

Synthesis, properties and bioconjugation of water-soluble asymmetric indodicarbocyanine dyes

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Experimental

The ^1H NMR spectra were recorded on a Bruker AMX-400 spectro-meter (400 MHz) in CDCl_3 with TMS as an internal standard in D_2O and $[\text{}^2\text{H}_6]\text{DMSO}$ solutions. Mass spectra were measured on a KOMPACT MALDI 4 mass spectrometer. Fluorescence spectra were recorded on an RF 5000 spectrofluorimeter (Shimadzu, Japan). Absorption spectra were measured using a Jasco V-550 spectrophotometer (Japan). Melting points were determined on a Kofler block and are uncorrected. TLC was performed on C18 reverse-phase plates (Merck) eluted with acetonitrile–water (3:1).

3-(4-Carboxybutyl)-2,3-dimethylindolenine 4a. A mixture containing **2** (0.72 g, 4.2 mmol), phenylhydrazine (0.4 ml, 4.2 mmol) and acetic acid (4.2 ml) was heated to 118 °C for 3.5 h. The solution was evaporated, the residue was dissolved in CHCl_3 , washed with water and then dried over anhydrous MgSO_4 . The solvent was removed on a rotary evaporator and residue was dissolved in ethyl acetate (0.6 ml) and reprecipitated with hexane (2 ml) to yield 0.8 g (78%) of indolenine **4a** as yellow-brown tint, mp 112–113 °C. UV-VIS [MeOH, λ/nm]: 256. MS (MALDI), m/z : 246.3 (M^+). ^1H NMR (CDCl_3) δ : 0.56–0.81 [m, 2H, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{COOH}$], 1.28 [s, 3H, Me(3)], 1.43–1.51 [m, 2H, $\text{CH}_2(\text{CH}_2)_3\text{COOH}$], 1.76–1.92 [m, 2H, $(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{COOH}$], 2.13–2.21 [m, 2H, $(\text{CH}_2)_3\text{CH}_2\text{COOH}$], 2.24 [s, 3H, Me(2)], 7.18–7.54 (br. m, 4H, ArH). Found (%): C, 73.68; H, 7.76; N, 5.62. Calc. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (%): C, 73.44; H, 7.81; N, 5.71.

Potassium salt of 3-(4-carboxybutyl)-2,3-dimethylindoleninium-5-sulfonate 4b: yield 83%, mp 198–200 °C, beige powder. UV-VIS [MeOH, λ/nm]: 258. MS (MALDI), m/z : 326.2 (M^+). ^1H NMR (D_2O) δ : 0.45–0.70 [m, 2H, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{COOH}$], 1.31 [s, 3H, Me(3)], 1.36 (m, 2H, $\text{CH}_2(\text{CH}_2)_3\text{COOH}$], 1.88–2.14 [m, 4H, $(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{COOH}$], 7.53 (d, 1H, ArH, J 9 Hz), 7.80 (m, 2H, ArH). Found (%): C, 49.38; H, 4.75; N, 3.71. Calc. for $\text{C}_{15}\text{H}_{18}\text{KNO}_5\text{S}$ (%): C, 49.57; H, 4.99; N, 3.85.

3-(4-Carboxybutyl)-2,3-dimethyl-1-ethylindoleninium iodide 5a. A mixture of 3-(4-carboxybutyl)-2,3-dimethylindolenine **4a** (49 mg, 0.2 mmol), acetonitrile (0.4 ml) and a large excess of ethyl iodide (1 ml) was heated at 70 °C for 20 h. The reaction mixture was cooled, solvent was decanted, and the residue was triturated with diethyl ether and acetone. The viscous brown mass (95%) was obtained and used in further experiments without additional purification. UV-VIS [MeOH, λ/nm]: 279. MS (MALDI), m/z : 274.4 (M^+). ^1H NMR (CDCl_3) δ : 0.52–0.78 [m, 2H, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{COOH}$], 1.25 [s, 3H, Me(3)], 1.38–1.49 [m, 2H, $\text{CH}_2(\text{CH}_2)_3\text{COOH}$], 1.62 (t, 3H, CH_2Me , J 7 Hz), 1.70–1.81 [m, 2H, $(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{COOH}$], 2.18 [m, 2H, $(\text{CH}_2)_3\text{CH}_2\text{COOH}$], 2.28 [s, 3H, Me(2)], 4.73 (m, 2H, CH_2Me), 7.50–7.68 (br. m, 4H, ArH).

