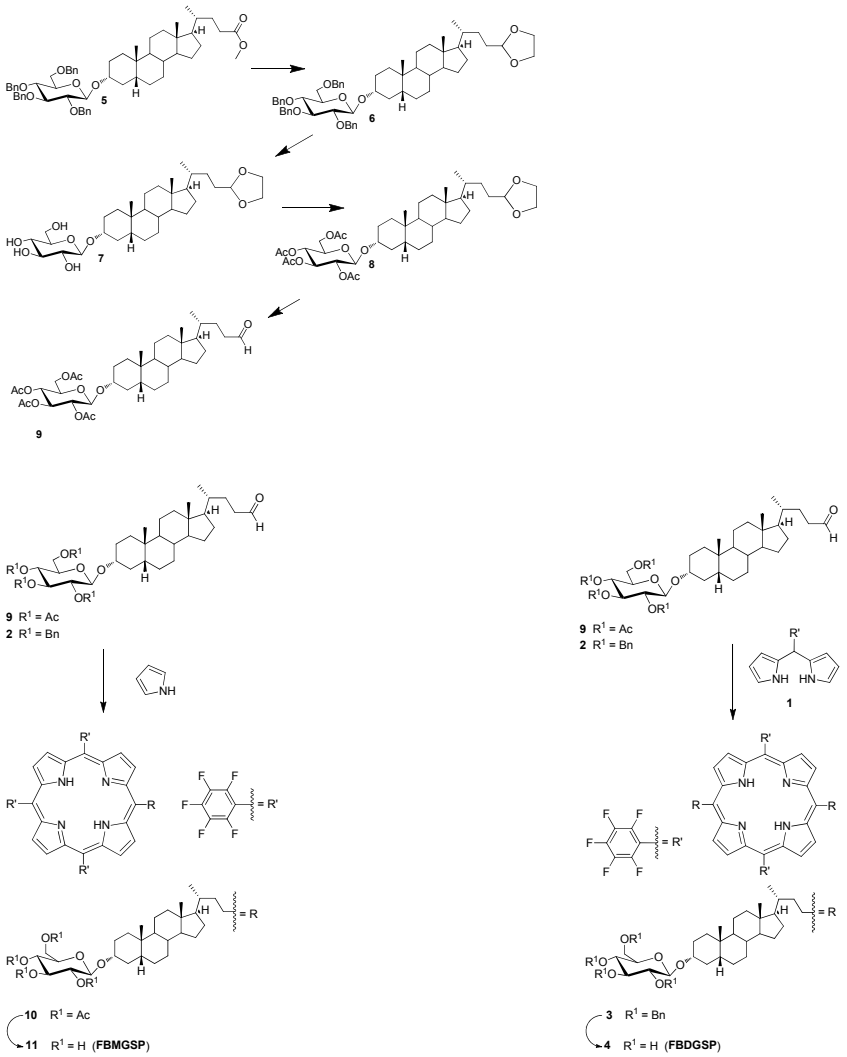
Electronic Supplementary Information (ESI):

1. Synthesis of glucosylated steroid porphyrins

Build-up of the porphyrin skeleton was achieved by the classic condensation reaction of aldehydes with dipyrrylmethane derivative **1**. Preparations of individual porphyrins were optimized. The last step of the synthesis was the deprotection of the saccharide-steroid moiety of porphyrins prepared, which was a key step. Thus were prepared trans-A2B2 type (FBDGSP) **4** and A3B type (FBMGSP) **3** porphyrins.

SYNTHESIS



5,15-Bis(pentafluorophenyl)-10,20-bis[3α-(β-D-glucopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin (FBDGSP) 4

To a solution of porphyrin 5,15-bis(pentafluorophenyl)-10,20-bis[3∀-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin **3** (40 mg) in mixture of dry dichloromethane (1.5 ml) and methanol (3 ml), 10% Pd(C) (40 mg) was added. Reaction mixture was stirred under H_2

