SUPPLEMENTARY MATERIAL

SYNTHESIS AND SOLVENT DRIVEN SELF-AGGREGATION STUDIES OF meso-“C-GLYCOSIDE”-PORPHYRIN DERIVATIVES

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5,10,15,20-Tetrakis-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl-methyl)porphyrin 2

IR (CHCl3) porphyrin: υ(NH): 3319 ω - free, 3229 ω, br - fixed; pyrrole υ(C=C): 1575 ω, υ(C=N): 1482 ω; 900 ω, 888 ω; BnO-: υas(CH2): 2922 m, br; υs(CH2): 2871 m; β(CH2): 1357 m; γ(CH2): 1334 ω; υas(COC): 1092 vs, 1125 s,sh; υ(C=H): 3090 ω (20a), 3067 ω (2), 3033 m (20b); (ring): 1604 ω (8a), 1585 ω (8b), 1497 (19a), 1454 vs (19b); 1078 s,sh (18b), 1028 m (7b), 699 s (4), 465 ω (6a). UV (CHCl3) λmax 422.5 (288000); 487.4 (3670); 520.3 (10190); 555.8 (5200); 599.1 (3395); 657.1 (3230). 1H NMR: porphyrin moiety -9.42 bs (8H, CH=), -2.82 bs (2H, NH); sugar moiety – 7.43-7.14 m (80H, aromatic H), 5.30 dd (4H, J = 6.3, 14.7, CH2-α), 5.22 dd (4H, J = 6.5, 14.7, CH2-α), 5.02 d (4H, J = 2.7, 6.4, 6.4 H-1), 4.53 d (4H, J = 4.4, 4.4, 8.8, H-5), 4.52 d (4H, J = 11.6, OCH2Ph), 4.47 d (4H, J = 11.6, OCH2Ph), 4.39 d (4H, J = 11.8, OCH2Ph), 4.37 d (4H, J = 11.8, OCH2Ph), 4.27 d (4H, J = 11.8, OCH2Ph), 4.24 d (4H, J = 11.8, OCH2Ph), 4.20 d (4H, J = 2.8, 4.9, H-4), 4.10 d (4H, J = 12.0, OCH2Ph), 3.96 d (4H, J = 12.0, OCH2Ph), 3.83 m (4H, H-3), 3.83 dd (4H, J = 8.8, 11.2, H-6a), 3.65 dd (4H, J = 3.8, 11.2, H-6b), 3.47 bs (4H, H-2). 13C NMR: porphyrin moiety – 114.43 (meso -C-); sugar moiety – 138.37, 138.30, 138.17, 138.06 (each 4C, ipso-C aromatic), 128.45, 128.27, 128.25, 128.14, 128.01, 127.91 (each 8C, CH aromatic), 127.80
(4C, CH aromatic), 127.56 (8C, CH aromatic), 127.53 (4C, CH aromatic), 127.25 (8C, CH aromatic), 127.19, 127.11 (each 4C, CH aromatic), 76.43 (4C, C-2), 75.54 (4C, C-1), 74.83 (4C, C-3), 74.51 (4C, C-5), 73.74 (4C, C-4), 73.20, 72.81, 72.59, 72.20 (each 4C, CH2Ph), 66.72 (4C, C-6), 34.25 (4C, CH2-α). MS (m/z, FAB, exact mass 2455.14) 2458.2 (M+3H)+.

5,10,15,20-Tetrakis-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl-methyl)porphyrin 4

