ISSN 1068-1620, Russian Journal of Bioorganic Chemistry, 2007, Vol. 33, No. 6, pp. 589–593. © Pleiades Publishing, Inc., 2007.
Original Russian Text © I.N. Fedulova, N.A. Bragina, N.V. Novikov, O.A. Ugol'nikova, A.F. Mironov, 2007, published in Bioorganicheskaya Khimiya, 2007, Vol. 33, No. 6, pp. 635–639.

Synthesis of Lipophilic Tetraphenylporphyrins to Design Lipid–Porphyrin Ensembles

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Received December 12, 2006; in final form, March 1, 2007

Abstract—Synthesis of symmetrical *meso*-arylsubstituted porphyrins with long chain hydrophobic substituents in the phenyl rings was achieved. The lipoporphyrins can be used to design supramolecular lipid ensembles of nanometer size.

Key words: lipoporphyrins, meso-aryltetraphenylporphyrins, meso-aryldipyrromethanes

DOI: 10.1134/S106816200706009X

INTRODUCTION

Porphyrins play an important role in the processes of energy transformation in nature. In biological systems, they usually function within the highly organized membrane complexes [1].[2] Such lipid–porphyrin ensembles have been used for the modeling of electron transfer processes and oxygen transport [2].

Supramolecular ensembles on the basis of amphiphilic porphyrin derivatives and lipids are prospective subjects for nanotechnology. The introduction of tetrapyrrol compounds in monolayer [3, 4], bilayer [5], and micellar [6] lipid aggregates allows the obtaining of supramolecular ensembles with unique physicochemical properties. These complexes can be widely applied to the modeling of biological processes, transport of medicinal preparations, diagnostics, and design of sensors for the registration of intermolecular interactions and devices for the transformation of energy and the storage of information.

The presence of a lipid constituent provides for the ability of such ensembles to self organization. At the same time, the porphyrin component permits the use of optical spectroscopy for the study of various processes of intermolecular recognition. The conjugated 20π-electron system of the porphyrin macrocycle serves as a convenient probe for the detection of weak intermolecular interactions with the host molecule by the main spectral methods. The aggregation–deaggregation processes of porphyrins at the interaction with ligands may be estimated according to fluorescence intensity and changes in the absorption spectrum in solution.

The necessary prerequisite for the obtaining of supramolecular ensembles in aqueous media is the amphiphility of the self-organizing molecules. Hence, structural fragments of lipids should be introduced into porphyrins, e.g., hydrocarbon residues with various chain lengths. It was shown that such compounds possess liquid-crystalline properties [7]. The liquid crystals on the basis of porphyrins are of interest for optoelectronics and devices to display and store information [8].

A wide use of porphyrins in technology and medicine is retarded by a low accessibility of the majority of them. In this connection, the problems of chemistry of synthetic porphyrins become important. The porphyrins containing aryl substituents in *meso*-positions are especially attractive, because they can be subjected to various chemical transformations [9].

RESULTS AND DISCUSSION

The goal of this study was the development of effective synthetic methods for lipophilic *meso*-aryl substituted porphyrins with various hydrophobic substituents. A combination of the methods of synthesis of *meso*-arylporphyrins with the modification of substituents in aromatic rings allows the obtaining of compounds with the required physicochemical characteristics.

Lipoporphyrins with four to eight residues of higher fatty alcohols, acids, steroids, or natural lipids had previously been synthesized on the basis of tetraphenylporphyrin [1, 9, 10]. The covalent binding of the residues of higher fatty acids and alcohols was achieved by acylation with higher fatty acid chlorides [8] or by alkylation with alkyl bromides of di-, tetra-, and

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[2] Abbreviations: DDQ, 2,3-dichloro-5,6-dicyanobenzoquinone; DMAP, 4-(dimethylamino)pyridine; and LPPC, *L*-*O*-palmitoyl-*sn*-glycero-3-phosphocholine.

