One-Pot Formation and Characterization of Macrocyclic Aromatic Tetrasulfonates

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Supporting Information
General Experimental Methods

All reactions were conducted with oven-dried glassware under an atmosphere of argon (Ar). Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Column chromatography was carried out using Silica gel (200-300 mesh). TLC was performed on glass-backed plates coated with silica gel 60 with F<sub>254</sub> indicator. The <sup>1</sup>H NMR spectra were measured at 400 MHz and <sup>13</sup>C NMR spectra were measured at 100 MHz using CDCl<sub>3</sub> as solvent. <sup>1</sup>H NMR chemical shifts are expressed in parts per million (δ) downfield to CHCl<sub>3</sub> (δ = 7.26); <sup>13</sup>C NMR chemical shifts are expressed in parts per million (δ) relative to the central CDCl<sub>3</sub> resonance (δ = 77.0). Coupling constant in <sup>1</sup>H NMR are expressed in Hertz. Melting points were measured on a microscope hot stage melting point apparatus and are uncorrected. MALDI-TOF MS spectra were recorded on a Bruker Daltonics Autoflex III MS spectrometer. a-Cyanocinnamic acid was used as matrix.

Experimental Procedures

![Compound 4a](image)

**Compound 4a:** 1, 3-Dihydroxybenzene (0.220 g, 2 mmol ) and 4, 6-Dialkoxy-1,3-disulfonyl chlorides (0.782 g, 2 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and then triethylamine (0.54 mL, 4 mmol) was added subsequently at room temperature, followed by heating the reaction mixture under refluxing for 30 hours. Then the solvent was evaporated, and the crude product was purified by chromatography on silica gel.
(ethyl acetate/petroleum ether, 1.5: 1, \( R_f \) 0.23) to give \( 4a \) as a white powder (21.6%, mp 294-295 °C). Single crystals of \( 4a \) were grown by slow cooling from acetone/petroleum ether, 10: 1. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 1.17 (t, \( J = 7.3 \) Hz, 2H), 1.96-2.05 (m, 8H), 4.20 (t, \( J = 6.0 \) Hz, 2H), 6.48 (s, 2H), 6.81 (d, \( J = 6.3 \) Hz, 2H), 6.93-7.00 (m, 4H), 7.93 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 10.5, 22.3, 72.1, 97.0, 113.8, 117.5, 118.1, 129.4, 136.8, 150.1, 163.4; IR (KBr, cm\(^{-1}\)): 1061, 1095, 1186, 1217, 1477, 1557, 1597; MS (MALDI-TOF): found 879.1 (M+Na\(^+\)), 895.1 (M+K\(^+\)); Anal. Calcd for C\(_{36}\)H\(_{40}\)O\(_6\)S\(_4\): N, 0.00; C, 50.47; H, 4.67; found N, 0.02; C, 50.50; H, 4.76.

\[ \text{4b} \]

**Compound 4b**: 3, 5-Dihydroxytoluene (0.426 g, 3 mmol) and 4, 6-Dialkoxy-1,3-disulfonyl chlorides(1.257 g, 3 mmol) were dissolved in CH\(_2\)Cl\(_2\) (30 mL) and then triethylamine (0.81 mL, 6 mmol) was added subsequently at room temperature, followed by heating the reaction mixture under refluxing for 30 hours. Then the solvent was evaporated, and the crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 3:1, \( R_f \) 0.22) and recrystallized with acetone to give compound \( 4b \) (24.9 %, mp 199-200 °C) as a white powder. Single crystals of compound \( 4b \) were obtained by cooling from acetone/ethyl acetate (1:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 1.00 (t, \( J = 7.2 \) Hz, 2H), 1.55-1.60 (m, 8H), 1.83-1.89 (m, 8H), 2.17 (s, 6H), 4.21 (t, \( J = 6.4 \) Hz, 2H), 6.51 (s, 2H), 6.64 (s, 2H), 6.80 (d, \( J = 1.6 \) Hz, 4H), 8.08 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 13.7, 18.9, 21.4, 30.7, 70.2, 97.3, 113.4, 114.6, 119.7, 135.9, 140.8, 149.8, 163.4; IR (KBr, cm\(^{-1}\)): 1061, 1095, 1140, 1186, 1217, 1477, 1557, 1594; MS (MALDI-TOF): found 963.3 (M+Na\(^+\)), 979.2 (M+K\(^+\)); Anal. Calcd for C\(_{42}\)H\(_{52}\)O\(_{16}\)S\(_4\).0.2H\(_2\)O: N, 0.00; C, 53.41; H, 5.55; found N, 0.00; C, 53.84; H, 6.05.
**Compound 5:** 2, 7-Dihydroxynaphthalene (0.640 g, 4 mmol) and 4, 6-Dialkoxy-1,3-disulfonyl chlorides (1.676 g, 4 mmol) were dissolved in CH$_2$Cl$_2$ (30 mL) and then triethylamine (1.08 mL, 8 mmol) was added subsequently at room temperature, followed by heating the reaction mixture under refluxing for 30 hours. Then the solvent was evaporated, and the crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 1.5:1, $R_f$ 0.25) to give compound 5 as a white powder. (13.2 % yield, mp 274-275 °C). Single crystals of 5 were grown by slow cooling from acetone/ethyl acetate/petroleum ether, 10:3:1. $^1$H NMR (400 MHz, CDCl$_3$): δ0.93 (t, $J$ = 7.2 Hz, 12H), 1.38-1.47 (m, 8H), 1.55-1.63 (m, 8H), 1.97-2.03 (m, 8H), 4.32 (t, $J$ = 6.4 Hz, 4H), 6.68 (s, 2H), 6.82 (d, $J$ = 8 Hz, 4H), 7.50 (d, $J$ = 1.2 Hz, 8H), 8.00 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ13.4, 21.9, 27.8, 28.3, 70.6, 99.7, 114.1, 120.0, 121.5, 130.1, 134.0, 135.5, 147.7, 164.0; IR (KBr, cm$^{-1}$): 1057, 1097, 1148, 1183, 1196, 1461, 1511, 1556, 1595; MS (MALDI-TOF): found 1091.1 (M+Na$^+$), 1107.1 (M+K$^+$); Anal.Calcd for C$_{52}$H$_{60}$O$_{16}$S$_4$: N, 0.00; C, 58.43; H, 5.62; found N, 0.04; C, 58.36; H, 5.40.
**Compound 6:** 4, 4-Dihydroxybiphenyl (0.186 g, 1 mmol) and 4, 6-Dialkoxy-1, 3-disulfonyl chlorides (0.447 g, 1 mmol) were dissolved in CH$_2$Cl$_2$ (30 mL) and then triethylamine (0.27 mL, 2 mmol) was added subsequently at room temperature, followed by heating the reaction mixture under refluxing for 24 hours. Then the solvent was evaporated, and the crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 3:1, $R_f$=0.27) and recrystallized with CHCl$_3$ to give compound 6 (23.5 %, mp 228-229 °C) as a white powder. Single crystals of compound 6 were obtained by cooling from acetone. $^1$H NMR (400 MHz, CDCl$_3$): $^13$C NMR (100 MHz, CDCl$_3$): IR (KBr, cm$^{-1}$): 1059, 1099, 1153, 1179, 1202, 1464, 1490, 1557, 1594; MS (MALDI-TOF): found 1142.8 (M+Na$^+$) 1158.7 (M+K$^+$); Anal.Calcd for C$_{56}$H$_{64}$O$_{16}$S$_4$•0.5 H$_2$O: N, 0.00; C, 59.52; H, 5.76; found N, 0.02; C, 59.51; H, 6.19.

