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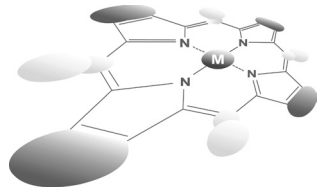

The synthesis of new potential photosensitizers [1–3]. Part 4. Photophysical properties of some monophenyltripyridyl-porphyrin derivatives

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ABSTRACT: Six monophenyltripyridylporphyrin derivatives were synthesized and characterized by spectroscopy in order to demonstrate their potential usefulness as photosensitizers for anticancer therapy purposes. Compounds **1** and **3–5** are amphiphilic, thus they may be suitable for transfer inside cells. Photochemical parameters such as fluorescence yield and singlet oxygen yield were determined. The former parameter does not exceed 10% which makes them unsuitable for photodynamic diagnosis (PDD). However, singlet oxygen yields are high and sufficient for these compounds to be considered as potential photodynamic therapy (PDT) photosensitizers.

KEYWORDS: photosensitizers, porphyrins, fluorescence, UV-vis, singlet oxygen, tetrapyrroles.

INTRODUCTION

We have been particularly interested by tetrapyrrole compounds suitable for PDD or PDT [1–3]. In particular, of interest to us have been their photochemical properties, including yield of singlet oxygen. The latter is generated during irradiation of the photosensitizer in the presence of triplet oxygen. This phenomenon, if occurring inside a cell or on a cell membrane, might result in cell death; as such it has been taken advantage of in anticancer therapy. Photofrin or Foscan, tetrapyrrole derivatives, are two well-known photosensitizers used for years in PDT.

The following derivatives: tripyridylmonohydroxyphenyl [4–6], tripyridylmonocarboxyphenyl [7–10] and tripyridylmonoaminophenylporphyrin [11–18] have been frequently reported and suggested as potentially photocytotoxic to cancer cells [5, 6, 9, 12]; as chemical shift reagents [7]; as multimodal agents for molecular imaging [10]; as biocatalysts [14, 16] and as compounds selectively binding to DNA [17, 18].

Compounds **1** and **2**, shown in Scheme 1, were earlier reported by us and had been characterized biologically as well as using crystallography and synchrotron radiation [19, 20].

Compound **1** demonstrated photodynamic activity causing cell death upon intracellular transfer and subsequent irradiation. Responsible for cell death was most likely singlet oxygen formed during the process. This phenomenon occurs for all porphyrins that can be transferred to the cell inside. Responsible for this process is the central porphyrin ring of the molecule. Substituents generally make introduction of porphyrin entity into biological material easier (or more difficult). A real challenge for synthesizing these compounds is such their modification that would allow them to be delivered only to cancer cells owing to their hydrophobic-hydrophilic nature or, perhaps, by using suitable carriers which they could be linked in various combinations. Our own attempts to obtain suitable porphyrin derivatives are geared towards use of liposomal carriers in which they could be "anchored." One of the features of a good photosensitizer is its easy procurement, *i.e*. simple synthetic procedure and uncomplicated structure. They ought to be very thoroughly characterized physico-chemically.

◊ SPP full member in good standing

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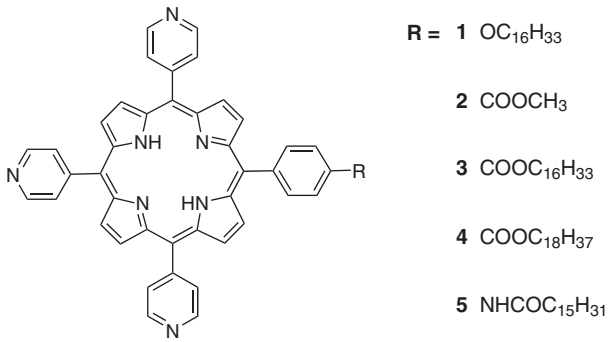

1-5

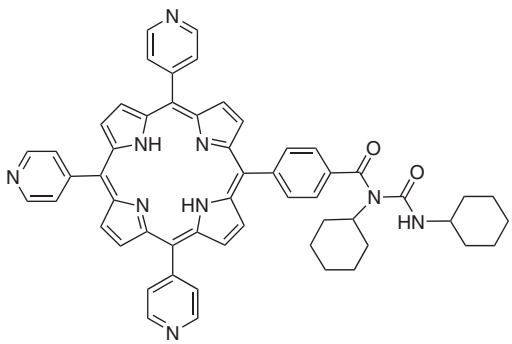

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Fig 1. Structures of **1–6**

