New strategy for targeting of photosensitizers. Synthesis of glycodendrimeric phenylporphyrins, incorporation into a liposome membrane and interaction with a specific lectin.

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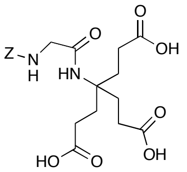
Electronic Supplementary Informations

Chemistry

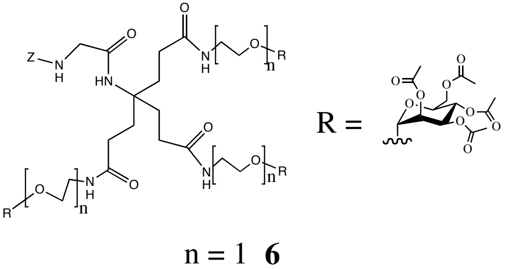
Compound 5 :



5

Compound **4** (2.9 g, 4.78 10^{-3} mole) in methylene chloride (120 mL) and trifluoroacetic acid (60 mL) was stirred one hour at room temperature then concentrated under vacuum. The crude product was diluted in methylene chloride, washed with aqueous sodium hydroxide (5 %). Aqueous phase was washed with methylene chloride (twice) and acidified by chlorhydric acid. The white precipitate was filtred, washed with water and dried under vacuum. Pure product was obtained as white crystals and used without other purification (1.926, yield 92 %), melting point 113 °C (pasty). Anal. ($C_{20}H_{26}N_2O_9$), 1.5 H_2O calc C 51.61, H 6.28, N 6.02 found C 51.86; H 6.20; N 6.21. ^{1}H NMR ($MeOD_{d4}$) δ (ppm) : 7.38-7.27 (m, 5 H, benzyloxycarbonyl), 5.10 (s, 2 H, CH_2 benzyloxycarbonyl), 3.70 (s, 2 H, HC glycine), 2.26 (t, 6 H, CH_2COOH), 2 [t, 6 H, $(CH_2)_3$-C)]. ^{13}C NMR ($MeOD_{d4}$) δ (ppm) : 176.8 (COOH), 171.1 (CO glycine), 159 (OCO benzyloxycarbonyl), 137.7 (C_1 benzyloxycarbonyl), 128.8 (*para*- and *meta*-benzyloxycarbonyl), 67.6 (CH_2 benzyloxy-carbonyl), 58.7 (C-NH), 45 (CH_2 glycine), 30.3 [$(CH_2)_3$-C], 29 (CH_2CO).

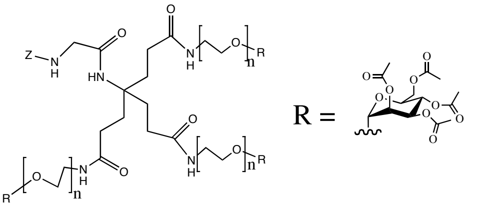
Compound 6 :



