Supplementary Material (ESI) for *Organic and Biomolecular Chemistry*

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 ($CHCl_3$) *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-*: $\upsilon_{as}(CH_2)$: 2922 m, br; $\upsilon_s(CH_2)$: 2871 m; $\beta_s(CH_2)$: 1357 m; $\gamma_s(CH_2)$: 1334 ω; υ_{as}(COC): 1092 vs, 1125 s,sh; υ(=C-H): 3090 ω (20a), 3067 ω (2), 3033 m (20b); υ(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 ($CHCl_3$) λ_{max} 422.5 (288000); 487.4 (3670); 520.3 (10190); 555.8 (5200); 599.1 (3395); 657.1 (3230). ^{1}H 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, CH_2-α), 5.22 dd (4H, *J* = 6.5, 14.7, CH_2-α), 5.02 ddd (4H, *J* = 2.7, 6.4, 6.4 H-1), 4.53 ddd (4H, *J* = 4.4, 4.4, 8.8, H-5), 4.52 d (4H, *J* = 11.6, OCH_2Ph), 4.47 d (4H, *J* = 11.6, OCH_2Ph), 4.39 d (4H, *J* = 11.8, OCH_2Ph), 4.37 d (4H, *J* = 11.8, OCH_2Ph), 4.27 d (4H, *J* = 11.8, OCH_2Ph), 4.24 d (4H, *J* = 11.8, OCH_2Ph), 4.20 dd (4H, *J* = 2.8, 4.9, H-4), 4.10 d (4H, *J* = 12.0, OCH_2Ph), 3.96 d (4H, *J* = 12.0, OCH_2Ph), 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). ^{13}C 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, $\underline{C}H_2Ph$), 66.72 (4C, C-6), 34.25 (4C, CH_2-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 ($CHCl_3$) *porphyrin:* υ(NH): 3414 *pyrrole*; υ(C-H): 3090 ω (20a), 3067 ω (2), 3033 ω (20b), υ(ring): 1560, 1468 m,sh, 1397 ω; benzene : 1607 m (8a), 1585 m,sh (8b), 1467 (19a), 1454 s (19b); *BnO-*: $\upsilon_{as}(CH_2)$: 2928 s; $\upsilon_s(CH_2)$: 2857 m; $\beta_s(CH_2)$: 1362 m; γ_{as}(ring-THP)+υ_{as}(COC): 1120 s,br,sh, 1088 vs. UV ($CHCl_3$) λ_{max} (ε) 426.3 (278000); 577.2 (4625); 612.8 (3210); 640.2 (3110). ^{1}H 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, CH_2-α), 5.12 dd (4H, *J* = 7.7, 14.8, CH_2-α), 5.11 d (4H, *J* = 11.2, OCH_2Ph), 5.07 ddd (4H, *J* = 3.6, 5.3, 7.7, H-1), 5.02 d (4H, *J* = 11.2, OCH_2Ph), 4.93 d (4H, *J* = 10.9, OCH_2Ph), 4.62 d (4H, *J* = 11.8, OCH_2Ph), 4.61 d (4H, *J* = 10.9, OCH_2Ph), 4.49 ddd (4H, *J* = 2.2, 3.8, 9.6, H-5), 4.46 d (4H, *J* = 11.8, OCH_2Ph), 4.35 dd (4H, *J* = 8.6, 9.2, H-3), 4.34 d (4H, *J* = 12.1, OCH_2Ph), 4.18 d (4H, *J* = 12.1, OCH_2Ph), 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* = 3.8, 10.7, H-6a), 3.55 dd (4H, *J* = 2.2, 10.7, H-6b). ^{13}C 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, $\underline{C}H_2Ph$), 73.08 (4C, C-5), 73.79, 73.38 (each 4C, $\underline{C}H_2Ph$), 69.08 (4C, C-6), 32.05 (4C, CH_2-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-1*H*-pyrrol-2-yl-D-*glycero*-L-*galacto*-octitol 5

IR ($CHCl_3$): *υ(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; υ_{as}*(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), β_s(*CH_2*) 1369 m, γ_s(*CH_2*): 1332 m; benzene: 1177 m (9a), 1071 m (18b), 1001 m (12), 699 vs (4); $\gamma_{as}(CH_2)$: 2924m; $\gamma_s(CH_2)$: 2807s. ^{1}H NMR: pyrrole moiety – 9.00 bs (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,