EXPERIMENTAL

General

All chemical reagents were purchased from Aldrich or Acros and were used without further purification. NMR spectra were recorded in $CDCl_3$ using a Brucker spectrometer (400 MHz). The peaks were referenced to the residual $CHCl_3$ resonances in ^1H and ^{13}C NMR (7.26 and 77.16 ppm, respectively). IR spectra were recorded on Bio-Rad FTS-600. UV-vis spectra were recorded in dichloromethane solutions using a Genesys 6 (ThermoSpectronic) spectrophotometer. Fluorescence spectra of the samples were taken on Varian Eclipse Cary — fluorescence spectrophotometer. ESI MS spectra were acquired using a LCQ DUO FINNINGAN THERMOQUEST spectrometer. The compounds to be studied were dissolved in a dichloromethane-methanol or acetone solutions and introduced into the source through a capillary at the rate of 20 μL.min^{-1}. The evaporation was assisted by an outflow of nitrogen heated at 200 °C. The ESI voltage 4.5 kV, current 58–60 μA, capillary voltage was 10.5 V, capillary temperature — 200 °C, collision gas — helium. For all compounds full-scan positive ion mass spectra were acquired. High resolution mass spectra were recorded on Bruker AD-604 spectrometer using electrosprey technique.

Synthesis

5-(4-Hexadecyloxyphenyl)-10,15,20-tri(4-pyridyl) porphyrin (1). 4-Hexadecyloxybenzaldehyde (3.46 g, 0.01 mol), 4-pyridylaldehyde (3.21 g, 0.03 mol) were dissolved in 300 mL of propionic acid and heated to reflux. Pyrrole (2.68 g, 0.04 mol) was added and the resulting mixture was heated under reflux for 2 h. 250 mL of propionic acid was removed by distillation. Rest of propionic acid was neutralized by saturated solution of sodium carbonate and the resulting mixture was extracted by dichloromethane. Organic layer was washed with water (5 × 100 mL) and dried with anhydrous $MgSO_4$. Dichloromethane was evaporated and the residue was chromatographed on silica gel with chloroform-ethyl acetate (2:1, v/v) mixture as eluent. Yield 0.21 g (2.5%). Anal. calcd. for. $C_{57}H_{59}N_7O$: C, 79.78; H, 6.93; N, 11.43. Found C, 79.49, H, 6.95, N, 11.20. ^1H NMR (400 MHz, $CDCl_3$): δ_H, ppm 9.02, 8.14 (dd, 12H, J = 5.4 Hz), 8.94, 8.78 (dd, 4H), 8.82 (bs, 4H), 8.07, 7.27 (dd, 4H, J = 8.4 Hz), 4.23 (t, 2H), 1.96 (q, 2H), 1.45 (q, 2H), 1.40–1.20 (m, 22H), 0.76 (t, 3H), -2.88 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ_C, ppm 14.2, 22.7, 26.3, 29.4, 29.6, 29.7, 29.8, 31.9, 68.4, 112.9, 116.8, 117.4, 121.9, 129.4, 133.5, 135.7, 148.2, 150.2, 159.3. MS (ESI): *m/z* 858.7 (calcd. for $[M + H]^+$ 858.5). HRMS (ESI^+): *m/z* calcd. for $[M + H]^+$ 858.4853, found 858.4746.

5-(4-Methoxycarbonylphenyl)-10,15,20-tri(4-pyridyl)porphyrin (2). 4-Methoxycarbonylbenzaldehyde (3.28 g, 0.02 mol), 4-pyridylaldehyde (6.43 g, 0.06 mol) were dissolved in 300 mL of propionic acid and heated to reflux. Pyrrole (5.37 g, 0.08 mol) was added and the resulting mixture was heated under reflux for 2 h. 250 mL of propionic acid was removed by distillation. Rest of propionic acid was neutralized by saturated solution of sodium carbonate and the resulting mixture was extracted by dichloromethane. Organic layer was washed with water (5 × 100 mL) and dried with anhydrous $MgSO_4$. Dichloromethane was evaporated and the residue was chromatographed on silica gel with chloroform-methanol (3:1, v/v) mixture as eluent. Yield 0.64 g (4.7%). Anal. calcd. for. $C_{43}H_{29}N_7O_2$: C, 76.43; H, 4.33; N, 14.51. Found C, 76.08, H, 4.25, N, 14.80. ^1H NMR (400 MHz, $CDCl_3$): δ_H, ppm 9.07, 8.20 (dd, 12H, J = 5.4 Hz), 8.86–8.83 (m, 8H), 8.30, 8.20 (dd, 4H, J = 10 Hz), 4.1 (s, 3H), -2.89 (bs, 2H). MS (ESI): *m/z* 676.4 (calcd. for $[M + H]^+$ 676).