1-(δ -Sulfonatobutyl)-3-(4-carboxybutyl)-2,3-dimethylindolenine 5b. A mixture of **4a** (0.64 g, 2.6 mmol), 1,4-butanediol (0.53 ml, 5.2 mmol) and 1,2-dichlorobenzene (4.2 ml) was heated at 118 °C for 25 h. The reaction mixture was cooled, 1,2-dichlorobenzene was decanted, and the solid was triturated with diethyl ether until free powder was obtained. The solid was filtered off and dried *in vacuo* to yield 0.98 g (99%) purple crystals, mp 48–50 °C. UV-VIS [MeOH, λ/nm]: 280. MS (MALDI), m/z : 382.0

(M⁺). ¹H NMR (D₂O) δ: 0.38–0.68 [m, 2H, CH₂CH₂(CH₂)₂COOH], 1.23–1.35 [m, 2H, CH₂(CH₂)₃COOH], 1.43 [s, 3H, Me(3)], 1.71–1.81 [m, 2H, CH₂CH₂(CH₂)₂SO₃], 1.92–2.20 [br. m, 6H, (CH₂)₂CH₂CH₂COOH, (CH₂)₂CH₂CH₂SO₃], 2.84 [t, 2H, (CH₂)₂CH₂SO₃, *J* 7.5 Hz], 4.41 [t, 2H, CH₂(CH₂)₃SO₃, *J* 7.5 Hz], 7.18–7.70 (br. m, 4H, ArH).

3-(4-Carboxybutyl)-2,3-dimethyl-1-ethylindoleninium-5-sulfonate 5c: yield 96%, mp 142–145 °C, dark brown powder. UV-VIS [MeOH, λ/nm]: 266. MS (MALDI), *m/z*: 354.2 (M⁺). ¹H NMR (D₂O) δ: 0.58–0.72 [m, 2H, CH₂CH₂(CH₂)₂COOH], 1.49 (t, 3H, CH₂Me, *J* 7 Hz), 1.56 [s, 3H, Me(3)], 1.61 [m, 2H, CH₂(CH₂)₃COOH], 2.14 (br. m, 4H, (CH₂)₂CH₂CH₂COOH), 4.5 (m, 2H, CH₂Me), 7.9 (d, 1H, ArH, *J* 9 Hz), 8.06 (m, 2H, ArH).

Potassium salt of 3-(4-carboxybutyl)-2,3-dimethyl-1-(δ-sulfonatobutyl)indoleninium-5-sulfonate 5d: yield 97%, mp 222–224 °C, dark brown powder. UV-VIS [MeOH, λ/nm]: 268. MS (MALDI), *m/z*: 461.1 (M⁺). ¹H NMR (D₂O) δ: 0.64–0.77 [m, 2H, CH₂CH₂(CH₂)₂COOH], 1.39 [m, 2H, CH₂(CH₂)₃COOH], 1.58 [s, 3H, Me(3)], 1.68–1.75 [m, 2H, CH₂CH₂(CH₂)₂SO₃], 1.95–2.31 [br. m, 6H, (CH₂)₂CH₂CH₂COOH, (CH₂)₂CH₂CH₂SO₃], 2.89 [t, 2H, (CH₂)₃CH₂SO₃, *J* 7.5 Hz], 4.51 [t, 2H, CH₂(CH₂)₃SO₃, *J* 7.5 Hz], 7.7 (d, 2H, ArH, *J* 9 Hz), 8.04 (s, 1H, ArH).

General procedure for the synthesis of cyanine dyes 9a and 9e–j. A solution of **6a–d** (0.2 mmol) and **7** (0.2 mmol) in a mixture of acetic anhydride (0.7 ml) and acetic acid (0.2 ml) was refluxed at 118 °C for 2 h. The indolenine **5a–d** (0.21 mmol), anhydrous potassium acetate (0.12 g, 1.2 mmol), acetic anhydride (0.7 ml) and acetic acid (0.35 ml) were added to the reaction mixture and heated at 118 °C for additional 2 h. Then, the solvent was evaporated and the cyanine dye was purified in reverse-phase (C18) chromatography.

General procedure for the synthesis of cyanine dyes 9b–d. A solution of indolenine **6a–d** (0.2 mmol) and malonaldehyde dianil hydrochloride **7** (0.2 mmol) in a mixture of acetic anhydride (0.7 ml) and acetic acid (0.3 ml) was heated at 118 °C for 2 h. The solvent was removed with rotary evaporator and crude product **8a–d** thus obtained was used without additional purification. A solution of indolenine **5a–d** (0.21 mmol) in acetic anhydride (0.8 ml) and diisopropylethylamine (0.2 ml) mixture was added to a solution of intermediate **8a–d** in acetic anhydride (1.7 ml). The reaction mixture was kept for 24 h at ~20 °C. After that, the solvent was evaporated and the cyanine dye was purified in reverse-phase (C18) chromatography.