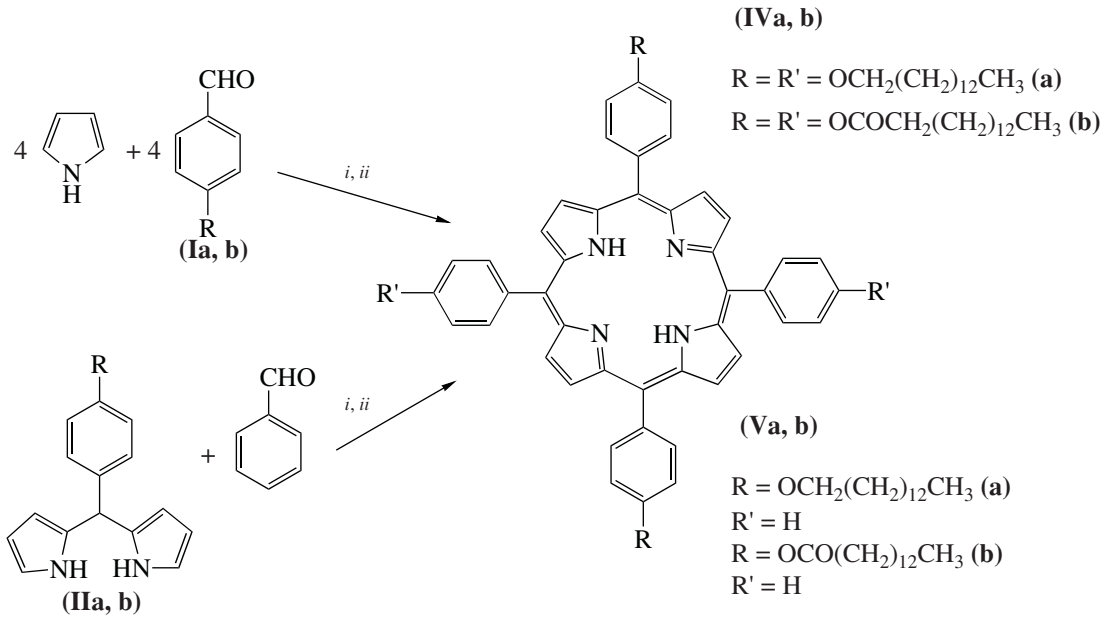
octa(hydroxyphenyl) derivatives of tetraphenylporphyrins [10, 11]. Hydroxyphenylporphyrins, which have a low solubility in organic solvents, were obtained by hydrolysis of tetraphenylporphyrin methoxy derivatives. In turn, these were synthesized by pyrrol condensation with methoxybenzaldehydes [12].

We suggest a more convenient scheme for the synthesis of lipoporphyrins according to which the residues of higher fatty acids and alcohols are introduced into the molecules of benzaldehydes at initial stages of synthesis. This allows the purposeful obtaining of the desired lipoporphyrins in high yields. The lengths of hydrophobic substituents in porphyrins were chosen in accordance with the size of hydrophobic area of natural phospholipids that form biological membranes.

The porphyrins were synthesized by two pathways: with the use of dipyrrometanes [13] and on the basis of monopyrrol condensation [14]. The synthesis via dipyrrolylmetanes has a number of advantages, which explains an elevated interest in it and its wide use [15]. The building up of the porphyrin molecule from *meso*-substituted dipyrrolylmetanes and substituted benzaldehydes allows the preparation of symmetrical structures with the required set of substituents. Moreover, the use of two different aldehydes at the condensation enables the preparation of asymmetric porphyrins of the AB_3 type [16].

We have obtained for the first time *meso*-aryldipyrrolylmetanes with long hydrophobic substituents [17]. The *meso*-aryl substituted dipyrrolylmetanes (**IIa**) and (**IIb**) were synthesized in 75 and 55% yields by the condensation of substituted benzaldehydes (**Ia**) and (**Ib**) with a large excess of pyrrol, which was also a solvent. The substituted benzaldehydes (**Ia**) and (**Ib**) were obtained by acylation or alkylation of *p*-hydroxybenzaldehyde with tetradecyl bromide and myristic acid chloride.

Porphyrins (**Va**) and (**Vb**) were obtained by the condensation of the corresponding *meso*-aryl substituted dipyrrolylmetanes (**IIa**) and (**IIb**) with benzaldehydes in the presence of trifluoroboron etherate, followed by oxidation of the resulting porphyrinogen to porphyrin under the action of DDQ (scheme). The yield of 5,15-bis(4-tetradecyloxyphenyl)-10,20-diphenylporphyrin was 54% and that of 5,15-bis(4-tetradecanoyloxyphenyl)-10,20-diphenylporphyrin 38%. The substitution of trifluoroacetic acid for trifluoroboron etherate leads to a decrease in the yield of the target product to 5–15%.