5-(4-Hexadecyloxycarbonylphenyl)-10,15,20-tri(4-pyridyl)porphyrin (3). 5-(4-Carboxyphenyl)-10,15,20-tri(4-pyridyl)porphyrin was obtained by hydrolysis of **2** in the solution of KOH in DMF in 85%. 5-(4-Carboxyphenyl)-10,15,20-tri(4-pyridyl)porphyrin (0.01 g, 0.015 mmol), 4-(dimethylamino)pyridine (DMAP) (0.0035 g, *ca* 0.03 mmol) and 1.5 mL of 0.01 M dicyclohexyl carbodiimide (DCC) solution (0.015 mmol) dissolved in 5 mL of dichloromethane were refrigerated for 2 days. After that haxadecan-1-ol (0.004 g, ~0.015 mmol) dissolved in 5 mL of dichloromethane was added and

the resulting mixture was refrigerated for next 4 days. Finally the mixture was stirred at room temperature for 2 days. 10 mL of dichloromethane was added to the mixture and the resulting solution was washed with water (2 × 20 mL) and dried with anhydrous $MgSO_4$. Dichloromethane was evaporated and the residue was separated on preparative silica gel plates with chloroform-methanol (200:3, v/v) as eluent. Yield 0.006 g (40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 9.04, 8.18 (dd, 12H, J = 5.5 Hz), 8.89–8.85 (m, 8H), 8.50, 8.32 (dd, 4H, J = 8 Hz), 4.54 (t, 2H), 1.94 (q, 2H), 1.61 (q, 2H), 1.48 (q, 2H), 1.35–1.21 (m, 22H), 0.87 (t, 3H), -2.88 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ_C, ppm 14.2, 22.7, 24.9, 26.2, 29.6, 29.7, 29.8, 31.2, 65.7, 117.2, 117.4, 120.6, 128.1, 129.6, 130.5, 132.4, 134.5, 145.9, 147.6, 149.9, 150.8, 166.7. MS (ESI): *m/z* 886 (calcd. for $[M + H]^+$ 886). HRMS (ESI^+): *m/z* calcd. for $[M + H]^+$ 886.4803, found 886.4706.

5-(4-Octadecyloxycarbonylphenyl)-10,15,20-tri(4-pyridyl)porphyrin (4). This compound was obtained similar to **3**, using octadecan-1-ol instead of hexadecane-1-ol. Product was chromatographed on silica gel with chloroform-methanol (200:3, v/v) mixture as eluent. Yield 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 9.09, 8.18 (dd, 12H, J = 5.5 Hz), 8.90-8.85 (m, 8H), 8.50, 8.30 (dd, 4H, J = 10.05), 4.54 (t, 2H), 1.95 (q, 2H), 1.61 (q, 2H), 1.38–1.21 (m, 28H), 0.87 (t, 3H), -2.86 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ_C, ppm 14.1, 22.7, 26.2, 28.9, 29.1, 29.3, 29.4, 29.6, 29.7, 31.9, 65.6, 117.4, 117.6, 120.2, 128.0, 129.3, 130.4, 131.3, 134.5, 146.1, 148.3, 149.9, 166.9. MS (ESI): *m/z* 914 (calcd. for $[M + H]^+$ 914). HRMS (ESI^+): *m/z* calcd. for $[M + H]^+$ 914.5116, found 914.5026.

5-(4-Hexadecanamidophenyl)-10,15,20-tri(4-pyridyl)porphyrin (5) was synthesized according to [21]. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 9.08–9.04 (m, 6H), 8.87 (bs, 4H), 8.98, 8.83 (dd, 4H), 8.20–8.14 (m, 8H), 8.00 (d, 2H), 7.81 (s, 1H), 2.6 (t, 2H), 1.91 (q, 2H), 1.41–1.28 (m, 24H), 0.89 (t, 3H), -2.86 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ_C, ppm 14.1, 22.7, 25.4, 25.6, 25.8, 29.4, 29.5, 29.6, 29.7, 31.9, 34.5, 38.1, 117.3, 118.1, 127.4, 128.2, 129.6, 131.0, 132.4, 135.2, 137.9, 138.3, 140.4, 147.6, 149.9, 171.9. MS (ESI): *m/z* 871 (calcd. for $[M + H]^+$ 871). HRMS (ESI^+): *m/z* calcd. for $[M + H]^+$ 871.4806, found 871.4706.