n = 1 **6**

Dry DMF (20 mL) was added on a mixture of triacid **5** (100 mg, $2.28\ 10^{-4}$ mol), 2-amino-ethoxy-O-2',3',4',6'-tetraacetyl-α-D-mannopyranose tosylate (0.398 g, $6.84\ 10^{-4}$ mol), HATU (0.260g, $6.84\ 10^{-4}$ mol) and DIPEA (1 mL). The solution was stirred under argon overnight at room temperature. The solution was concentrated under vacuum. Crude product was dissolved in methylene chloride, washed with water, diluted aqueous chlorhydric acid, water, aqueous sodium hydroxide (5 %), water and dried on sodium sulfate then filtered and concentrated. Pure titled compound **6** was obtained after crystallization from a mixture of methylene chloride/ether as brown powder (yield 70 %). Anal. ($C_{68}H_{95}N_5O_{36}$), 3 H_2O calc C 50.65, H 6.31, N 4.34 found C 50.73; H 6.13; N 4.41. ^{1}H NMR ($CDCl_3$) δ (ppm) : 7.35 (m, 5 H, benzyloxycarbonyl), 6.62 (broad t, 3 H, CH_2-NH), 5.90 (broad t, 1 H, NH glycine), 5.32 (dd, 3 H, HC_3), 5.28 (dd, 3 H, HC_4), 5.25 (dd, 3 H, HC_2), 5.12 (s, 2 H, CH_2 benzyloxycarbonyl), 4.90 (d, 3 H, J = 2 Hz, HC_1), 4.2 (dd, 3 H, J = 5 and 12 Hz, H_aC_6), 4.12 (dd, 3 H, J = 12 Hz, H_bC_6), 4.04 (m, 3 H, HC_5), 3.78 (m, 3 H, CH_{2a}-O-mannosyl), 3.72 (d, 2 H, HC glycine), 3.67 (m, 3 H, CH_{2b}-O-mannosyl), 3.39 (m, 6 H, CH_2-NH), 2.21 [m, 6 H, $(C\underline{H}_2)_3$-C], 2.16 (s, 9 H, CH_3CO), 2.10 (s, 9 H, CH_3CO), 2.05 (s, 9 H, CH_3CO), 2.00 (s, 9 H, CH_3CO), 2.00 (m, 6 H, CH_2CO). ^{13}C NMR ($CDCl_3$) δ (ppm) : 173.30 ($COCH_3$), 170.74 ($COCH_3$), 170.27 ($COCH_3$), 170.11 ($COCH_3$), 169.75 ($COCH_3$), 168.67 (CO glycine), 156.86 (OCO benzyloxycarbonyl), 136.42 (C_1 benzyloxycarbonyl), 128.51 (*ortho*-benzyloxycarbonyl), 128.12 (*para*-benzyloxycarbonyl), 127.94 (*meta*-benzyloxycarbonyl), 97.56 (C_1), 69.62 (C_2), 69.08 (C_3), 68.42 (C_5), 67.09 (CH_2-O-mannosyl), 66.90 (CH_2 benzyloxycarbonyl), 66.17 (C_4), 62.53 (C_6), 58.18 (C-NH), 45 (CH_2 glycine), 39.34 (CH_2-NH), 31 (CH_2CO), 30.63 [$(CH_2)_3$-C], 20.77 (CH_3), 20.71 (CH_3).

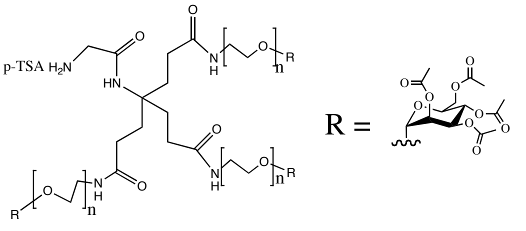
Compound 7:



n = 2 **7**

Prepared as **6** from 2-amino-ethoxy-ethoxy-O-2',3',4',6'-tetraacetyl-α-D-mannopyranose tosylate. Pure titled compound was obtained after crystallization from a mixture of methylene chloride/ether as brown powder (yield 72 %). Anal. ($C_{74}H_{107}N_5O_{39}$), $3H_2O$ calc C 50.94, H 6.53, N 4.01 found C 50.98; H 6.55; N 3.84. ^{1}H NMR ($CDCl_3$) δ (ppm) : 7.35 (m, 5 H, benzyloxycarbonyl), 7.24 (broad s, 1 H, NH-C), 6.62 (broad t, 1 H, NH-CH_2), 5.90 (broad t, 1 H, NH-glycine), 5.32 (m, 3 H, HC_3), 5.28 (m, 3 H, HC_4), 5.25 (m, 3 H, HC_2), 5.12 (s, 2 H, CH_2-benzyloxycarbonyl), 4.90 (s, 3 H, HC_1), 4.27 (dd, 3 H, J = 12 and 5 Hz, H_aC_6), 4.12 (d, 3H, J = 12 Hz, H_bC_6), 4.04 (m, 3 H, HC_5), 3.78 (m, 3 H, CH_{2a}-O-mannosyl), 3.74 (d, 2 H, HC-glycine), 3.67 (m, 3 H, CH_{2b}-O-mannosyl), 3.63 (m, 6 H, CH-O), 3.52 (m, 9H, NH-CH_{2a} and NH-CH_2-CH_2-O), 3.39 (m, 3 H, (m, 9H, NH-CH_{2b}), 2.21 (m, 2 H, CH_2), 2.16 (s, 9 H, $COCH_3$), 2.10 (s, 9 H, $COCH_3$), 2.05 (s, 9 H, $COCH_3$),), 2.00 (m, 9 H, $COCH_3$), 2.00 (m, 6 H, CH_2-CO). ^{13}C NMR ($CDCl_3$) δ (ppm) : 173.30 ($COCH_3$), 170.74 ($COCH_3$),170.27 ($COCH_3$), 170.11 ($COCH_3$), 169.75 ($COCH_3$), 168.67 (CO glycine), 156.86 (COO-Cbz), 136.42 (C_1 benzyloxycarbonyl), 128.51 (*ortho*-benzyloxycarbonyl), 128.14 (*para*-benzyloxycarbonyl), 127.94 (*meta*-benzyloxycarbonyl), 97.56 (C_1), 69.84 (C-NH), 69.62 (C-O-mannosyl), 69.62 (C_2), 69.08 (C_3), 68.42 (C_5), 67.09 (C-O-mannosyle), 66.90 (CH_2- benzyloxycarbonyl), 66.17 (C_4), 62.53 (C_6), 58.18 [C-(NH)], 45 (HC glycine), 39.34 [CH-(NH)], 21 (CO-CH_2), 30.63 (HC-C), 27.71 (CH_3).

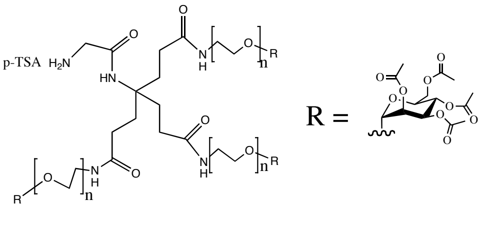
Compound 8 :



n = 1 **8**

Product **6** (0.5 g, 0.32 mmol), palladium on activated carbon (Pd/C 10 %, 270 mg) and *para*-toluenesulfonic acid (100 mg) were dissolved in methanol (200 mL). The solution was stirred under hydrogen atmosphere (3 bars) at room temperature for 24 hours. The suspension was filtered under celite and concentrated under vacuum. Pure product was crystallized from methylene chloride/ether mixture. 413 mg of yellow crystals was obtained by filtration and dried under vacuum (yield 96 %). Anal. ($C_{67}H_{97}N_5O_{37}S$), 4 H_2O calc C 48.23, H 6.34, N 4.20, found C 47.81; H 6.13; N 4.11. ^1H NMR ($CDCl_3$) δ (ppm) : 7.66 (d, 2 H, J = 7.1 Hz, *meta*-phenyl), 7.20 (d, 2 H, J = 7 Hz, *ortho*-phenyl), 5.24 (m, 9 H, $HC_{2,3,4}$), 4.81 (s, 3 H, HC_1), 4.26 (d, 3 H, J = 11 Hz, H_aC_6), 4.09 (d, 3 H, J = 11 Hz, H_bC_6), 3.97 (d, 2 H, HC glycine), 3.97 (m, 3 H, HC_5), 3.69 (m, 3 H, HC_a-O-mannosyl), 3.46 (m, 3 H, HC_a-NH), 3.46 (m, 3 H, HC_b-O-mannosyl), 3.28 (m, 3 H, HC_b-NH), 2.34 (s, 3 H, CH_3-phenyl), 2.20 [m, 6 H, HC-(C)], 2.13 (s, 9 H, CH_3CO), 2.09 (s, 9 H, CH_3CO), 2.04 (s, 9 H, CH_3CO), 2.00 (m, 6 H, HC-CO), 1.97 (s, 9 H, CH_3CO). ^{13}C NMR ($CDCl_3$) δ (ppm) : 174.45 ($COCH_3$), 170.82 ($COCH_3$), 170.51 ($COCH_3$), 170.32 ($COCH_3$), 169.65 ($COCH_3$), 166.17 (CO glycine), 141.61 (C-SO_3H), 140.52 (*para*-phenyl), 129.01 (*meta*-phenyl), 125.84 (*ortho*-phenyl), 97.35 (C_1), 69.39 ($C_{2,3,4}$), 68.53 (C_5), 66.53 (C-O-mannosyl), 65.84 ($C_{2,3,4}$), 62.36 (C_6), 58.85 (C-NH), 41.54 (CH_2-glycine), 38.73 (C-NH), 30.86 (CO-CH_2), 30.37 (CH_2-C), 21.25 (CH_3-phenyl), 20.87 (CH_3), 20.70 (CH_3).