Preparation of *meso*-aryl-substituted porphyrins (**IVa**),(**IVb**) and (**Va**), (**Vb**). Reagents: *i*, $CHCl_3$, $BF_3 \cdot OEt_2$, EtOH; *ii,* DDQ.

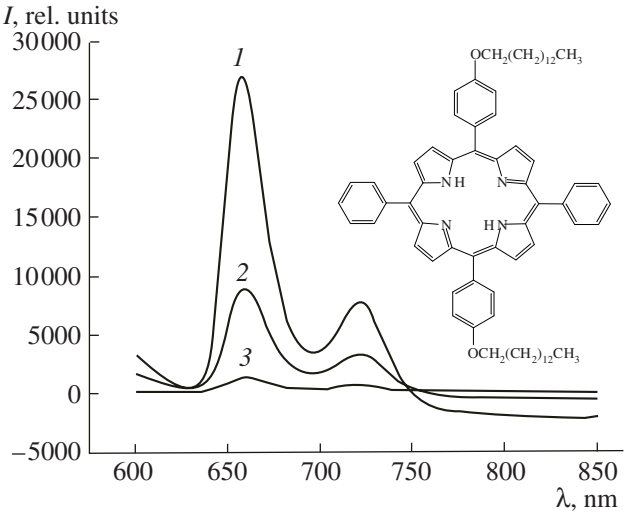
We used a modified method of monopyrrol condensation for the obtaining of 5,10,15,20-tetraphenylporphyrins. It was shown under the conditions that the maximal yields of porphyrins are achieved at the concentrations of benzaldehyde and pyrrol equal to 10^{-2} M [10]. The symmetrical porphyrins (**IVa**) and (**IVb**)

were obtained from the substituted benzaldehydes (**Ia**) and (**Ib**) in 30–35% yields.

The homogeneity and structure of the compounds were confirmed by TLC and electronic and ^{1}H NMR spectroscopies.

Literature data [18] indicate that lipoporphyrins (**Va**) and (**Vb**) should possess liquid crystalline properties, which opens an opportunity of their use as materials for nanotechnology, e.g., in the high density devices for information storage [8].

We carried out preliminary experiments on the porphyrin (**Va**) solubilization in micelles at the porphyrin–detergent ratios of 1 : 100, 1 : 200, and 1 : 400, LPPC being used as a detergent. An analysis of fluorescence spectra of (**Va**) at its various concentrations within the LPPC micelles showed that an increase in the porphyrin content in micelle lead to self quenching of fluorescence (figure). The tendency to the decrease of fluorescence at an increase in porphyrin concentration points out to the inclusion of several (more than one) porphyrin molecules at the porphyrin–detergent ratios.



Fluorescence spectra of porphyrin (**Va**) at various porphyrin concentrations within the LPPC micelles in water at porphyrin–detergent molar ratios: *1*, 400; *2*, 200; and *3*, 100. λ_{ex} 513 nm; temperature 20°C.

EXPERIMENTAL

We used in this work: triethylamine, calcium hydride, phosphorus pentoxide, trifluoroboron etherate, and organic solvents of domestic production; pyrrol and TFA (Fluka); tetradecyl bromide (Merck); DDQ, 4-hydroxybenzaldehyde, benzaldehyde, and DMAP (Aldrich); and potassium carbonate (Sigma). Myristic acid chloride was obtained by a standard procedure [19]. Chloroform and dichloromethane were distilled over phosphorus pentoxide; triethylamine and pyrrol, over calcium hydride. IR spectra were recorded on a Fourier Bruker EQUINOX 55 spectrometer (Germany). NMR spectra were obtained on a pulse Fourier Bruker MSL-500 spectrometer (Germany) with the working frequency 500 MHz; chemical shifts are given in δ scale; internal standard was Me_4Si; and solvent, $CDCl_3$. Electron spectra were registered on a Jasko UV-7800 spectrometer in dichloromethane. Silufol UV-254 (Kavalier, Czech Republic) was used for TLC. Chromatographic purification of compounds was carried out on open columns with silica gel G 60 (Sigma). Elution systems were (A) 15 : 1 petroleum ether–diethyl ether, (B) 4 : 1 : 0.1 chloroform–hexane–triethylamine, and (C) 4 : 1 chloroform–hexane.