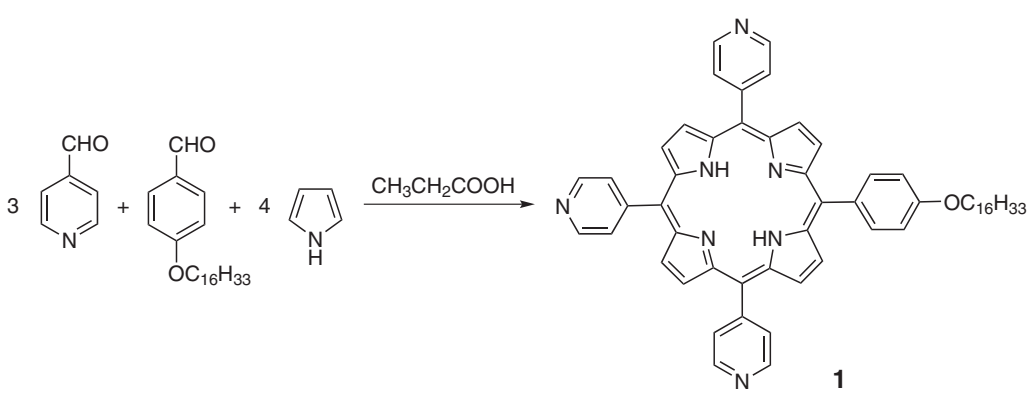
N-[5-(4-Carbonylphenyl)-10,15,20-tri(4-pyridyl) porphyrin]-N,N′-dicyclohexylurea (6). This compound was isolated (*ca*. 20% yield) during preparative chromatographic separation of compounds **3** and **4**. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 9.06, 8.17 (dd, 12H, J = 6 Hz), 8.88–8.84 (m, 8H), 8.30, 8.02 (dd, 4H, J = 10.05 Hz), 6.27 (m, 1H), 4.43 (m, 1H), 3.75 (m, 1H), 2.20–1.20 (m, 20H), -2.87 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ_C, ppm 24.7, 25.4, 25.5, 26.4, 29.7, 30.9, 32.7, 50.0, 57.3, 117.4, 117.6, 120.1, 125.6, 129.4, 134.6, 136.8, 144.1, 148.2, 150.0, 150.1, 154.4, 170.7. MS ESI: *m/z* 868 (calcd. for $[M + H]^+$ 868). HRMS (ESI^+): *m/z* calcd. for $[M + H]^+$ 868.4081, found 868.3965. Anal. calcd. for $C_{55}H_{49}N_9O_2$:C, 76.10; H, 5.69; N, 14.52. Found C, 76.02, H, 5.80, N, 14.76.

5,10,15,20-Tetra(9-phenanthrenyl)porphyrin (7). This compound was synthesized according to [26]. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 8.96 (t, 8H), 8.64 (bs, 8H), 8.60 (d, 4H), 8.05 (d, 4H), 7.85 (t, 4H), 7.76 (t, 4H), 7.63 (t, 4H), 7.40–7.20 (m, 8H), -2.1 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ_C, ppm 117.7, 122.5, 122.8, 126.3, 126.7, 127.3, 127.4, 129.0, 129.6, 130.0, 130.1, 130.7, 130.8, 133.5, 133.6, 133.8, 136.2, 137.5, 137.6. MS (ESI): *m/z* 1015 (calcd. for $[M + H]^+$ 1015). HRMS (ESI^+): *m/z* calcd. for $[M + H]^+$ 1015.3795, found 1015.3678.