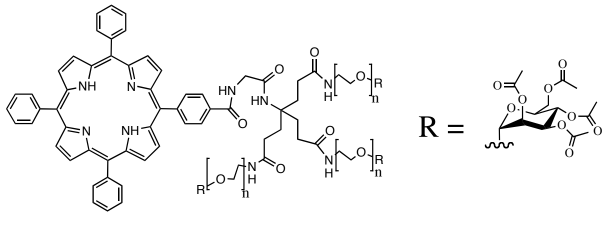
Compound 9 :



n = 2 **9**

Prepared as compound **8** from **7**. Pure title compound was obtained as white crystals in yield 82 %. Anal. ($C_{73}H_{109}N_5O_{40}S$), 10 H_2O calc C 45.93, H 6.81, N 3.67, found C 46; H 6.28; N 3.87. ^1H NMR ($CDCl_3$) δ (ppm) : 5.29 (m, 9 H, $HC_{2,3,4}$), 4.89 (s, 3 H, HC_1), 4.27 (m, 3 H, H_aC_6), 4.07 (m, 6 H, H_bC_6), 4.07 (m, 3 H, HC_5), 3.64 (m, 6 H, HC-NH), 3.64 (m, 6 H, HC-O-mannosyl), 2.37 (m, 6 H, HC-C), 2.16 (s, 9 H, CH_3CO), 2.11 (s, 9 H, CH_3CO), 2.06 (s, 9 H, CH_3CO), 2 (s, 9 H, CH_3CO), 2 (m, 6 H, CH-CO). ^{13}C NMR ($CDCl_3$) δ (ppm) : 174.09 (CO), 170.77 ($COCH_3$), 170.21 ($COCH_3$), 170.14 ($COCH_3$), 169.75 ($COCH_3$), 166.23 (CO glycine), 97.61 (C_1), 69.74 (C-CH_2-NH), 69.74 (C-CH_2-O-mannosyl), 69.52 ($C_{2,3,4}$), 69.20($C_{2,3,4}$), 68.44 (C_5), 67.23 (C-O-mannosyl), 66.05 ($C_{2,3,4}$), 62.52 (C_6), 59.16 (C-NH), 39.34(C-NH), 30.91 (CH_2-C), 30.91 (C-CO), 20.99 (CH_3), 20.87 (CH_3), 20.80 (CH_3).

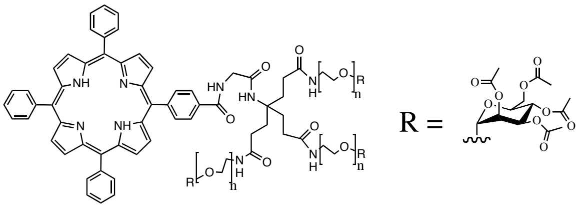
Compound 10 :