4-Tetradecyloxybenzaldehyde (Ia). Potassium carbonate (1.39 g, 10.02 mmol) in acetone (30 ml) was added to a solution of *p*–hydroxybenzaldehyde (0.7 g, 5.73 mmol) and tetradecyl bromide (1.59 g, 5.73 mmol). The mixture was refluxed for 15 h, diluted with water (60 ml), and extracted with ether (2 × 50 ml). The combined extract was shaken with 10% NaOH (2 × 50 ml), washed with water (100 ml), dried with anhydrous sodium sulfate, and evaporated in a vacuum. The residue was chromatographed on a silica gel column eluted with system A; yield 0.41 g (71%); R_f 0.5 (1 : 1 petroleum ether–diethyl ether); mp 37°C; IR (ν, cm^{-1}): 2914, 2851, 1468, 734 ($(CH_2)_{13}CH_3$), 1676 (C=O), 1601, 824 (Ar), 1275, 1033 (C–O). Calc., %: C 79.19, H 10.76; Found, %: 79.16, H 10.81.

4-Tetradecanoyloxybenzaldehyde (Ib). A solution of myristoyl chloride (0.62 g, 2.46 mmol) was added dropwise for 30 min to a solution of *p*-hydroxybenzaldehyde (0.25 g, 2.05 mmol) and DMAP (0.19 g, 1.54 mmol) in dichloromethane (10 ml). The solution was stirred at room temperature for 20 h, evaporated in a vacuum, and the residue was chromatographed on silica gel eluting with system C. Yield of (**Ib**) 0.59 g (82%); R_f 0.65 (C), mp 43°C; IR (ν,$^{-1}$): 2925, 2853 ($(CH_2)_{12}CH_3$), 1757, 1744 (C=O), 1463 (Ar), 1025, 1200 (C–O). Calc., %: C 75.97, H 9.64. Found, %: C 75.93, H 9.75.

***meso*-Tetradecyloxyphenyl)dipyrromethane (IIa).** An inert gas was passed through a mixture of tetradecyloxybenzaldehyde (0.4 g, 1.25 mmol) and pyrrol (3.5 ml, 50.2 mmol) for 5 min. TFA (9.3 μl, 0.013 mmol) was added, and the mixture was stirred for 30 min at room temperature. The reaction mixture was diluted with dichloromethane (60 ml), washed with 0.1 N NaOH and water to neutral reaction, and dried with sodium sulfate. (**IIa**) was isolated by flash chromatography eluting with system B. Solvent and unreacted pyrrol were removed in a vacuum at 40°C. The residue was dissolved in dichloromethane (1 ml) and ethanol (7 ml) was added. The precipitated solid was filtered and dried in a vacuum; yield 0.41 g (75%); R_f 0.6 (4 : 1 : 0.1 chloroform–hexane–triethylamine); mp 41°C; IR (ν, cm^{-1}): 3420 (NH, pyrrol), 3124 (CH, pyrrol), 2920, 2857, 1468, 734 ($(CH_2)_{13}CH_3$), 1595, 824 (Ar), 1513, 1324 (C–C, pyrrol), 1262, 1031 (C–C); ^{1}H NMR: 0.89 (3 H, t, CH_3), 1.24 [20 H, m, $(CH_2)_{10}$),

1.85 [2 H, q, *J* 7, $OCH_2C\underline{H}_2CH_2(CH_2)_{10}CH_3$), 1.45 [2 H, q, *J* 7, $OCH_2CH_2C\underline{H}_2(CH_2)_{10}CH_3$), 3.97 [2 H, t, *J* 7, $OC\underline{H}_2CH_2CH_2(CH_2)_{10}CH_3$), 5.4 (1 H, s, *meso*-C<u>H</u>), 5.89–5.94(2 H, m, βCH), 6.17 (2 H, m, βCH), 6.68–6.72 (2 H, m, αCH), 6.75–6.82 (4 H, m, ArH), 7.9 (2 H, s, NH).