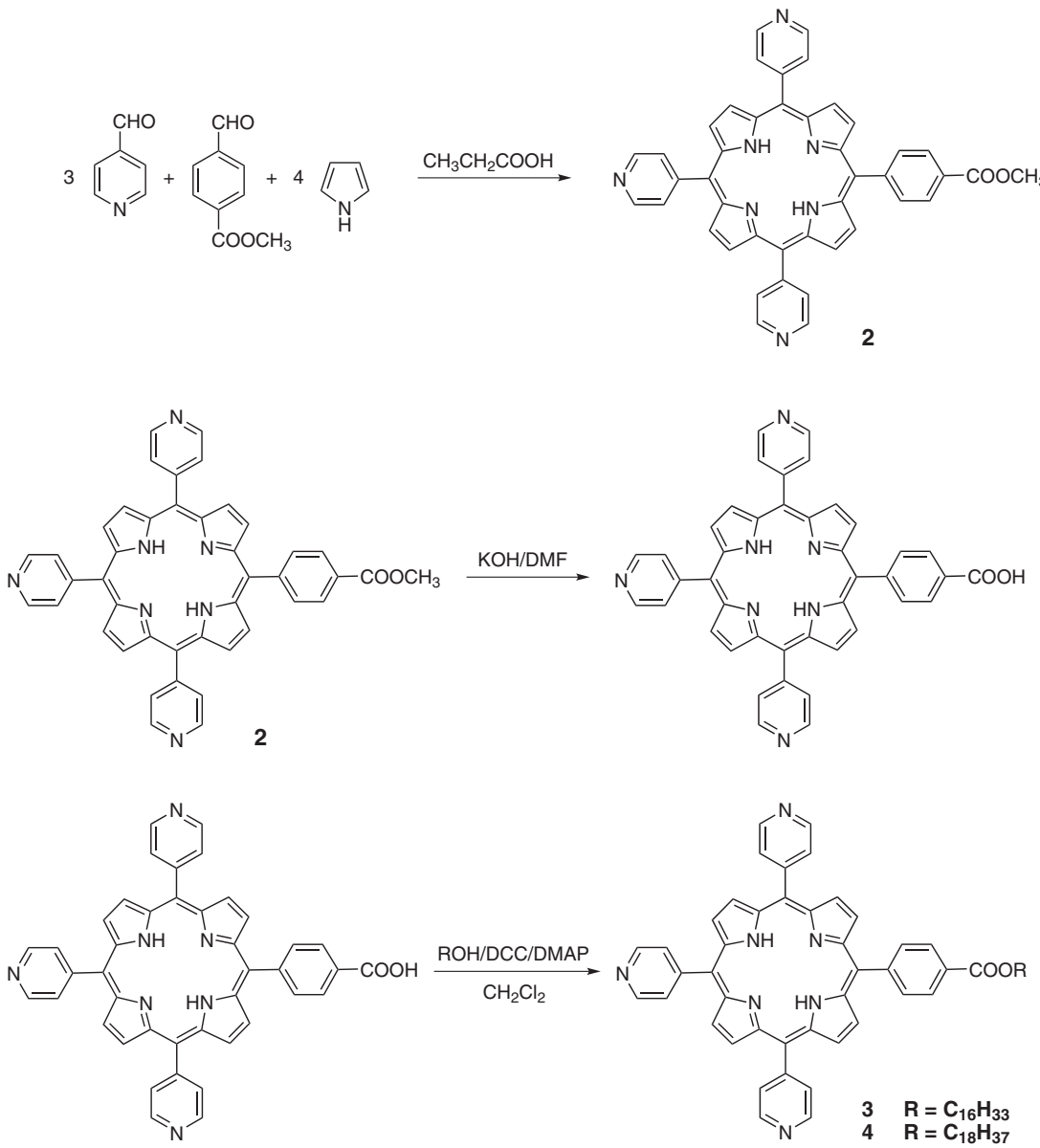
RESULTS AND DISCUSSION

Synthesis

Compounds **1**–**5** were obtained in a series of reactions shown in Schemes 1–3. All of them display asymmetry and have three pyridine substituents and a phenyl one substituted in *para*-position. Derivatives of this kind are obtained in reactions of mixed aldehydes with pyrrole (yields of these reactions are most frequently very low since six various porphyrin derivatives are obtained) or by modifying functional groups or