IR (CHCl3) porphyrin: ν(NH): 3414 pyrrole; ν(C-H): 3068 (20a), 3067 (2), 3033 (20b), ν(=C-H): 1696, 1468, 1397; benzene : 1607 m (8a), 1585 m,sh (8b), 1467 (19a), 1454 s (19b); BnO-: νas(CH2): 2928 s; νs(CH2): 2857 m; βs(CH2): 1362 m; γas(ring-THP)+νas(COC): 1120 s,br,sh, 1088 vs. UV (CHCl3) λmax (ε) 426.3 (278000); 577.2 (4625); 612.8 (3210); 640.2 (3110). 1H NMR: porphyrin moiety -9.41 bs (8H, CH=), -2.76 bs (2H, NH); sugar moiety 7.41–7.26 m (48H, aromatic H), 7.14–7.04 m (32H, aromatic H), 5.49 dd (4H, J = 3.6, 14.8, CH2-α), 5.12 dd (4H, J = 7.7, 14.8, CH2-α), 5.11 d (4H, J = 11.2, OCH2Ph), 5.07 ddd (4H, J = 3.6, 5.3, 7.7, H-I), 5.02 d (4H, J = 11.2, OCH2Ph), 4.93 d (4H, J = 10.9, OCH2Ph), 4.62 d (4H, J = 11.8, OCH2Ph), 4.61 d (4H, J = 10.9, OCH2Ph), 4.49 ddd (4H, J = 2.2, 3.8, 9.6, H-5), 4.46 d (4H, J = 11.8, OCH2Ph), 4.35 dd (4H, J = 8.6, 9.2, H-3), 4.34 d (4H, J = 12.1, OCH2Ph), 4.18 d (4H, J = 12.1, OCH2Ph), 3.90 dd (4H, J = 5.3, 9.2, H-2), 3.82 dd (4H, J = 8.6, 9.6, H-4), 3.82 dd (4H, J = 3.6, 10.7, H-6a), 3.55 dd (4H, J = 2.2, 10.7, H-6b). 13C NMR: porphyrin moiety – 115.62 (meso-C=); sugar moiety – 138.64, 138.27, 138.05, 137.87 (each 4C, ipso-C aromatic), 128.45, 128.44, 128.24, 128.15, 128.06, 127.94, 127.91 (each 8C, CH aromatic), 127.77, 127.66, 127.63, 127.60, 127.40 (each 4C, CH aromatic), 82.38 (4C, C-3), 80.48 (4C, C-1), 80.43 (4C, C-2), 78.18 (4C, C-4), 75.27, 75.04 (each 4C, CH2Ph), 73.08 (4C, C-5), 73.79, 73.38 (each 4C, CH2Ph), 69.08 (4C, C-6), 32.05 (4C, CH2-α). MS (m/z, FAB, exact mass 2455.14) 2458.2 (M+3H)+.

2,6-anhydro-1,3,4,5-tetra-O-benzyl-7,8-dideoxy-8,8-di-1H-pyrrl-2-yl-D-glycero-L-galacto-octitol 5

IR (CHCl3): ν(NH): 3464 s - free, 3357 m, br ; pyrrole: υ(ring): 1564 ω, 1400 m; β(C-H): 1271 s; 1253 m,sh; 1028 vs (+benzene 18a), 884 m; 719 vs; υas(COC) 1121 vs, sh; 1093 vs, 884 m, 719 vs; -OBn: υ(=C-H): 3090 m (20a), 3067 m (2+pyrrole), 3033 m (20b); υ(ring): 1603 ω (8a), 1586 ω (8b), 1497 (19a), 1454 s (19b), βs(CH2) 1369 m, γ(CH2): 1332 m; benzene: 1177 m (9a), 1071 m (18b), 1001 m (12), 699 vs (4); γas(CH2): 2924m; γ(CH2): 2807s. 1H NMR: pyrrole moiety – 9.00 brs (2H, NH), 6.57 dt (1H, J = 1.6, 2.6, 2.6, H-5), 6.54 dt (1H, J = 1.6, 2.6, 2.6, H-5), 6.12 t (1H, J = 2.7, H-4), 6.11 t (1H, J = 2.7, H-4), 6.01 bdt (1H, J = 1.6, 2.8, 2.8, H-3), 5.81 bdt (1H, J = 1.6, 2.8,
2,6-anhydro-1,3,4,5-tetra-O-benzyl-7,8-dideoxy-8,8-di-1H-pyrrol-2-yl-D-glycero-L-gulo-octitol