***meso*-Tetradecanoyloxyphenyl)dipyrromethane (IIb)** was synthesized as described for (**IIa**) from 4-tetradecanoyloxybenzaldehyde (0.25 g, 0.753 mmol) and pyrrol (3 ml, 43 mmol) in the presence of TFA (5.6 μl, 0.075 mmol). Ammonia was used for the treatment of reaction mixture. Yield of (**IIb**) 0.23 g, 55%); R_f 0.62 (B); mp 52°C; IR (ν, cm^{-1}): 3344 (CH, pyrrol), 3320, 1600 (CH, pyrrol), 2925; 2853 ($(CH_2)_{12}CH_3$), 1757 (C=O), 1555 (N–N, pyrrol); 1463 (Ar); 1200, 1025 (C–O); ^{1}H NMR: 0.89 (3 H, t, CH_3), 1.27 [2 H, m, $(CH_2)_{10}$), 1.91 (2 H, q, *J* 7, $OCOCH_2C\underline{H}_2(CH_2)_{10}$), 2.51 (2 H, t, *J* 7, $OCOC\underline{H}_2$), 5.47 (1 H, s, *meso*-CH), 5.76–5.91 (2 H, m, βCH), 6.12–6.25 (2 H, m, βCH), 6.65–6.75 (2 H, m, αCH), 7.0–7.30 (4 H, m, ArH), 7.91 (2 H, s, NH).

5,15-Bis(4-tetradecyloxyphenyl)-10,20-diphenylporphyrin (Va). Trifluoroboron etherate (16 μl, 0.12 mmol) and absolute ethanol (20 μl) were added to a solution of *meso*-(4-tetradecyloxyphenyl)dipyrromethane (0.33 g, 0.76 mmol) (**IIa**) and benzaldehyde (0.12 g, 1.14 mmol) in chloroform (50 ml) in argon atmosphere. The reaction mixture was stirred for 1 h, DDQ (0.16 g, 0.68 mmol) was added, and stirring was continued for 1 h at room temperature. Oligomeric products were separated by flash chromatography at system C elution. The target product (**IVa**) was purified by chromatography on a column eluted with system C; yield 0.2 g (54%); R_f 0.68 (chloroform); electron spectrum, (λ_{max}, nm ($\varepsilon \times 10^{-3}$): 418.0 (616), 515.2 (28.3), 550.6 (15.8), 590.4 (9.1), 646.2 (7.47); ^{1}H NMR: –2.72 (2 H, s, NH), 0.91 (6 H, t, $C\underline{H}_3$), 1.31 [40 H, m, $(C\underline{H}_2)_{10}$), 1.60 [4 H, q, *J* 7, $OCH_2CH_2C\underline{H}_2(CH_2)_{10}CH_3$), 2.01 [4 H, m, *J* 7, $OCH_2C\underline{H}_2CH_2(CH_2)_{10}CH_3$), 4.27 [4 H, t, *J* 7, $OC\underline{H}_2CH_2CH_2(CH_2)_{10}CH_3$), 7.78 [10 H, m, *J* 7, 10,20-(ArH)], 8.23 [8 I, m, *J* 7, 5,15-(ArH)], 8.85 (8 H, m, β-H, pyrrol); MS, *m/z*: calc. for $C_{72}N_4O_2H_{86}$: 1039, found: 1038.781 (M^+).

5,15-Bis(4-tetradecyloxyphenyl)-10,20-diphenylporphyrin (Vb) was synthesized like (**Va**) from *meso*-(4-tetradecanoyloxyphenyl)dipyrromethane (**IIb**) (0.225 g, 0.50 mmol), and benzaldehyde (0.08 g, 0.75 mmol) in chloroform (50 ml) in the presence of trifluoroboron etherate (11 μl, 0.08 mmol) and absolute ethanol (20 μl). The reaction mixture was stirred for 2 h in argon flow at room temperature; DDQ (0.103 g, 0.45 mmol) was added; and stirred at room temperature for 1 h. Oligomeric products were separated by flash chromatography at elution with dichloromethane. The target product was purified by chromatography on a column eluted with system C; yield 0.101 g (38%); R_f 0.6 (chloroform); electron spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$): 418.00 (530), 514.00 (24.8), 548.80 (16.1), 589.20 (14.4), 644.80 (7.18); ^{1}H NMR: –2.8 (2 H, s, NH), 0.89 (6 H, t, CH_3), 1.27 [40 H, m, $(CH_2)_{10}$), 1.91 (4 H, q, *J* 7, $OCOCH_2C\underline{H}_2(CH_2)_{10}$), 2.75 (4 H, t, *J* 7, $OCOC\underline{H}_2$), 7.48–7.75 [10 H, m, 10,20-(ArH)], 8.2 (8 H, m, 5,15-(ArH)), 8.85 (8 H, m, pyrrol); MS (*m/z*): calc. for $C_{72}N_4O_4H_{82}$: 1066, found: 1065.936 (M^+).

