Synthesis, Spectroscopy, and Photocytotoxicity of Glycosylated Amino Acid Porphyrin Derivatives as Promising Molecules for Cancer Phototherapy

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Received December 23, 1998

To obtain molecules that can target malignant cells, two series of new *meso* glucosylporphyrins bearing amino acid residues are synthesized in four steps. The first series contained *n meso* glycosyl moieties and (4 − *n*) alanyl groups on the *ortho* or *para* positions of the *meso* phenyl. In the second series, the carbohydrate moiety is separated from the aryl substituent by a serine unit. Starting from *p*- or *o*-nitrobenzaldehyde, *p*- or *o*-acetylbenzaldehyde or -tolualdehyde, and pyrrole, the glycosylnitrophenylporphyrins **3**−**6** and tritolylporphyrins **8a,b** are synthesized under optimized conditions tailored from Lindsey's method. The nitro function is then reduced and *N*-Fmoc-L-alanine or acetylglycosylated *N*-Fmoc-serine are coupled on the amino function. A detailed ^{1}H and ^{13}C NMR study allows complete structural elucidation. The UV−visible fluorescence and MALDI mass spectra are presented. Compounds **19**−**22** produced $^1O_2$, and photocytotoxicities against the K562 leukemia cell line are compared to hematoporphyrin. As a result of their sensitizing abilities, these resultant compounds are of considerable interest for photodynamic therapy.

The chemistry of porphyrins bearing glycosylated groups has made rapid progress during recent years owing to the development of new photosensitizers being applied in cancer photochemotherapy.[1] Photodynamic therapy (PDT) is based on the principle that porphyrins become concentrated in tumor cells and, upon subsequent irradiation with visible light in the presence of oxygen, specifically destroy the cells.[2] Although the exact mechanism of PDT in cancer treatment is unknown, there is scope for exploring new variations to amplify the therapeutic efficiency of the senzitizer.

It occurred to us that porphyrins linked to a cellular recognition element and an hydrophilic moiety could appear as promising candidates for an application in PDT. Thus, porphyrins with sugar moieties have not only good solubility in aqueous solutions but also possible specific membrane interaction.[3] This property can be enhanced by use of appropriately selected short oligopeptides. Indeed, it was recently shown that two tripeptides (Arg-Gly-Asp and Asn-Gly-Arg) linked to a chemotherapeutic molecule (doxorubicin) targets the drug to the new blood vessels that nourish the tumor.[4b,c] This demonstrates that attaching small peptides to cancer drugs can enhance their efficacy, reduce their toxicity,[4] and also improve tumor cell targeting. Moreover, as glycopeptides and glycoproteins have been involved in important biological recognition phenomena and transport processes,[5] they have been used as carriers of metabolite inhibitors and toxic drugs; from this perspective and as a first approach, we have synthesized (i) mono-, di-, and tri-alanine glycoporphyrin derivatives **19a,b**, **20**, **21**, and **22a,b** (Scheme 1). Indeed, the free α-amino group of alanine is known to improve specific cancer cells targeting.[4a] In a second step, (ii) two tristolylporphyrins are substituted by a glycosylated serine **23a,b** because the presence of lipophilic aryl groups and hydrophilic substituents could increase the interaction with the