![Compound 6](image)

**Compound 7:** 3, 6-bis-(3-methyl-butoxy)-naphthalene-2, 7-disulfonyl dichloride (0.496 g, 1 mmol) and naphthalene-2,7-diol (0.160 g, 1 mmol) were dissolved in CH$_2$Cl$_2$ (30 mL) and then triethylamine (0.27 mL, 2 mmol) was added subsequently at room temperature, followed by heating the reaction mixture under refluxing for 24 hours. Then the solvent was evaporated, and the crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 3:1, $R_f$=0.19) to give compound 7 (15.5 % yield, mp 378-379 °C) as a white powder. Single crystals of 7 were
grown by slow cooling from methanol/DMF, 10: 1. $^1$H NMR (CDCl$_3$, 400 MHz): $^\text{m} 1.03$

(d, $J = 6.4$ Hz, 24H), 1.90-1.95 (m, 8H), 2.02-2.12 (m, 8H), 4.36 (t, $J = 6.4$ Hz, 8H),

8.30 (s, 4H), 6.80-6.83 (dd, $J = 2$ Hz, 4H), 7.20 (s, 4H), 7.37 (d, $J = 8.8$ Hz, 4H), 7.79 (d, $J = 2$ Hz, 8.05 (s, 4H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $^\text{m} 162.4, 155.4, 147.1, 142.2, 135.8, 133.7, 130.1, 129.9, 122.1, 121.9, 120.7, 119.1, 107.8, 67.7, 37.1, 30.7, 24.2, 22.2.

IR(KBr, cm$^{-1}$): 1680, 1620, 1428, 1377, 1185, 1147, 1052, 851, 804, 709, 550, 474. MS (MALDI-TOF): found 1191.5 (M+Na$^+$), 1208.4 (M+K$^+$). Anal. Calcd for $C_{60}H_{64}O_{16}S_4\cdot2$ DMF: N, 2.13; C, 60.25; H, 5.98; found N, 1.84; C, 60.05; H, 4.50.
NMR and MS Spectra

Compound 4a: $^1$H NMR Spectrum
Compound 4a: $^{13}$C NMR Spectrum

MALDI–TOF, CCA, ZDC – 2 – 63, 2006, 6, 21

[M+Na$^+$]

[M+K$^+$]

Compound 4a: MALDI Spectrum
Compound 4b: $^1$H NMR Spectrum

Compound 4b: $^{13}$C NMR Spectrum
Compound 4b: MALDI Spectrum
Compound 5: $^1$H NMR Spectrum

Compound 5: $^{13}$C NMR Spectrum
Compound 5: MALDI spectrum
Compound 6: $^1$H NMR Spectrum

Compound 6: $^{13}$C NMR Spectrum
MALDI-TOF, CCA, ZDC - 2 - 81, 2006, 8, 22

Compound 6: MALDI spectrum
Compound 7: $^1$H NMR Spectrum

Compound 7: $^{13}$C NMR Spectrum
Compound 7: MALDI spectrum