Sodium salt of 3-(4-carboxybutyl)-1,1'-di(δ-sulfonatobutyl)-3,3',3'-trimethylindodicarbocyanine 9a: yield 48%, mp 184–186 °C, dark-blue powder. MS-MALDI, *m/z*: 712.1 (M⁺). ¹H NMR (DMSO-*d*₆) δ: 0.45 (m, 1H, CH₂CH₂CH₂CH₂COOH), 0.77 (m, 1H, CH₂CH₂CH₂CH₂COOH), 1.32 (m, 2H, CH₂CH₂CH₂CH₂COOH), 1.65–1.8 [s, 17H, CH₃(3,3), CH₃(3'), CH₂CH₂CH₂CH₂SO₃], 1.91 (m, 2H, CH₂CH₂CH₂CH₂COOH), 2.17 (m, 1H, CH₂CH₂CH₂CH₂COOH), 2.42 (m, 5H, CH₂CH₂CH₂CH₂COOH, CH₂CH₂CH₂CH₂SO₃), 4.09 (m, 4H, CH₂CH₂CH₂CH₂SO₃), 6.37 (m, 2H, α,α'-CH), 6.57 (t, 1H, γ-CH, *J* 12.0 Hz), 7.21–7.6 (br. m, 8H, ArH), 8.3 (m, 2H, β,β'-CH). Found (%): C, 60.21; H, 6.58; N, 3.93. Calc. for C₃₇H₄₇N₂NaO₈S₂ (%): C, 60.47; H, 6.45; N, 3.81.

3-(4-Carboxybutyl)-1-ethyl-1'-(δ-sulfonatobutyl)-3,3',3'-trimethylindodicarbocyanine 9b: yield 28%, mp 175–177 °C, dark-blue powder. MS-MALDI, *m/z*: 605.7 (M⁺). ¹H NMR (DMSO-*d*₆) δ: 0.48 (m, 1H, CH₂CH₂CH₂CH₂COOH), 0.79 (m, 1H, CH₂CH₂CH₂CH₂COOH), 1.2–1.35 (m, 5H, CH₂CH₃, CH₂CH₂CH₂CH₂COOH), 1.65–1.81 [m, 13H, CH₃(3,3), CH₃(3'), CH₂CH₂CH₂CH₂SO₃], 2.02 (m, 2H, CH₂CH₂CH₂CH₂COOH), 2.17 (m, 1H, CH₂CH₂CH₂CH₂COOH), 2.34 (m, 3H, CH₂CH₂CH₂CH₂COOH, CH₂CH₂CH₂CH₂SO₃), 4.12 (m, 4H, CH₂CH₃, CH₂CH₂CH₂CH₂SO₃), 6.35 (m, 2H, α,α'-CH), 6.58 (m, 1H, γ-CH), 7.22–7.61 (br. m, 8H, ArH), 8.3 (m, 2H, β,β'-CH). Found (%): C, 69.35; H, 7.46; N, 4.75. Calc. for C₃₅H₄₄N₂O₅S (%): C, 69.51; H, 7.33; N, 4.63.

3-(4-Carboxybutyl)-1'-ethyl-1-(δ-sulfonatobutyl)-3,3',3'-trimethylindodicarbocyanine 9c: yield 38%, mp 172–173 °C, dark-blue powder. MS-MALDI, *m/z*: 605.5 (M⁺). ¹H NMR (DMSO-*d*₆) δ: 0.43 (m, 1H, CH₂CH₂CH₂CH₂COOH), 0.78 (m, 1H, CH₂CH₂CH₂CH₂COOH), 1.24–1.31 (m, 5H, CH₂CH₃, CH₂CH₂CH₂CH₂COOH), 1.64 [s, 9H, CH₃(3,3), CH₃(3')], 1.73 (m, 4H, CH₂CH₂CH₂CH₂SO₃), 1.89 (m, 2H, CH₂CH₂CH₂CH₂COOH), 2.18 (m, 1H, CH₂CH₂CH₂CH₂COOH), 2.41 (m, 3H, CH₂CH₂CH₂CH₂COOH, CH₂CH₂CH₂CH₂SO₃), 4.12 (m, 4H, CH₂CH₃, CH₂CH₂CH₂CH₂SO₃), 6.26 (d, 1H, α'-CH, *J* 13.5 Hz), 6.41 (d, 1H, α-

CH, *J* 13.5 Hz), 6.57 (t, 1H, γ -*CH*, *J* 12.0 Hz), 7.21-7.61 (br. m, 8H, *ArH*), 8.32 (m, 2H, β,β' -*CH*). Found (%): C, 69.28; H, 7.21; N, 4.69. Calc. for $C_{35}H_{44}N_2O_5S$ (%): C, 69.51; H, 7.33; N, 4.63.