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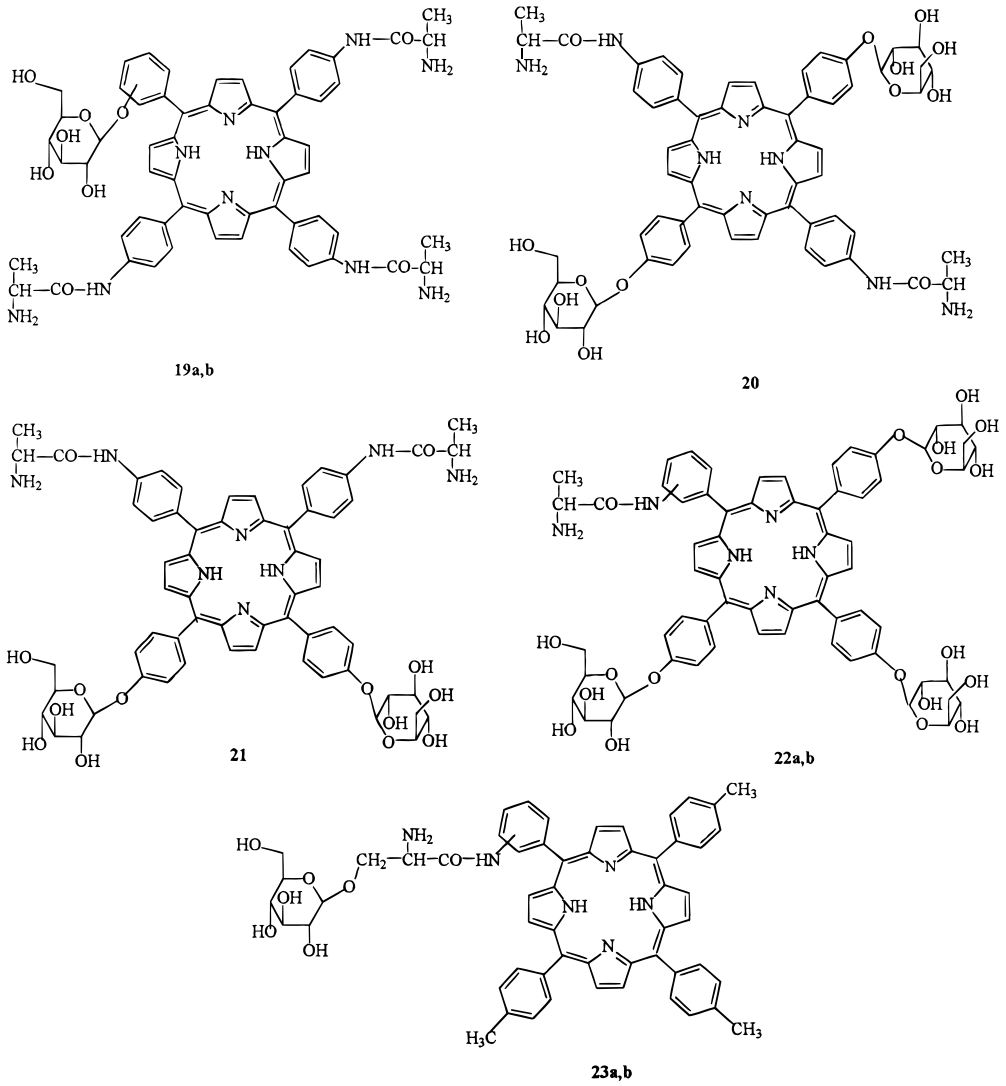
10.1021/jo982499+ CCC: $18.00
Published on Web 05/15/1999

Scheme 1[a]



[a] **a** and **b** refer to *ortho* and *para* position, respectively.

lipidic membrane. Several examples of coupling of amino acids to porphyrins have been reported in the literature, the great majority of which have been designed as models of hematoproteins[6] or for studies in electron-transfer reactions.[7] They have been also used in magnetic resonance imaging[8] and in DNA sequence recognition.[9]

In the present paper, we report full experimental data concerning the synthesis and characterization of amino acid glycosylporphyrin derivatives **19a,b**, **20**, **21**, **22a,b**, and **23a,b** (Scheme 1) and compare their in vitro photocytotoxic activities with hematoporphyrin (HP).

Results and Discussion

Synthesis. The different porphyrins were prepared according to the general route outlined in Schemes 2 and 3. Aldehyde **1a** was prepared from commercially available helicin (2-(*β*-D-glucopyranosyloxy)benzaldehyde) by acetylation at 0 °C during 50 min with acetic anhydride in dry pyridine (yield 80%). 4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)benzaldehyde **1b** was synthesized from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide and 4-hydroxybenzaldehyde (3 equiv) in acetone in the presence of 7% aqueous NaOH.[10] After 24 h, the expected compound was obtained in 35% yield. Compound **2** (Scheme 3) was prepared from *β*-D-glucose peracetate and *N*-Fmoc-L-serine with $BF_3 \cdot Et_2O$ (3 equiv) in acetonitrile for 2 h at room temperature.[11] Workup gave compound **2** in a 30% yield. Nitrophenylporphyrin derivatives **3**−**8** were synthesized following Lindsey's method.[12] This