n = 1 **10**

Compound **8** (200 mg, 0.14 mmol) was added after 5 minutes to a solution of 10,15,20-triphenyl porphyrin-5-*para*-benzoic acid (46 mg, 7 10^{-5} mol) containing HOBT (14.6 mg, 0.105 mmol), EDC (20 mg, 0.105 mmol) and Et_3N (45 µL) in dry methylene chloride (20 mL) under argon. The solution was stirred overnight under argon at room temperature. The crude mixture was washed with aqueous chlorhydric acid (10 %), water, aqueous sodium hydrogenocarbonte (10 %) and water then dried on sodium sulfate and filtered. The solution was concentrated under vacuum. The pure compound **10** was obtained by preparative thin layer chromatography (silica gel, methylene chloride/acetone, 1/1, v/v) and crystallization from a mixture of methylene chloride/heptane (red powder, yield 74 %). Anal. ($C_{105}H_{117}N_9O_{35}$), 3 H_2O calc C 59.51, H 5.85, N 5.95, found C 59.58; H 6.19; N 5.57. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε $L.mmol^{-1}.cm^{-1}$) : 417.5 (411.9), 515 (10.1), 549.5 (8.2), 590.5 (6), 645.5 (4.7). ^1H NMR ($CDCl_3$) δ (ppm) : 8.85 (s, 6 H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.80 (d, 2 H, $HC_{3,7}$ pyrrole, J = 4.6 Hz), 8.31 (s, 4 H, *ortho*- and *meta*-carboxyphenyl), 8.20 (d, 6 H, J = 5.9 Hz, *ortho*-phenyl), 8.01 (broad t, J = 5 Hz, NH glycine), 7.75 (m, 9 H, *meta*- and *para*-phenyl), 7.32 (broad s, 1 H, NH), 7.22 (broad t, 1 H, J = 5.5 Hz, CH_2NH), 5.36-5.32-5.28 (m, 9 H, HC_{2-3-4}), 4.88 (d, 3 H, HC_1), 4.28 (dd, 3 H, J = 12 and 5 Hz, H_aC_6), 4.21 (d, 2 H, CH glycine), 4.13 (d, 3 H, J = 12 Hz, H_bC_6), 4.06 (m, 3 H, HC_5), 3.81 (m, 3 H, CH_{2a}-O-mannosyl), 3.61 (m, 6 H, HC_{2a}-NH and CH_{2b}-O-mannosyl), 3.42 (m, 3 H, HC_{2b}-NH), 2.37 (t, 6 H, J = 7.5 Hz, CH_2CO dendrimer), 2.14 (s, 9 H, CH_3CO), 2.12 (m, 6 H, CH_2C dendrimer), 2. 09 (s, 9 H, CH_3CO), 2.02 (s, 9 H, CH_3CO), 2.00 (s, 9 H, CH_3CO), -2.78 (s, 2 H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) :173.86 (CO-CH_2CH_2), 170.81 ($COCH_3$), 170.42 ($COCH_3$), 170.26 ($COCH_3$), 169.76 ($COCH_3$), 169.07 (CO glycine), 168.40 (CO phenyl), 145.95 (C1 carboxyphenyl), 141,98 (C1 phenyl), 134.67, (*ortho*-carboxyphenyl), 134.67 (*ortho*-phenyl), 132.81 (*para*-carboxyphenyl), 131.25 (C pyrrole), 127.77 (*para*-phenyl), 126.70 (*meta*-phenyl), 125.74 (*meta*-carboxyphenyl), 120.54 (*meso*-C_{15}), 120.34 (*meso*-$C_{15,20}$), 118.49 (*meso*-C_5), 97.56 (C_1), 69.41-69.33 (C_{2-3-4}), 68.67 (C_5), 67 (CH_2-O-glucosyl), 65.98 (C_{2-3-4}), 62.46 (C_6), 58.73 (C-NH), 44.51 (CH_2 glycine), 38.93 (CH_2-NH), 31.35 [$(CH_2)_3C$], 30.89 ($COCH_2$), 20.90 (CH_3), 20.79 (CH_3), 20.77 (CH_3), 20.70 (CH_3).

