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Synthesis and liquid-crystal properties of new amphiphilic long-chain derivatives of *meso*-arylporphyrins with terminal polar groups

Kirill A. Formirovsky, Natalya A. Bragina, Andrey F. Mironov, Galina A. Anan'eva, Venera V. Bykova and Nadezhda V. Usol'tseva

Experimental

IR spectra were measured in thin film or in KBr pellets using a Bruker EQUINOX 55 Fourier spectrometer (Germany). NMR spectra (δ scale) were recorded on a Bruker MSL-300 instrument (Germany) at a working frequency of 300 MHz. TMS was the internal reference, $CDCl_3$ and CD_3OD were the solvents. Electronic spectra were recorded in CH_2Cl_2 using a Jasko UV-7800 spectrophotometer (Japan). Mass spectra of the compounds were obtained using an Agilent Technologies 1100 LCMSD instrument. Mesomorphic properties were studied by optical polarisation microscopy. Thermotropic mesomorphism was studied using a Leitz Laborlux 12 Pol optical thermopolarisation microscope equipped with a Mettler FP 82 hot stage, whereas lyotropic mesomorphism was studied by the method of contact agents with organic solvents.

General procedure for the preparation of substituted benzaldehydes **1a**,**b**.

A solution (20 ml) of methyl 6-bromohexanoate (2.52 g, 11.8 mmol) or 3.35 g (11.8 mmol) of methyl 11-bromoundecanoate in dichloromethane (10 ml) was added to a solution (25 ml) of 4-hydroxybenzaldehyde (1.2 g, 9.83 mmol) and DBU (0.9 g, 7.37 mmol) in dichloromethane. The mixture was stirred for 24 h with heating. The excess solvent was removed *in vacuo*. To purify the compound, the reaction mixture was extracted in a water–dichloromethane system, then subjected to column chromatography on G 60 silica gel, eluting with dichloromethane–hexane (6:1).

4-(5-Methoxycarbonylpentyloxy)benzaldehyde **1a**. Yield 2.35 g (80%), R_f 0.3 (chloroform); IR (ν/cm^{-1}): 1734 ($COOCH_3$), 1683 (CHO), 1255, 1013 (C–O).

4-(10-Methoxycarbonyldecyloxy)benzaldehyde **1b**. Yield 3.41 g (94%), R_f 0.4 (chloroform–hexane, 7:3); IR (ν/cm^{-1}): 1734 ($COOCH_3$), 1683 (CHO), 1253, 1013 (C–O).

5,10,15,20-Tetrakis[4-(10-carboxydecyloxy)phenyl]porphyrin **3b.** Yield 76 mg (88%), R_f 0.14 (CH_2Cl_2–MeOH, 9:1). Electronic spectrum [λ_{max} / nm, ($\varepsilon\times10^{-3}$)]: 422 (386), 515 (11.2), 550 (5.08), 590 (3.49), 646 (2.51). ^{1}H NMR: −2.81 (2H, s, NH), 1.61 [48H, m, $OCH_2CH_2(CH_2)_6$], 1.76 [8H, m, J 7 Hz, $O(CH_2)_2CH_2CH_2COOH$], 1.95 (8H, m, J 7 Hz, OCH_2CH_2), 2.39 [8H, t, J 7 Hz, $O(CH_2)_2CH_2CH_2COOCH_3$], 4.16 (8H, t, J 7 Hz, OCH_2), 7.18 [8H, d, J 7 Hz, (ArH)], 8.04 [8H, d, J 7 Hz, (ArH)], 8.8 (8H, s, pyrrole). MS (*m/z*): 1415.4 [M^++1].

5,10,15,20-Tetrakis[4-(11-hydroxyundecyloxy)phenyl]porphyrin **4b** was obtained similarly to compound **4a** from porphyrin **2b** (50 mg, 0.035 mmol) and $LiAlH_4$ (12 mg, 0.17 mmol). Yield 42 mg (83%), R_f 0.2 (CH_2Cl_2–MeOH, 9:1). Electronic spectrum [λ_{max} / nm, ($\varepsilon\times10^{-3}$)]: 418 (385), 516 (14), 550 (5.5), 590 (3.78), 646 (3.12). ^{1}H NMR: −2.81 (2H, s, NH) 8.68–8.51 (s, 8H pyrrole), 7.86–7.69 [d, 8H, (ArH)], 6.98–6.86 [d, 8H, (ArH)], 3.88 [t, *J* 6.4 Hz, 8H, ($HOCH_2$)], 3.41 [t, *J* 6.6 Hz, 8H, (OCH_2)], 1.69 [m, *J* 6.2 Hz, 8H, ($HOCH_2CH_2$)], 1.53–1.18 [m, 24H, ($HOCH_2CH_2(\underline{CH_2})_9$]. MS (*m/z*): 1359.7 [$M^+$+1].