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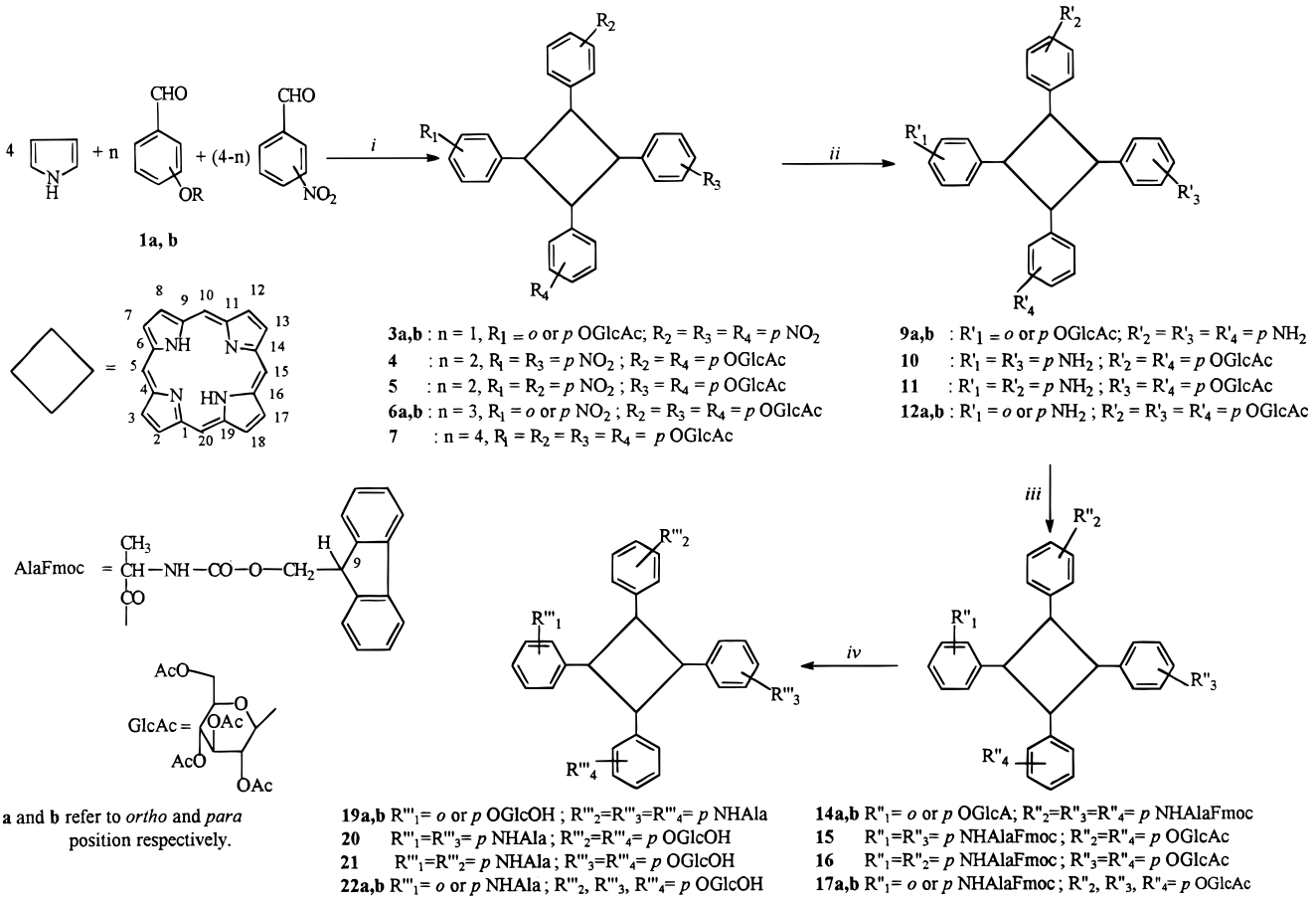
Scheme 2[a]



[a] Reaction conditions: (i) BF_3OEt_2/CH_2Cl_2, 18 h, then *p*-choranil; (ii) H_2, 10% Pd-C, THF, rt, 5 h; (iii) CH_2Cl_2, DCC, Fmoc-L-Ala, 15 h, rt; (iv) morpholine, then NaOMe/MeOH/CH_2Cl_2.