Scheme 1. Synthesis of compound **1**



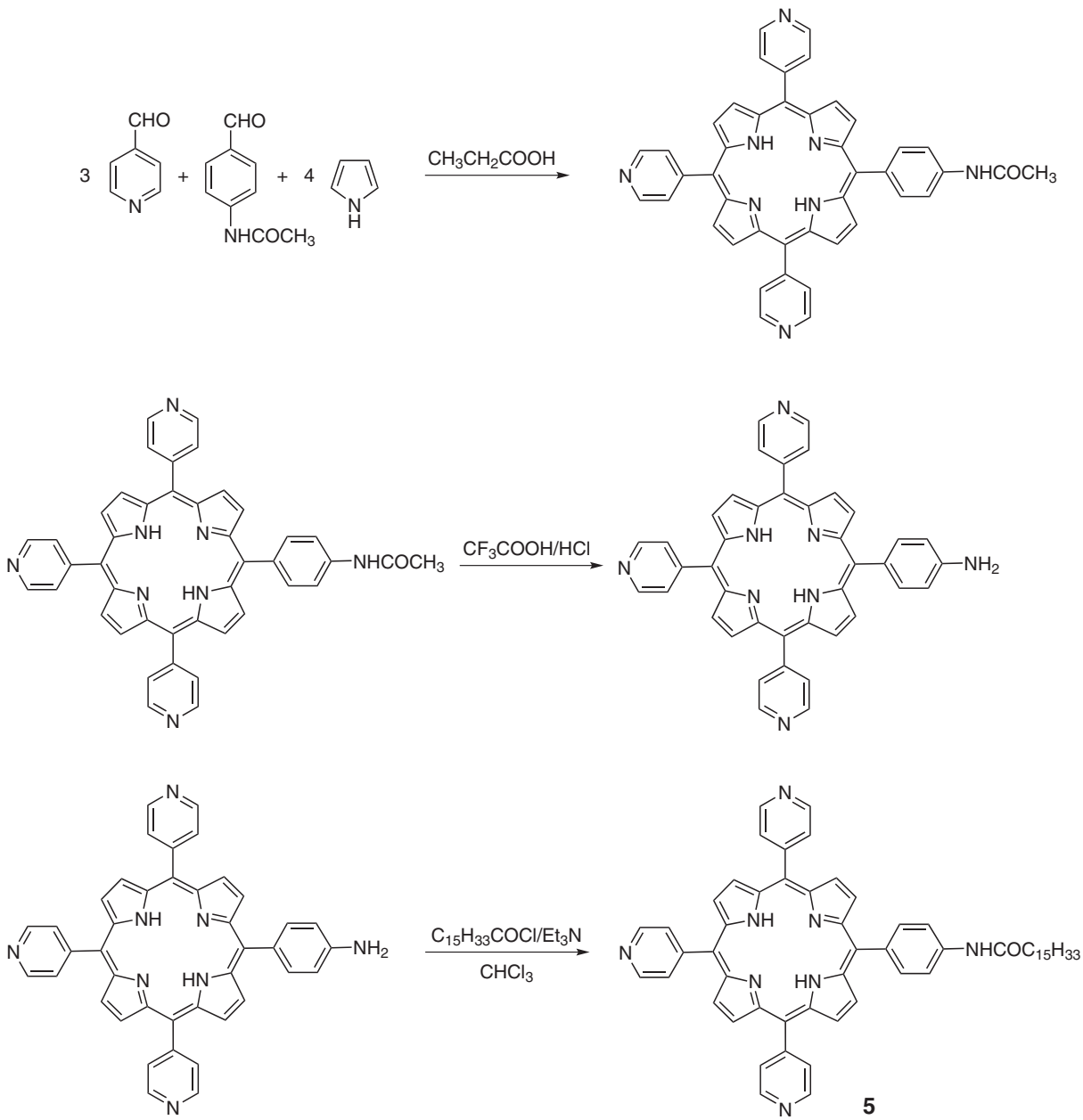
Scheme 2. Synthesis of compounds **2**, **3** and **4**

porphyrin-type compounds (in these cases yields are higher since one of the substrates is porphyrin). Compound **1** was obtained directly in the reaction of mixed aldehydes (4-hexadecyloxybenzaldehyde and 4-pyridylaldehyde) with a yield of 2.5%. Likewise, compound **2** was obtained (from 4-pyridylaldehyde and 4-methoxycarbonylbenzaldehyde) with *ca*. 5% yield. Compound **2** was the starting point for obtaining 5-(4-carboxyphenyl)-10,15,20-tri(4-pyridyl)porphyrin *via* hydrolysis of ester moiety. The carboxylic derivative was transformed by esterification, into compounds **3** and **4** with *ca*. 40% yield. Compound **5** was obtained in a three-stage procedure reported in [21] and shown in Scheme 3.

Compound **6** was obtained (accidentally) with a good yield (*ca*. 20% with respect to the main product) during preparation of a mixture of carboxyporphyrin and DCC. In the case of carboxylic derivatives of tetraphenylporphyrin greater yield is obtained for stable N-acylurea species than for O-acylurea [22]. This type of reaction when making esters or amides is not favorable since it lowers total yield of the reaction. This compound is a stable product with defined structure. We therefore decided to check its physicochemical and photooptical properties.