(atmospheric pressure) at r.t. over night. Then few drops of triethylamine were added and mixture was filtered over Celite and washed with mixture of chloroform-methanol (4:1), the filtrate was evaporated to dryness under reduced pressure. Residue was suspended in toluene and filtered over cotton wool. Elution with mixture of chloroform-methanol (4:1) and evaporation to dryness gave porphyrin 5,15-bis(pentafluorophenyl)-10,20-bis[3α-(β-D-glucopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin (20 mg, 72 %) as an amorphous brown powder. UV-Vis: (pyridine) λ_{max} 417 nm (log ε = 5.29). ^{1}H NMR (400 MHz, C_5D_5N): -2.26 bs, 2 H (2 × NH-pyrrole); 0.74 s, 6 H (2 × H-18); 0.90 s, 6 H (2 × H-19); 1.58 d, 6 H (*J* = 6.0, 2 × H-21); 0.80-2.80, 52 H (2 × steroid fingerprint); 3.98-4.64, 14 H (2 × H-3β, 2 × H-2', H-3', H-4', H-5', H-6a', H-6b'); 5.00 bm, 2 H (2 × H-23a); 5.07 d, 2 H (*J* = 7.2, 2 × H-1'); 5.26 bm, 2 H (2 × H-23b). 9.43 d, 4 H (*J* = 4.2, 4 × H-pyrrole), 9.94 d, 4H (*J* = 4.9, 4 × H-pyrrole). ^{13}C NMR (100 MHz, C_5D_5N): 12.30, 19.47, 21.10, 23.51, 24.47, 26.54, 27.28, 27.40, 28.91, 32.70, 34.66, 34.82, 35.38, 35.86, 37.93, 40.33, 40.60, 42.28, 43.06, 46.56, 56.33, 56.49, 62.94, 71.81, 75.41, 77.86, 78.55, 78.71, 101.48, 102.04, 117.40, 122.96, 130.38, 131.16, 145.94, 148.29. ^{19}F NMR (376 MHz, C_5D_5N): -138.61 m, 4 F; -153.89 m, 2 F; -163.01 m, 4 F. For $C_{90}H_{108}F_{10}N_4O_{12}$ calculated Exact Mass: 1626.78; Mol. Wt. 1627.82, *m/z*: 1626.78 (100.0 %), 1627.78 (99.3 %), 1628.79 (48.5 %), 1629.79 (18.1 %), 1630.79 (5.0 %), 1628.78 (3.9 %), 1627.79 (1.2 %); found MS (FAB, MeOH), *m/z*: 1627.6 (M^+). MS (ESI, MeOH/$CHCl_3$): 1627.3 (M^+).

5,10,15-Tris(pentafluorophenyl)-20-[3α-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin 10

Vessel with aldehyde 3α-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5β-cholan-24-yl]-porphyrin **9** (240 mg, 0.34 mmol), pyrrole (95 mg, 100 µl, 1.39 mmol) and pentafluorobenzaldehyde (210 mg, 1.04 mmol) in dry dichloromethane (140 ml) was bubbled with argon for 15 min. $BF_3.Et_2O$ (20 mg, 18 µl, 0.14 mmol) was added through rubber septum and mixture was shielded from light. Reaction mixture was stirred under argon at r.t. After 4 hours, DDQ (410 mg, 1.8 mmol) was added and mixture was stirred over night. Then triethylamine (20 µl, 0.14 mmol) was added, mixture stirred for 5 minutes. Solvents were removed under reduced pressure. Residue was dissolved in chloroform, silica gel (2 g) was added and solvent evaporated to dryness. Chromatography on a silica gel (30g) column (1. toluene-ethyl acetate 25:1, second porphyrin fraction collected, 2-3. 2. toluene-ethyl acetate 19:1) gave porphyrin 5,10,15-tris(pentafluorophenyl)-20-[3α-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin (65 mg, 12 %) as pale red-violet solid. UV-Vis: ($CHCl_3$) λ_{max} 415 nm (log ε = 5.69). ^{1}H NMR (300 MHz, C_6D_6): -2.71 bs, 2 H (2 × NH-pyrrole); 0.66 s, 3 H (H-18); 0.91 s, 3 H (H-19); 1.35 d, 3 H (*J* = 6.3, H-21); 1.68 s, 6 H; 1.70 s, 3 H; 1.76 s, 3 H (4 × OAc); 0.80-2.54, 26 H (steroid fingerprint); 3.53 ddd, 1 H (J_1 = 9.9, J_2 = 4.5, J_3 = 2.4, H-5'); 3.60 m, 1 H (H-3β); 4.11 dd, 1 H (J_1 = 12.3, J_2 = 2.4, H-6a'); 4.30 dd, 1 H (J_1 = 12.3, J_2 = 4.5, H-6b'); 4.37 bm, 1 H (H-23a); 4.48 d, 1 H (*J* = 7.8, H-1'); 4.64 bm, 1 H (H-23b); 5.29 t, 1 H (*J* = 9.6, H-4'); 5.33 dd, 1 H (J_1 = 9.3, J_2 = 7.8, H-2'); 5.48 t, 1 H (*J* = 9.6, H-3'); 8.62 d, 2 H (*J* = 4.8); 8.70 d, 2 H (*J* = 5.1); 8.74 d, 2 H (*J* = 4.8); 9.29 d, 2 H (*J* = 4.8) (8 × H-pyrrole). ^{13}C NMR (75 MHz, C_6D_6): 12.95, 20.10, 20.83, 20.91, 20.93, 21.08, 21.94, 24.29, 25.03, 27.05, 28.12, 28.33, 29.59, 33.35, 35.32, 35.49, 36.28, 36.63, 38.31, 40.96, 41.20, 43.18, 43.65, 47.01,56.53, 56.69, 62.70, 69.63, 72.86, 73.04, 74.21, 80.61, 100.61, 102.11, 103.38, 116.83, 117.47, 125.43, 130.96, 131.96, 136.80, 140.16, 141.28, 144.67, 145.85, 149.14, 169.42, 169.73, 170.70, 170.73. ^{19}F NMR (282 MHz, C_6D_6): -137.30 m, 6 F; -151.47 t, 1 F (*J* = 22.0), -151.79 t, 2 F (*J* = 21.7), -161.91 m, 6 F. For $C_{75}H_{67}F_{15}N_4O_{10}$ calculated Exact Mass: 1468.46; Mol. Wt. 1469.33, *m/z*: 1468.46 (100.0 %), 1469.47 (82.3 %), 1470.47 (35.5 %), 1471.47 (11.1 %), 1472.48 (1.8 %), 1469.46 (1.5 %), 1470.46 (1.2 %); found MS (ESI, MeOH), *m/z*: 1492.3 ($M + Na^+$).