procedure (Schemes 2 and 3) consists of the condensation of a suitable aldehyde with pyrrole in the presence of BF_3/etherate (formation of porphyrinogen) followed by oxidation by *p*-chloranil to afford the porphyrin **3**−**8**. The condensation of pyrrole (4 equiv) with *para* nitrobenzaldehyde (3 equiv) and 2- or 4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)benzaldehyde **1a,b** (1 equiv) gave compounds **3a,b** (14% and 16% yield, respectively). The relative proportion (Table 1) of reagents (pyrrole/4-nitrobenzaldehyde/**1b**) have been studied in order to increase the yields of compounds **3b**, **4**, **5**, and **6b**. In all cases, these reagents were added to CH_2Cl_2 as solvent under argon at room temperature. After usual workup,[1d] porphyrins were purified by a silica gel column and PLC and then individually characterized by ^1H NMR analysis. For *meso*-tetraglucosylarylporphyrin **7**,[1d] it was iolated as a byproduct from the synthesis of **6b**. The yields are shown in Table 1. The synthesis of mononitrophenyltristolylporphyrins **8a,b** are shown in Scheme 3. For the preparation of these compounds, pyrrole was condensed with *p*-tolualdehyde and 2- or 4-nitrobenzaldehyde in a relative proportion of 4/3/1, but only mononitrophenyltristolylporphyrins were isolated by silica gel column and purified by PLC. Porphyrins **8a,b** were obtained in 14% and 15% yield, respectively. The usual reduction of the nitro function with $SnCl_2$/HCl could not be used because sugar moieties are sensitive under strongly acidic conditions. So the amino functions were obtained by reduction with H_2/Pd−C in THF for 5 h.[13] Glycosylated aminoporphyrins **9a,b**, **10**, **11**, and **12a,b** were obtained after purification on PLC, in 56−76% yield (Scheme 2). Unlike glycosylated porphyrins, mononitrophenyltristolylporphyrins were reduced in $CHCl_3$/acetic acid by the usual procedure ($SnCl_2$/HCl) (Scheme 3).[14] The mixture was stirred under reflux overnight and then was neutralized with NaOH. After extraction and purification on PLC, compounds **13a,b**[15] were obtained in 90% yield.

Two series of amino acid porphyrins have been synthesized. The first involves the coupling of **9a,b**, **10**, **11**, or **12a,b** with *N*-Fmoc-L-alanine to give mono-, di-, or triamino acid porphyrins glycosylated with protected NH_2 groups **14a,b**, **15**, **16**, and **17a,b** (Scheme 2). The second results from the coupling of **13a,b** with **2** to give monoglucosylamino acid porphyrin derivatives **18a,b** with a protected NH_2 group (Fmoc) (Scheme 3).

The general coupling method involves the formation of a symmetrical anhydride as a coupling agent with dicyclohexylcarbodiimide (DCC) and *N*-Fmoc-L-alanine in CH_2Cl_2 (15 h in darkness), which reacts with porphyrin derivatives. After removing the insoluble dicyclohexylurea by filtration, compounds **14**−**18** were obtained after purification on TLC in 90% yield.[15] The *N*-9-fluorenyl-

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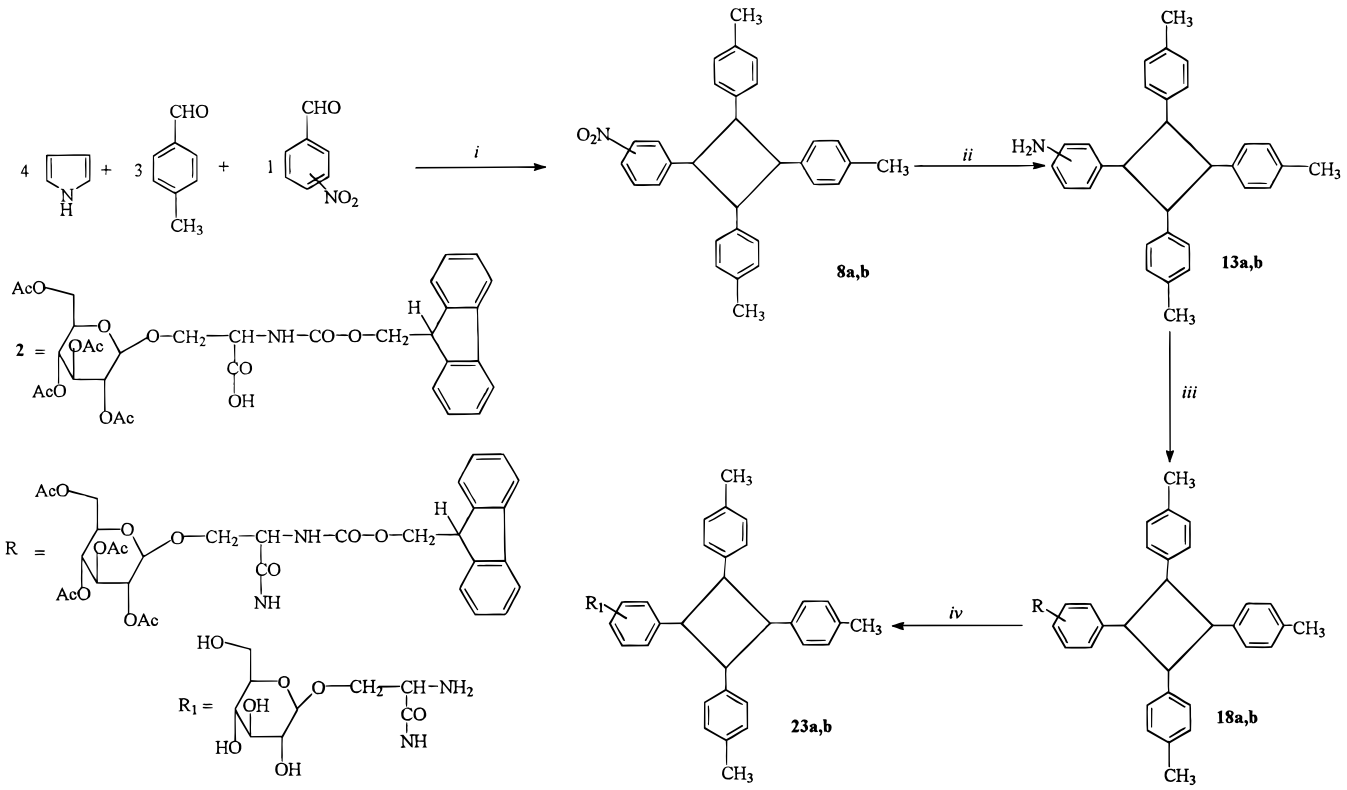
Scheme 3[a]