UV-vis spectra

All porphyrin conjugates show typical electronic spectra. A Soret band appears near 420 nm and four less intense Q-bands are present at 513, 548, 589 and 645 nm



Scheme 3. Synthesis of compound **5**

with an *ethio* outline. For all the examined compounds there is little difference in extinction coefficients. The UV-vis data are shown in Table 1.

IR spectra

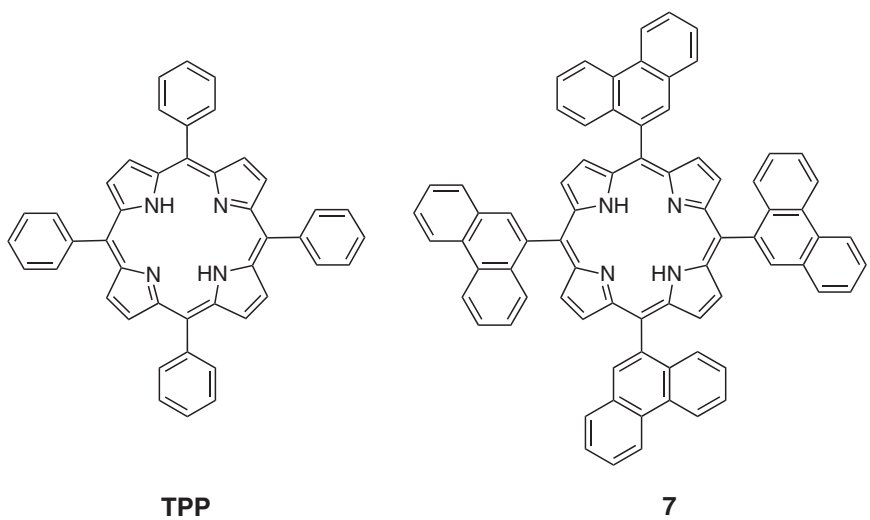
Porphyrin compounds show very strong absorption in the infrared range. The best solution to obtain high-quality spectra is to use ATR (Attenuated Total Reflection) technique. Our spectra were recorded for powdered sample using Bio-Rad FTS-600 spectrometer equipped with ATR Miracle accessory and KRS5 lenses. All samples showed presence of vibrations in the 3315–3331 cm^{-1} range which corresponds to vibration values for N–H groups present in the porphyrin ring. In the case of compounds **5** and **6** with additional amide groups, there are additional vibrations of N–H groups at 3349 and 3442 cm^{-1}, respectively. In spectra of all compounds with pyridine substituents, characteristic strong stretching vibrations $\nu_{Cpyr\text{-}Cpyr}$ are seen in a very narrow range (1590–1609 cm^{-1}).

Fluorescence and singlet oxygen

Fluorescence spectra of the investigated compounds, as well as tetraphenylporphyrin (TPP) are shown in

Table 1. UV-vis spectra of compounds **1–7** [λ_{nm} (log ε)] in chloroform solutions

Derivatives	λ_{Soret}	$Q_y(1–0)$	$Q_y(0–0)$	$Q_x(1–0)$	$Q_x(0–0)$
1	420 (5.33)	514 (4.26)	549 (3.86)	591 (3.74)	648 (3.46)
2	419 (6.94)	513 (4.24)	547 (3.76)	588 (3.72)	645 (3.36)
3	417 (5.51)	513 (4.10)	548 (3.62)	588 (3.61)	643 (3.23)
4	419 (5.73)	513 (4.28)	546 (3.86)	589 (3.80)	645 (3.46)
5	420 (5.61)	514 (4.17)	549 (3.75)	589 (3.63)	647 (3.32)
6	419 (5.38)	513 (4.18)	547 (3.72)	589 (3.66)	646 (3.36)
7	427 (5.74)	516 (4.35)	550 (3.65)	591 (3.81)	648 (3.18)



TPP **7**

Fig 2. Structures of tetrakis-5,10,15,20-phenylporphyrin (**TPP**) and tetrakis-5,10,15,20-(9 phenanthrenyl)porphyrin (**7**)

Table 2. Selected IR data for compounds **1–7** (cm^{-1})

	1	**2**	**3**	**4**	**5**	**6**	**7**
νN-H	3315	3320	3324	3331	3320	3315	3315
$\nu_{sym}CH_2$	2853	—	2851	2851	2851	2863	—
$\nu_{asym}CH_2$	2924	—	2918	2915	2921	2930	—
νC=O	—	1721	1720	1719	1716	1724	—
$\nu C_{pyr}C_{pyr}$	1593	1592	1609	1590	1592	1591	—

Table 3. Emission bands for all the compounds occur at 650 ± 2 and 717 ± 2 nm. Fluorescence yields of these compounds, determined by a comparative method (with TPP used as a reference) did not exceed a 10% threshold. Such values preclude use of these compounds in photodynamic diagnostics; at the same time it suggests that they can generate greater amounts of singlet oxygen since there is a greater probability of intercombinatory transitions responsible for this process.