Compound 11 :



n = 2 **11**

Prepared as compound **10** from **8**. The pure compound **11** was obtained by preparative thin layer chromatography (silica gel, methylene chloride/acetone, 1/1, v/v) and crystallization from a mixture of methylene chloride/heptane (red powder, 93 mg, yield 57 %). Anal. ($C_{111}H_{129}N_9O_{38}$), 4 H_2O calc C 58.75, H 6.09, N 5.56, found C 58.30; H 6.40; N 5.51. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε $L.mmol^{-1}.cm^{-1}$) : 417.5 (402.7), 514.5 (15.9), 549.5 (6.9), 590 (4.7), 645 (3.5). ^1H NMR ($CDCl_3$) δ (ppm) : 8.85 (s, 6 H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.80 (d, 2 H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 8.31 (s, 4 H, *meta* and *ortho*-carboxyphenyl), 8.21 (d, 6 H, J = 5.9 Hz, *ortho*-phenyl), 7.80 (broad, 1 H, NH-glycine), 7.75 (m, 9 H, *meta*- and *para*-phenyl), 7.59 (broad s, 1 H, NH), 6.86 (broad t, 3 H, J = 5 Hz, NH-CH_2), 5.35 (t, 3 H, HC_3), 5.30 (t, 3 H, HC_4), 5.27 (t, 3 H, HC_2), 4.92 (d, 3 H, J = 1.9 Hz, HC_1), 4.27 (dd, 3 H, J = 5.1 and 12.3 Hz, H_aC_6), 4.22 (d, 2 H, HC glycine), 4.12 (dd, 3 H, J = 12.3 and 1.7 Hz, H_bC_6), 4.06 (m, 3 H, HC_5), 3.80 (m, 3 H, CH_{2a}-O-mannosyl), 3.69 (m, 3 H, CH_{2b}-O-mannosyl), 3.46 (t, 6 H, J = 5.1 Hz, CH_2NH), 2.37 (t, 6 H, J = 3.7 Hz, CH_2CO), 2.15 [m, 6 H, $(CH_2)_3C$], 2.15 (s, 9 H, CH_3CO), 2.08 (s, 9 H, CH_3CO), 2.03 (s, 9 H, CH_3CO), 2.00 (s, 9 H, CH_3CO), -2.78 (s, 2 H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 173.59 (CO-CH_2CH_2), 170.77 ($COCH_3$), 170.32 ($COCH_3$), 170.19 ($COCH_3$), 169.78 ($COCH_3$), 168.80 (CO glycine), 168.07 (CO phenyl), 145.89 (C1 carboxyphenyl), 142,03 (C1 phenyl), 134.67, (*ortho*-carboxyphenyl), 134.54 (*ortho*-phenyl), 133.06 (*para*-carboxyphenyl), 131.3 (C pyrrole), 127.80 (*para*-phenyl), 126.73 (*meta*-phenyl), 125.75 (*meta*-carboxyphenyl), 120.55 (*meso*-C_{15}), 120.36 (*meso*-$C_{15,20}$), 118.56 (*meso*-C_5), 97.59 (C_1), 69.64 (C_2), 69.14 (C_3), 68.46 (C_5), 67.13 (CH_2-O-glucosyl), 66.18 (C_4), 62.55 (C_6), 58.48 (C-NH), 44.40 (CH_2 glycine), 39.46 (CH_2-NH), 31.09 [$(CH_2)_3C$], 30.78 ($COCH_2$), 20.95 (CH_3), 20.79 (CH_3), 20.74 (CH_3).

Compound 1:

To a solution of **10** (68 mg, 3.3 10^{-5} mol) in dry MeOH (10 mL) and dry THF (0.5 mL) was added a solution of NaOMe in MeOH (100 µL, 1 M), and the mixture was stirred overnight at room temperature. IWT TMD-8 ion-exchange resin (1 g) was then added and gentle stirring was continued for 30 min. The reaction mixture was filtered, and the recovered resin was washed with MeOH and pyridine. The combined filtrate and washings were then evaporated to dryness. Product **1** (98%) was obtained as a red powder without other purification. MALDI-TOF MS calc for $C_{81}H_{93}N_9O_{23}$ (MH^+), 1560.64; found, 1560.68. Anal. ($C_{81}H_{93}N_9O_{23}$), 7 H_2O calc C 57.68, H 6.39, N 7.47, found C 57.81; H 6.21; N 7.39. UV-vis spectrum in MeOH/pyridine (24/1, v/v) : λ_{max}, nm (ε $L.mmol^{-1}.cm^{-1}$) : 414 (274.4), 514.5 (12.2), 548 (5.3), 588.5 (3.6), 645.5 (2.4). ^1H NMR (Pyridine$_{d5}$) δ (ppm) : 10 (broad s, 1 H, NH glycine), 9.05 (m, 8 H, HC pyrrole), 8.78 (s, 2 H, *meta*-carboxyphenyl), 8.73 (m, 1 H, NH-CH_2), 8.42 (s, 2 H, *ortho*-carboxyphenyl), 8.37 (m, 6 H, *ortho*-phenyl), 7.81 (m, 9 H, *meta*- and *para*-phenyl), 6.97 (t, 3 H, OH), 6.77 (t, 3 H, OH), 6.70 (t, 3 H, OH), 6.56 (t, 3 H, OH), 5.41 (s, 3 H, HC_1), 4.58 (d, 2 H, CH_2 glycine), 4.58 (m, 12 H, $HC_{2,3,4,6a}$), 4.39 (m, 6 H, $HC_{5,6b}$), 4.12 (m, 3 H, HC_{2a}-O-mannosyl), 3.80 (m, 3 H, HC_{2b}-O-mannosyl), 3.74 (m, 6 H, CH-NH), 2.71 (m, 6 H, CH-CO), 2.60 (m, 6 H, CH-C), -2.41 (s, 2 H, NH). ^{13}C NMR (Pyridine$_{d5}$) δ (ppm) : 173.97 (CO), 169.91 (CO glycine), 168.64 (CO carboxyphenyl), 145.39 (C$_1$ carboxyphenyl), 142.38 (C$_1$ phenyl), 135 (*ortho*-phenyl), 135 (*ortho*-carboxyphenyl), 134.34 (*para*-carboxyphenyl), 131.75 (C pyrrole), 128.32 (*para*-phenyl), 127.35 (*meta*-phenyl), 126.93 (*meta*-carboxyphenyl), 120.90 (*meso*-C$_{10,15,20}$), 119.83 (*meso*-C$_5$), 101.85 (C$_1$), 75.46 (C$_5$), 72.84 (C$_{2,3,4}$), 72.03 (C$_{2,3,4}$), 69.10 (C$_{2,3,4}$), 67.07 (CH$_2$-O-mannosyl), 63.11 (C$_6$), 59.03 (C-NH), 44.87 (CH$_2$ glycine), 39.95 (C-NH), 31.71 [(CH$_2$)$_3$C], 31.16 (COCH$_2$).

Compound 2 :