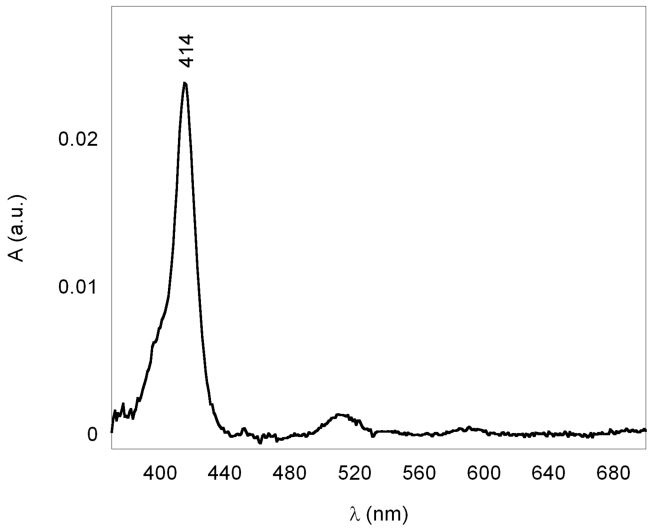
5,10,15-Tris(pentafluorophenyl)-20-[3α-(β-D-glucopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin (FBMGSP) 11

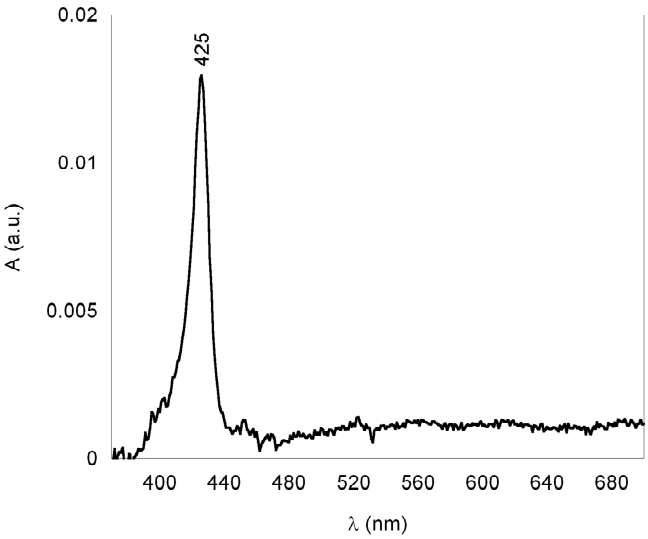
To a stirred solution of porphyrin 5,10,15-tris(pentafluorophenyl)-20-[3α-(2,3,4,6-tetra-*O*-acetyl-β-D-glukopyranosyloxy)-5β-24-norcholan-23-yl]-porphyrin **10** (50 mg, 34 µmol) in mixture of dry methanol (25 ml) and dichloromethane (5 ml), sodium methylate (5 mg) was added and mixture was

allowed to stir 4 hours. Mixture was neutralized with addition of Dowex 50 in H^+ cycle (25 mg). Then dichloromethane (20 ml) was added, and mixture filtered over cotton wool. Solvents were evaporated to dryness under reduced pressure. Residue was dissolved in mixture of chloroform and methanol (9:1) and the solution was filtered over short silica gel column (0.5 g). Solvents were evaporated to give porphyrin **11** (**FBMGSP**, 38 mg, 85 %) as a pale red-brown solid.