3-(4-Carboxybutyl)-1,1'-diethyl-5'-sulfo-3,3',3'-trimethylindodicarbocyanine 9d: yield 27%, mp 168-170°C, dark-blue powder. MS-MALDI, *m/z*: 577.0 (M^+). 1H NMR (DMSO- d_6) δ : 0.46 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.75 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.23-1.33 (m, 8H, CH_2CH_3 , $CH_2CH_2CH_2CH_2COOH$), 1.68 [s, 9H, $CH_3(3,3)$, $CH_3(3')$], 1.89 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.16 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.4 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 4.13 (m, 4H, CH_2CH_3), 6.26 (d, 1H, α' -*CH*, *J* 13.5 Hz), 6.34 (d, 1H, α -*CH*, *J* 13.5), 6.56 (t, 1H, γ -*CH*, *J* 12.0 Hz), 7.2-7.8 (br. m, 7H, *ArH*), 8.35 (t, 2H, β,β' -*CH*, *J* 13.5 Hz). Found (%): C, 68.91; H, 7.18; N, 4.95. Calc. for $C_{33}H_{40}N_2O_5S$ (%): C, 68.72; H, 6.99; N, 4.86.

3-(4-Carboxybutyl)-1,1'-diethyl-5'-sulfo-3,3',3'-trimethylindodicarbocyanine 9e: yield 18%, mp 169-172°C, dark-blue powder. MS-MALDI, *m/z*: 577.3 (M^+). 1H NMR (DMSO- d_6) δ : 0.47 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.77 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.24-1.36 (m, 8H, CH_2CH_3 , $CH_2CH_2CH_2CH_2COOH$), 1.7 [s, 9H, $CH_3(3,3)$, $CH_3(3')$], 1.9 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.16 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.42 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 4.13 (m, 4H, CH_2CH_3), 6.27 (d, 1H, α' -*CH*, *J* 13.5 Hz), 6.35 (d, 1H, α -*CH*, *J* 13.5 Hz), 6.57 (t, 1H, γ -*CH*, *J* 12.0 Hz), 7.21-7.75 (br. m, 7H, *ArH*), 8.34 (t, 2H, β,β' -*CH*, *J* 13.0 Hz). Found (%): C, 68.51; H, 6.76; N, 4.75. Calc. for $C_{33}H_{40}N_2O_5S$ (%): C, 68.72; H, 6.99; N, 4.86.

Sodium salt of 3-(4-carboxybutyl)-1,1'-diethyl-5,5'-disulfo-3,3',3'-trimethylindodicarbocyanine 9f: yield 14%, mp >250°C, dark-blue powder. MS-MALDI, *m/z*: 656.5 (M^+). 1H NMR (DMSO- d_6) δ : 0.51 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.75 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.22-1.38 (m, 8H, CH_2CH_3 , $CH_2CH_2CH_2CH_2COOH$), 1.69 [s, 9H, $CH_3(3,3)$, $CH_3(3')$], 2.04 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.21 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.43 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 4.14 (m, 4H, CH_2CH_3), 6.33 (m, 2H, α,α' -*CH*), 6.57 (t, 1H, γ -*CH*, *J* 12.0 Hz), 7.28-7.82 (br. m, 6H, *ArH*), 8.35 (m, 2H, β,β' -*CH*), 11.88 (s, 1H, *COOH*). Found (%): C, 58.57; H, 5.91; N, 4.25. Calc. for $C_{33}H_{39}N_2NaO_8S_2$ (%): C, 58.39; H, 5.79; N, 4.13.

Sodium salt of 3-(4-carboxybutyl)-1-ethyl-1'-(δ -sulfonatobutyl)-5'-sulfo-3,3',3'-trimethylindodicarbocyanine 9g: yield 20%, mp 166-168°C, dark-blue powder. MS-MALDI, *m/z*: 684.2 (M^+). 1H NMR (DMSO- d_6) δ : 0.5 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.77 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.21 (t, 3H, CH_2CH_3 , *J* 7 Hz), 1.34 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 1.66-1.79 [m, 13H, $CH_3(3,3)$, $CH_3(3')$, $CH_2CH_2CH_2CH_2SO_3$], 2.02 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.19 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.43 (m, 3H, $CH_2CH_2CH_2CH_2COOH$, $CH_2CH_2CH_2CH_2SO_3$), 4.12 (m, 4H, CH_2CH_3 , $CH_2CH_2CH_2CH_2SO_3$), 6.3 (d, 1H, α' -*CH*, *J* 13.5 Hz), 6.4 (d, 1H, α -*CH*, *J* 13.5 Hz), 6.58 (t, 1H, γ -*CH*, *J* 12.0 Hz), 7.24-7.75 (br. m, 7H, *ArH*), 8.35 (m, 2H, β,β' -*CH*). Found (%): C, 59.21; H, 6.27; N, 4.13. Calc. for $C_{35}H_{43}N_2NaO_8S_2$ (%): C, 59.47; H, 6.13; N, 3.96.