IR (CHCl₃): ν(NH): 3461 s - free, 3376 m, br - fixed; β(NH): 1121 vs,sh; γ(NH): 554 m,br, sh, pyrrole: ν(C-H): 3106 ω; ν(ring): 1563 ω, 1468 m,sh, 1400 m; β(C-H): 1271 m; γ(C-H): 884 ω; β(ring)+ γ(C-H): 718 vs; γ(ring): 634 ω; ν₃o(COC), ν₃o(ring) THP: 1087 vs, br, 1121 vs, sh; benzene: ν(C-H): 3090 m (20a), 3067 m (2), 3033 m (20b); ν(ring): 1604 ω (8a), 1586 ω (8b), 1497 (19a), 1454 s (19b), 1178 m, sh (9a), 1155 s (9b), 1074 vs,sh (18b), 1028 vs (18a), 912 m (17b), 700 vs (4), 467 m (6a). ¹H NMR: pyrrole moiety – 8.27 bs (1H, NH), 7.92 bs (1H, NH), 6.57 dt (1H, J = 1.5, 2.7, 2.7, H-5), 6.55 dt (1H, J = 1.5, 2.7, 2.7, H-5), 6.12 t (1H, J = 2.7, H-4), 6.11 t (1H, J = 2.7, H-4), 6.04 btd (1H, J = 1.5, 2.7, 2.7, H-3), 5.97 bdt (1H, J = 1.5, 2.7, 2.7, H-3); sugar moiety – 7.36-7.13 m (20H, aromatic H), 4.91 d (1H, J = 10.9, OCH₂Ph), 4.82 d (1H, J = 10.9, OCH₂Ph), 4.77 d (1H, J = 10.9, OCH₂Ph), 4.60 d (1H, J = 10.9, OCH₂Ph), 4.54 d (1H, J = 11.6, OCH₂Ph), 4.51 d (1H, J = 12.0, OCH₂Ph), 4.48 d (1H, J = 10.9, OCH₂Ph), 4.44 d (1H, J = 11.6, OCH₂Ph), 4.20 dd (1H, J = 3.9, 11.5, CH-β), 4.00 ddd (1H, J = 3.1, 5.9, 11.7, H-1), 3.80 t (1H, J = 9.0, H-3), 3.73 ddd (1H, J = 2.1, 5.2, 9.8, H-5), 3.67 dd (1H, J = 2.1, 10.3, H-6b), 3.66 dd (1H, J = 5.9, 9.2, H-2), 3.63 dd (1H, J = 5.2, 10.3, H-6a), 3.50 dd (1H, J = 8.7, 9.8, H-4), 2.43 ddd (1H, J = 3.9, 11.7, 14.6, CH₂-α), 2.17 ddd (1H, J = 3.1, 11.5, 14.6, CH₂-α). ¹³C NMR: pyrrole moiety – 132.17 and 133.73 (C-2), 116.70 and 116.87 (C-5), 108.17 and 108.08 (C-4), 105.84 and 104.66 (C-3); sugar moiety – 138.60, 138.10, 138.02, 137.89 (each C, ipso-C aromatic), 128.42, 128.39, 128.37, 128.37, 127.90,
127.89, 127.85 (each 2C, CH aromatic), 127.78, 127.74 (each C, CH aromatic), 127.74 (2C, CH aromatic), 127.71, 127.60 (each C, CH aromatic), 82.43 (C-3), 79.72 (C-2), 78.32 (C-4), 75.34, 74.94, 73.46, 72.78 (CH2Ph), 71.38 (C-5), 71.28 (C-1), 69.54 (C-6), 33.37 (C-β), 30.63 (C-α). MS (m/z, FAB, Exact Mass 682.34): 682.5 (M+) 

5,15-[Bis-(pentafluorophenyl)]-10,20-[bis-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl-methyl)porphyrin 7

IR (CHCl3) porphyrin: υ(NH): 3414 ω; υ(ring): 1567 ω, 1470 m,sh; β(ring): 803 ω, 715 ω (8a), 1498 ω (19b); 1315 ω (13), 1248 ω (14), 1142 m (7b), 1121 s (7a), 990 s (20b) 919 m, 924 m,sh (20a); BnO-: υ(C-H): 3090 ω, 3067 ω (2), 3033 ω (20b); υ(ring): 1604 ω,sh (8a), 1568 ω (8b), 1455 m (19b); 1280 ω (13) 1029 m (18a), 699 s (4), 464 ω (6a); υ(ν(COC)): 1090s, 1090s; υ(=C=H): 3090 ω (20a), 3067 ω (2), 3033 ω (20b); υ(ring): 1604 ω,sh (8a), 1568 ω (8b), 1455 m (19b); 1280 ω (13) 1029 m (18a), 699 s (4), 464 ω (6a); υ(ν(COC)): 1090s, 1121 s; υ(ν(α)): 2932 ω; υ(ν(β)): 2874 m; υ(βs): 1366 m; υ(γs): 1333 m. UV (CHCl 3) λmax 417.0 (249000); 480 (12800); 513 (19800); 546 (9530); 589 (7909); 647 (4967). 