5,10,15,20-Tetra(4-tetradecyloxyphenyl)porphyrin (IVa). Trifluoroboron etherate (13 μl, 0.1 mmol) and absolute ethanol (30 μl) were added to a solution of 4-tetradecyloxybenzaldehyde (**Ia**) (0.319 g, 1 mmol) and pyrrol (0.067 g, 1 mmol) in dichloromethane (100 ml) in argon atmosphere at room temperature. The reaction mixture was strirred for 1 h in an inert gas flow at room temperature; DDQ (0.204 g, 0.09 mmol) was added, and stirring was continued for additional 1 h. Oligomeric products were separated by flash chromatography in system C. The target product (**IVa**) was purified by chromatography on a column eluted with system C; yield 0.12 g (33%); R_f 0.9 (chloroform); electron spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$): 418.2 (300); 515.4 (26.3); 550.4 (10.8); 590.6 (7.1); 646 (6.3); ^{1}H NMR spectrum: –3.36 (2 H, s, NH), 0.29 (12 H, t, CH_3), 0.91 (80 H, m, $(C\underline{H}_2)_{10}$), 1.02 (8 H, q, *J* 7, $OCH_2CH_2C\underline{H}_2(CH_2)_{10}CH_3$), 1.4 (8 H, q, *J* 7, $OCH_2C\underline{H}_2CH_2(CH_2)_{10}CH_3$), 3.65 [8 H, t, *J* 7 $OC\underline{H}_2CH_2CH_2(CH_2)_{10}CH_3$), 6.65–7.15 [16 H, m, *meso*-(ArH)], 8.25 (8 H, m, pyrrol); MS (*m/z*): calc. for $C_{100}N_4O_4H_{142}$: 1462, found: 1461.682 (M^+).

5,10,15,20-Tetra(4-tetradecanoyloxyphenyl)porphyrin (IVb) was synthesized as described for (**IVa**) from 4-tetradecanoyloxybenzaldehyde (0.332 g, 1 mmol) and pyrrol (0.067 g, 1 mmol) in dichloromethane (100 ml) in the presence of trifluoroboron etherate (13 μl, 0.1 mmol) and absolute ethanol (30 μl); yield 0.162 g (35%); electron spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$): 418.0 (380), 516.0 (23.6), 551.6 (11.2), 590.0 (7.4), 646.80 (6.42); ^{1}H NMR spectrum: –2.8 (2 H, s, NH), 0.89 (12 H, t, CH_3), 1.27 [80 H, m, $(CH_2)_{10}$), 1.91 (8 H, q, *J* 7, $OCOCH_2C\underline{H}_2(CH_2)_{10}$), 2.75 (8 HI, t, *J* 7, $OCOC\underline{H}_2$), 7.48–8.25 (16 H, m, *meso*-(ArH)], 8.85 (8 H, m, pyrrol); MS (*m/z*): calc. for $C_{72}N_4O_4H_{82}$: 1518, found: 1517.675 (M^+).

Inclusion of porphyrins in micelles. An aliquot of porphyrin dissolved in chloroform was added to LPPC (10 mg) in a 4 : 1 chloroform–methanol mixture. The solvents were removed in a vacuum, and the residue was thoroughly dried. The resulting thin film was intensively shaken with warm water (55°C) for 10 min. The samples contained 5 mg/ml (0.01 M) LPPC; porphyrin concentrations varied from 2×10^{-4} to -2.5×10^{-5} M. The fluorescence spectra were measured for the freshly prepared micellar dispersions. The samples remained transparent for a month after the preparation; no porphyrin precipitation was observed.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation for Basic Research, project no. 04-03-33064.

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