Sodium salt of 3-(4-carboxybutyl)-1-ethyl-1'-(δ -sulfonatobutyl)-5'-sulfo-3,3',3'-trimethylindodicarbocyanine 9h: yield 22%, mp 139-141°C, dark-blue powder. MS-MALDI, *m/z*: 684.3 (M^+). 1H NMR (DMSO- d_6) δ : 0.47 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.77 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.24-1.38 (br. m, 5H, CH_2CH_3 , $CH_2CH_2CH_2CH_2COOH$), 1.68 [s, 13H, $CH_3(3,3)$, $CH_3(3')$, $CH_2CH_2CH_2CH_2SO_3$], 2.0 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.19 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.4 (m, 3H, $CH_2CH_2CH_2CH_2COOH$, $CH_2CH_2CH_2CH_2SO_3$), 4.13 (m, 4H, CH_2CH_3 , $CH_2CH_2CH_2CH_2SO_3$), 6.26 (d, 1H, α' -*CH*, *J* 13.5 Hz), 6.43 (d, 1H, α -*CH*, *J* 13.5 Hz), 6.57 (t, 1H, γ -*CH*, *J* 12.0 Hz), 7.23-7.79 (br. m, 7H, *ArH*), 8.33 (m, 2H, β,β' -*CH*). Found (%): C, 59.68; H, 6.34; N, 4.09. Calc. for $C_{35}H_{43}N_2NaO_8S_2$ (%): C, 59.47; H, 6.13; N, 3.96.

Disodium salt of 3-(4-carboxybutyl)-5,5'-disulfo-1-ethyl-1'-(δ -sulfonatobutyl)-3,3',3'-trimethylindodicarbocyanine 9i: yield 19%, mp >250°C, dark-blue powder. MS-MALDI, *m/z*: 763.2 (M^+). 1H NMR (DMSO- d_6) δ : 0.52 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.73 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.22-1.35 (m, 5H, CH_2CH_3 , $CH_2CH_2CH_2CH_2COOH$), 1.68 [m, 15H, $CH_3(3,3)$, $CH_3(3')$, $CH_2CH_2CH_2CH_2SO_3$], 2.02 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.18 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.37 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 4.12 (m, 4H, CH_2CH_3 , $CH_2CH_2CH_2CH_2SO_3$), 6.36 (m, 2H, α,α' -*CH*), 6.59 (m, 1H, γ -*CH*), 7.0-7.79 (m, 6H, *ArH*), 8.35 (m, 2H, β,β' -*CH*). Found (%): C, 51.65; H, 5.12; N, 3.33. Calc. for $C_{35}H_{42}N_2Na_2O_{11}S_3$ (%): C, 51.97; H, 5.23; N, 3.46.

Trisodium salt of 3-(4-carboxybutyl)-5,5'-disulfo-1,1'-di-(δ -sulfonatobutyl)-3,3',3'-trimethylindodicarbocyanine 9j: yield 42%, mp 145-148°C, dark-blue powder. MS-MALDI, *m/z*: 870.0 (M^+). 1H NMR (DMSO- d_6) δ : 0.53 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 0.78 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 1.39 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 1.67-1.81 (m, 21H, $3,3',3'$ - CH_3 , $CH_2CH_2CH_2CH_2SO_3$), 1.92 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 2.17 (m, 2H, $CH_2CH_2CH_2CH_2COOH$), 2.41 (m, 1H, $CH_2CH_2CH_2CH_2COOH$), 4.12 (m, 4H, $CH_2CH_2CH_2CH_2SO_3$), 6.39 (m, 2H, α,α' -*CH*), 6.64 (m, 1H, γ -*CH*), 7.25-7.81 (m, 6H, *ArH*), 8.33 (m, 2H, β,β' -*CH*). Found (%): C, 47.08; H, 4.69; N, 2.83. Calc. for $C_{37}H_{45}N_2Na_3O_{14}S_4$ (%): C, 47.33; H, 4.83; N, 2.98.