1H NMR: porphyrin moiety – 9.54 d (4H, J = 4.9, CH=), 8.63 d (4H, J = 4.9, CH=), -2.73 bs (2H, NH); sugar moiety – 7.40-7.26 m (48H, aromatic H), 6.75–7.05 m (32H, aromatic H), 5.30 dd (4H, J = 5.5, 14.8, CH2-α), 5.22 dd (4H, J = 6.5, 14.8, CH2-α), 5.10 dt (4H, J = 3.0, 6.1, 6.1, H-1), 4.67 d (4H, J = 11.8, OCH2Ph), 4.61 d (4H, J = 11.6, OCH2Ph), 4.61 d (4H, J = 12.0, OCH2Ph), 4.60 d (4H, J = 11.6, OCH2Ph), 4.44 d (4H, J = 12.0, OCH2Ph), 4.27 dd (4H, J = 2.7, 4.6, H-4), 4.09 d (4H, J = 12.0, OCH2Ph), 4.05 d (4H, J = 12.0, OCH2Ph), 4.00 dd (4H, J = 2.7, 6.0, H-3), 3.89 dd (4H, J = 7.9, 11.1, H-6a), 3.75-3.78 m (4H, H-2), 3.70 dd (4H, J = 3.6, 11.1, H-6b). 

13C NMR: porphyrin moiety – 147.55 (4C, -(N)C=), 145.60 (4C, -(N)C=), 130.38 (4C, -(N)C=), 129.92 (4C, -(N)C=), 117.77 (2C, meso -C=), 117.07 (2C, JCF = 20.0, meso -C=); sugar moiety – 138.33, 138.20, 138.13, 138.11 (each 2C, ipso-C aromatic), 128.49, 128.33, 128.21, 128.06, 127.90, 127.69, 127.52 (each 4C, CH aromatic), 127.00, 126.77 (each 2C, CH aromatic), 76.74 (2C, C-2), 76.11 (2C, C-1), 75.62 (2C, C-3), 74.49 (2C, C-5), 73.96 (2C, C-4), 73.30, 72.59, 72.97, 72.84 (each 2C, CH2Ph), 67.14 (2C, C-6). MS (m/z, FAB, Exact Mass 1714.60): 1716.7 (M+2H) + 

5,15-[Bis-(pentafluorophenyl)]-10,20-[bis-(α-D-galactopyranosyl-methyl)porphyrin 10

To a solution of porphyrin 7 (100 mg, 0.058 mmol) in CH2Cl2 1 ml and MeOH 2 ml 10% Pd(C) 90 mg was added. The reaction mixture was stirred under H2 (atmospheric pressure) at ambient temperature for one night. After filtration silica gel was added and solvents were evaporated under reduced pressure. Resulting powder was posed at the top of a short silica gel
column. Increasing polarity elution with CHCl₃, CHCl₃:MeOH 2:1 gave porphyrin 10 (37 mg, 63%) as dark green amorphous solid.

UV (MeOH) $\lambda_{max}$ 410 (54600); 510 (5180); 543 (2340); 589 (1950); 647 (1970). $^1$H NMR 300 MHz (CD₃OD): porhyrin moiety – 9.90 bs (4H), 9.05 bs (4H); sugar moiety – 4.05-3.52 m (18H). $^{13}$C NMR 75 MHz (CD₃OD): 151.17, 149.11, 145.19, 141.17, 137.73, 133.72, 129.79, 129.66, 71.51, .71.12, 70.89, 70.67, 70.55, 70.21, 69.97, 37.76. For C₄₆H₃₆F₁₀N₄O₁₀ (Exact Mass 994.23) MS (m/z, FAB): 995.0 (M+H)$^+$, 1011.1 (M+H₂O)$^+$.

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REFERENCES