2.8, H-3); sugar moiety – 7.35-7.18 m (20H, aromatic H), 4.62 d (1H, *J* = 11.8, OCH_2Ph), 4.59 d (1H, *J* = 11.8, OCH_2Ph), 4.58 d (1H, *J* = 11.9, OCH_2Ph), 4.57 d (1H, *J* = 11.8, OCH_2Ph), 4.52 d (1H, *J* = 11.8, OCH_2Ph), 4.50 d (1H, *J* = 11.9, OCH_2Ph), 4.49 d (1H, *J* = 11.9, OCH_2Ph), 4.39 d (1H, *J* = 11.9, OCH_2Ph), 4.23 dd (1H, *J* = 3.9, 11.3, CH-β), 4.18 ddd (1H, *J* = 3.2, 4.6, 8.0, H-5), 4.07 dd (1H, *J* = 8.0, 11.2, H-6b), 3.98 dd (1H, *J* = 2.9, 4.6, H-4), 3.88 dt (1H, *J* = 2.0, 2.0, 11.1, H-1), 3.71 dd (1H, *J* = 2.9, 6.1, H-3), 3.57 dd (1H, *J* = 3.2, 11.2, H-6a), 3.52 dd (1H, *J* = 2.0, 6.1, H-2), 2.44 ddd (1H, *J* = 3.9, 11.3, 13.8, CH_2-α), 1.77 bt (1H, *J* = 12.6, CH_2-α). ^{13}C NMR: pyrrole moiety – 133.09 and 133.88 (C-2), 116.39 and 116.65 (C-5), 107.75 and 107.93 (C-4), 104.56 and 105.25 (C-3); sugar moiety – 138.36, 138.18, 137.91, 137.87 (each C, *ipso*-C aromatic), 128.45, 128.36 (each 2C, CH aromatic), 128.31 (4C, CH aromatic), 128.06 (2C, CH aromatic), 127.83 (3C, CH aromatic), 127.73, 127.69 (each C, CH aromatic), 127.65 (2C, CH aromatic), 127.53 (1C, CH aromatic), 127.46 (2C, CH aromatic), 76.66 (C-2), 75.21 (C-3), 73.93 (C-4), 72.95, 72.95, 72.93, 72.90 ($\underline{C}H_2Ph$), 72.46 (C-5), 67.11 (C-6), 34.53 (C-α), 33.58 (C-β). MS (m/z, FAB, Exact Mass 682.34): 682.5 $(M)^+$.

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

IR ($CHCl_3$): *υ(NH)*: 3461 s - free, 3376 m, br - fixed; β(NH): 1121 vs,sh; γ(NH): 554 m,br, sh, *pyrrole: υ(C-H)*: 3106 ω; υ(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; υ_{as}*(COC), υ(ring) THP*: 1087 vs, br, 1121 vs, sh; *benzene: υ(C-H)*: 3090 m (20a), 3067 m (2), 3033 m (20b); υ(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). ^{1}H 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 bdt (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, OCH_2Ph), 4.82 d (1H, *J* = 10.9, OCH_2Ph), 4.77 d (1H, *J* = 10.9, OCH_2Ph), 4.60 d (1H, *J* = 12.0, OCH_2Ph), 4.54 d (1H, *J* = 11.6, OCH_2Ph), 4.51 d (1H, *J* = 12.0, OCH_2Ph), 4.48 d (1H, *J* = 10.9, OCH_2Ph), 4.44 d (1H, *J* = 11.6, OCH_2Ph), 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, CH_2-α), 2.17 ddd (1H, *J* = 3.1, 11.5, 14.6, CH_2-α). ^{13}C 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 ($\underline{C}H_2Ph$), 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 ($CHCl_3$) *porphyrin:* υ(NH): 3414 ω; υ(ring): 1567 ω, 1470 m,sh; β(ring): 803 ω ;C_6F_5-: υ(ring): 1651 ω (8a),1520 s (19a) 1498 vs (19b); 1437 ω (2), 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 (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_{as}(COC): 1090s, 1121 s; $\upsilon_{as}(CH_2)$: 2932 ω; $\upsilon_s(CH_2)$: 2874 m; $\beta_s(CH_2)$: 1366 m; $\gamma_s(CH_2)$1333 m. UV ($CHCl_3$) λ_{max} 417.0 (249000); 480 (12800); 513 (19800); 546 (9530); 589 (7909); 647 (4967). ^{1}H NMR: porhyrin 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, CH_2-α), 5.22 dd (4H, *J* = 6.5, 14.8, CH_2-α), 5.10 dt (4H, *J* = 3.0, 6.1, 6.1, H-1), 4.67 d (4H, *J* = 11.8, OCH_2Ph), 4.61 d (4H, *J* = 11.6, OCH_2Ph), 4.61 d (4H, *J* = 12.0, OCH_2Ph), 4.60 ddd (4H, *J* = 3.6, 4.6, 7.9, H-5), 4.60 d (4H, *J* = 11.8, OCH_2Ph), 4.47 d (4H, *J* = 11.6, OCH_2Ph), 4.44 d (4H, *J* = 12.0, OCH_2Ph), 4.27 dd (4H, *J* = 2.7, 4.6, H-4), 4.09 d (4H, *J* = 12.0, OCH_2Ph), 4.05 d (4H, *J* = 12.0, OCH_2Ph), 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). ^{13}C NMR: porphyrin moiety – 147.55 (4C, -(N)C=), 145.60 (4C, -(N)C=), 130.38 (4C, -CH=), 129.92 (4C, -CH=), 117.77 (2C, *meso* -C=), 117.07 (2C, J_{CF} = 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, $\underline{C}H_2Ph$), 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 CH_2Cl_2 1 ml and MeOH 2 ml 10% Pd(C) 90 mg was added. The reaction mixture was stirred under H_2 (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 $CHCl_3$, $CHCl_3$:MeOH 2:1 gave porphyrin **10** (37 mg, 63%) as dark green amorphous solid.

UV (MeOH) λ_{max} 410 (54600); 510 (5180); 543 (2340); 589 (1950); 647 (1970). ^{1}H NMR 300 MHz (CD_3OD): porhyrin moiety – 9.90 bs (4H), 9.05 bs (4H); sugar moiety – 4.05-3.52 m (18H). ^{13}C NMR 75 MHz (CD_3OD): 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 $C_{46}H_{36}F_{10}N_4O_{10}$ (Exact Mass 994.23) MS (m/z, FAB): 995.0 $(M+H)^+$, 1011.1 $(M+H_2O)^+$.

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