Prepared as porphyrin **1** in quantitative yield. Compound **2** was obtained as red powder without other purification. MALDI-TOF MS calc for $C_{87}H_{105}N_9O_{26}$ (MH$^+$), 1693.81; found, 1693.78. Anal. ($C_{87}H_{105}N_9O_{26}$), 8 H_2O calc C 56.88, H 6.64, N 6.86, found C 56.31; H 6.53; N 6.75. UV-vis spectrum in MeOH/pyridine (24/1, v/v) : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}): 414 (347.0), 513 (14.2), 546.5 (6.4), 589 (4.3), 644.5 (3.1). ^{1}H NMR (Pyridine$_{d5}$) δ (ppm) : 9.88 (t, 1 H, J = 5.1 Hz, NH glycine), 9.08 (d, 2 H, J = 4.4 Hz, HC$_{3,7}$ pyrrole), 9.03 (s, 4 H, HC$_{12,13,17,18}$ pyrrole), 9.02 (d, 2 H, HC$_{2,8}$ pyrrole), 8.76 (d, 2 H, J = 8 Hz, *meta*-carboxyphenyl), 8.64 (broad s, 1 H, NH), 8.58 (broad s, 1 H, NH-CH$_2$), 8.40 (d, 2 H, *ortho*-carboxyphenyl), 8.36 (m, 6 H, *ortho*-phenyl), 7.80 (m, 9 H, *meta*- and *para*-phenyl), 5.39 (s, 3 H, HC$_1$), 4.61 (d, 2 H, CH$_2$ glycine), 4.55 (m, 15 H, HC$_{2,3,4,6a}$), 4.36 (m, 6 H, HC$_{5,6b}$), 4.06 (m, 3 H, CH$_{2a}$-O-mannosyl), 3.72 (m, 3 H, CH$_{2b}$-O-mannosyl), 3.63 (m, 6 H, CH-NH), 3.63 (m, 12 H, CH$_2$-O), 2.70 (m, 6 H, CH-CO), 2.58 (m, 6 H, CH-C), -2.42 (s, 2 H, NH). ^{13}C NMR (Pyridine$_{d5}$) δ (ppm) : 173.88 (CO), 169.67 (CO glycine), 168.39 (CO carboxyphenyl), 145.38 (C$_1$ carboxyphenyl), 142.39 (C$_1$ phenyl), 13.99 (*ortho*-phenyl), 134.99 (*ortho*-carboxyphenyl), 134.50 (*para*-carboxyphenyl), 131.8 (C pyrrole), 128.35 (*para*-phenyl), 127.37 (*meta*-phenyl), 126.88 (*meta*-carboxyphenyl), 121.02 (*meso*-C$_{15}$), 120.93 (*meso*-C$_{10,20}$), 119.80 (*meso*-C$_5$), 101.63 (C$_1$), 75.30 (C$_5$), 72.95 (C$_{2,3,4}$), 72.05 (C$_{2,3,4}$), 70.36 (CH$_2$-O), 70.19 (CH$_2$-O), 69.20 (C$_{2,3,4}$), 66.76 (CH$_2$-O-mannosyl), 63.26 (C$_6$), 58.82 (C-NH), 44.77 (CH$_2$ glycine), 39.96 (C-NH), 31.53 [(CH$_2$)$_3$C], 31.02 (COCH$_2$).

Preparation and characterization of liposomes

A homemade auto-recording Langmuir-type film trough coupled to a R&K Wilhelmy device (Riegler and Kirstein, GmbH, Germany) was used to record compression isotherms of monolayers of the porphyrin derivatives and mixtures with DMPC, spread from a chloroform/methanol (9:1) solution onto the aqueous subphase (160 cm^3, 217.2 cm^2). After the deposition of the studied solution, the solvents were allowed to evaporate for 15 min before the beginning of compression (1 cm/min). All experiments were run at 22±1°C, and the results are mean values of at least three measurements. The experimental uncertainty was estimated to be 0.2 mN/m. Ultrapure water (γ = 72.4 mN/m at 22°C) produced by a Millipore Synergy 185 apparatus coupled with a RiOs5^{TM}, with a resistivity of 18,2 MΩ/cm. was used in all experiments.

A 10 mM HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid, Sigma, Saint-Louis, USA) buffer solution containing 1mM $CaCl_2$, 2H_2O and 1mM $NiCl_2$, 6H_2O (VWR International, West Chester, USA), was used for liposome preparation. The pH was adjusted to 6.5 by addition of NaOH 1M (Merck, Darmstadt, Germany). Concanavalin A (Type IV) was purchased from Sigma (Saint-Louis, USA).

Liposomes were formed by solvent evaporation from DMPC-porphyrin mixed solutions (500:1) in chloroform-methanol (9:1), hydration of the resulting dry lipid film, and then extrusion of vesicles ten times through polycarbonate membranes of 200 nm pores diameter, using an extruder (Whitley, Lipex).[1] The size of the obtained multilamellar vesicles was measured by the Zetasizer Nano-ZS90 (Malvern).

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[1] V. Faivre, M. L. Costa, P. Boullanger, A. Baszkin, V. Rosilio. *Chem. Phys. Lipids,* 2003*,* **125**, 147.