Singlet oxygen quantum yield was determined in an identical manner as described in part 2 of our publication. To this purpose we used laser flash photolysis and measurement of characteristic emission of singlet oxygen at *ca*. 1280 nm. This is a relative value and in our case we made use of a previously determined singlet oxygen quantum yield for TPP (Φ_Δ = 0.62) [23] as a reference value. Samples of compounds in toluene with absorbance of ~0.35 [Soret band] were subjected to oxygen saturation for *ca*. 2 min and then they were excited with a laser flash of λ = 355 nm. Emission spectrum of samples was recorded in the 1245–1320 nm range. Measurements were repeated 30–50 times. Values of relative effectiveness of generating singlet oxygen for all the compounds are comparable and average *ca*. 60%.

Table 3. Fluorescence emission maximums, wavelengths (Λ_{max}), fluorescence quantum yields (Δ_F), Stokes shifts (nm) between the Q(0–0) and Q_x(0–0) band and quantum yield of singlet oxygen Φ_Δ for compound **1**–**7** and tetraphenylporphyrine (TPP)

Photosensitizers	Q(0–0)	Q(0–1)	Φ_F (420 nm)	Φ_Δ	Stokes shift
1	651	718	0.09	0.61	3
2	648	716	0.10	0.60	3
3	651	717	0.08	0.61	8
4	651	716	0.08	0.61	6
5	651	717	0.08	0.59	4
6	650	717	0.10	0.62	4
TPP	651	719	0.100	0.62	—
7	651	719	0.09	0.63	3

This value indicates that they may be potentially useful in PDT.

For compound **1** oxygen quantum yield was earlier determined by us using a different method and 1-H-phenalen-1-one as a reference [19]. The value of Φ_Δ determined with this method was 0.66, so it does not differ substantially from the value determined and cited in this paper. Both determined values are higher than that of Photofrin (Φ_Δ = 0.32 [19]). Oxygen quantum yield determined in the same way for tetra-phenanthrenylporphyrin (**7**) has a similar value to those of the remaining compounds discussed in this paper, to TPP reference (Φ_Δ = 0.66, determined acc. to [24]), and to tetra-α-naphthylporphyrin (Φ_Δ = 0.97, determined acc. to [25]). Both Φ_Δ values were measured by a photoacoustic method.

Stokes shift, which characterizes magnitude of the shift between Q (0–0) band of the fluorescence spectrum and Q_x (0–0) band of the absorbance spectrum is for our compounds small. This can reflect small structural changes occurring in porphyrin molecules during excitation process.

Mass spectra

The ESI mass spectra were recorded using LCQ DUO FINNINGAN THERMOQUEST spectrometer. The compounds to be studied were dissolved in dichloromethane/methanol or acetone solutions and introduced into the source through a capillary at the rate of 20 μL.min^{-1}. Only positive mode electrospray ionization method could be used in analysis of porphyrins **1**–**7**. The base peaks corresponding to $[M + H]^+$ ions for all compounds were observed (data are in the Experimental section accompanying description of particular compounds). No presence of fragmentary ions was detected. Peaks corresponding to the formation of ion clusters were not observed.

Spectra of this kind allow determining in a very simple manner approximate purity of the obtained compound which may be important for procurement on a larger scale.

CONCLUSION

Porphyrins obtained by us with three pyridine substituents and one substituent of hydrophobic nature show similar photochemical properties. These compounds might be used as potential photosensitizers in PDT since they show great capacity to form singlet oxygen which is one of the most important factors mediating targeted cell death. Low fluorescence quantum yield suggests that they are not suitable for PDD. The hydrophobic-hydrophilic nature of the obtained compounds, on the other hand, makes feasible using liposomes as their carrier for *in vivo* applications. Our observations suggest that these compounds are stable solids and their solutions in neutral solvents do not show changes in UV spectra after storage for several days at room temperature.

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