UV-Vis: ($CHCl_3$) λ_{max} 415 nm (log ε = 5.48). ^{1}H NMR (300 MHz, C_5D_5N): -2.49 bs, 2 H (2 × NH-pyrrole); 0.73 s, 3 H (H-18); 0.90 s, 3 H (H-19); 1.59 d, 3 H (*J* = 6.3, H-21); 0.80-2.85, 26 H (steroid fingerprint); 3.96-4.68, 7 H (H-3β, H-2‘, H-3‘, H-4‘, H-5‘, H-6a‘, H-6b‘); 4.90-5.40, 3 H (H-1‘, H-23a,b); 6.52 bs, 1 H; 7.05 bs, 1 H; 7.16 bs, 2H (4 × OH); 9.49 d, 2 H (*J* = 4.8); 9.54 d, 2 H (*J* = 4.8); 9.57 d, 2 H (*J* = 4.8); 10.03 d, 2 H (*J* = 4.8) (8 × H-pyrrole). ^{13}C NMR (75 MHz, C_5D_5N): 12.27, 19.45, 21.09, 23.50, 24.46, 26.54, 27.29, 27.41, 28.89, 33.12, 34.66, 34.82, 35.39, 35.86, 37.95, 40.34, 40.60, 42.28, 43.06, 46.84, 56.29, 56.48, 62.94, 71.81, 75.40, 77.88, 78.54, 78.71, 101.61, 102.04, 102.99, 116.08, 116.68, 125.85, 131.41, 132.44, 139.73, 140.70, 144.07, 145.46, 148.67. ^{19}F NMR (282 MHz, C_5D_5N): -138.15 m , 6 F; -152.99 t, 1 F (*J* = 21.2), -153.01 t, 2 F (*J* = 22.0), -162.38 m, 6 F. For $C_{67}H_{59}F_{15}N_4O_6$ calculated Exact Mass: 1300.42; Mol. Wt. 1301.18, *m/z*: 1300.42 (100.0 %), 1301.42 (74.2 %), 1302.43 (26.5 %), 1303.43 (7.2 %), 1302.42 (2.3 %), 1304.43 (1.5 %); found MS (ESI, MeCN/$CHCl_3$), *m/z*: 1302.0 (M^+). MS (ESI, MeOH) 1301.9 (M^+) 1323.9 ($M + Na^+$).

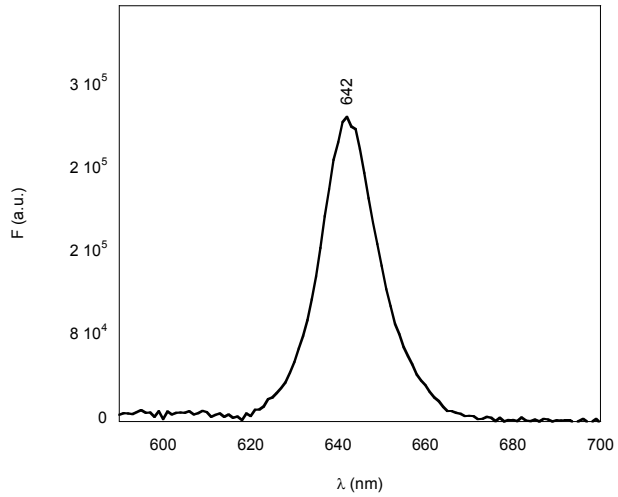
Absorption spectra of FBDGSP and FBMGSP in POPC

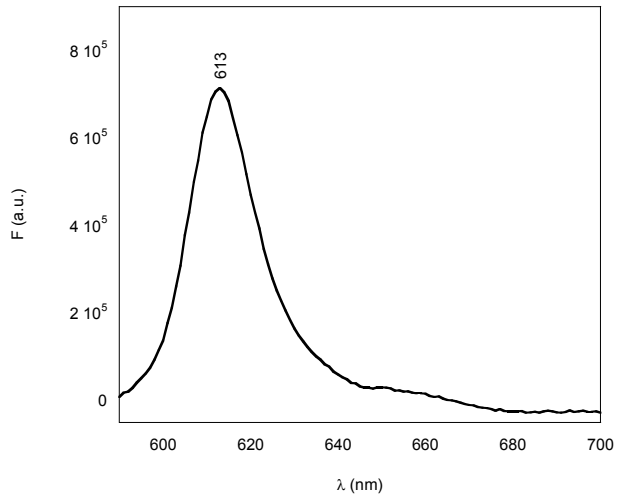




UV-Vis spectra of FBMGSP (top) and FBDGSP (down) included into the double layer of POPC unilamellar liposomes (porphyrin/lipid 1:1000 molar ratio).

Fluorescence spectra of FBDGSP and FBMGSP in POPC





Fluorescence emission spectra of FBMGSP (top) and FBDGSP (down) included into the double layer of POPC unilamellar liposomes (porphyrin/lipid 1:1000 molar ratio).