[a] Reaction conditions: (i) BF_3OEt_2/CH_2Cl_2, 18 h, then *p*-chloranil, reflux, 1 h; (ii) $SnCl_2/HCl$, reflux, 15 h; (iii) DCC, **2**, 15 h, rt; (iv) morpholine, then $H_2N\text{-}NH_2/MeOH/CH_2Cl_2$.

Table 1. Effect of Ratio of Reagents on the Yields of *para* Polyglucosylated 4-Nitrophenylporphyrins

porphyrins obtained	4/3/1[a]	4/2/2[a]	4/1/3[a]
3b	16[b]	2	1
4	1.8	14	1
5	1	10	1
6b	1	2	16
7	4	3.5	11
total yield	23.8	31.5	30

[a] Ratio of pyrrole/*p*-nitrobenzaldehyde/**1b**. [b] Yield of pure isolated compounds in %.

methoxycarbonyl (Fmoc) protective group of the α-amino function is frequently used in peptide chemistry and was selectively removed in high yield with a weak base (50% morpholine in CH_2Cl_2, rt, 1 h).[16] According to the literature,[17] the acetate groups of glucose moieties (**14**−**17**) were easily removed by treatment at room temperature (1 h) with NaOMe in $MeOH/CH_2Cl_2$ (8/2), yielding compounds **19**−**22** in 75−64% (Scheme 2). However, for compounds **18a,b**, deacetylation of the glucose moieties was not obvious because the usual basic condition leads to *β*-elimination.[18] We therefore utilized a procedure developed by Kunz[18a,b] that relies upon hydrazine in $MeOH/CH_2Cl_2$ to remove the acetates nucleophilically. Deacetylation was complete after 2 h at 25 °C, and compounds **23a,b** were obtained in 71% and 57% yield, respectively (Scheme 3).

Mass Characterization. Mass spectrometry of all porphyrin derivatives was performed using the MALDI (matrix-assisted laser desorption ionization) technique.[19] Positive ion mass spectra exhibited a base peak corresponding to the intact porphyrin, and no fragment ions were detected. The analysis of the isotopic components indicated the presence of a protonated species $(M + H)^+$ with a minor contribution of the radical cation $M^{+\bullet}$ (Figure 1), allowing the determination of the molecular mass with an accuracy generally around 0.001%.

^{1}H NMR Characterization. ^{1}H NMR spectra recorded at 400 MHz were used for characterization of compounds **3**−**18** in $CDCl_3$. The detailed resonance assignments are based on integration and selective homonuclear decoupling, as well as NOE and 2D homonuclear COSY experiments. The spectra of these compounds are governed by the symmetry properties of the product[1e] and by the orientation of the carbohydrates **3a,b**, **9a,b**, **14a,b**, *N*-Fmoc-L-alanine **17a,b**, and glycosylated serine **18a,b**. For *meso*-tetraglucosylarylporphyrins **7**,[1d] the resonances of the eight equivalent pyrrolic protons appear as a single peak at 8.90 ppm. In contrast, the pyrrolic proton resonances of the others compounds are more complicated. They depend on the number, the linking position, and the nature of *meso* substituents. For porphyrin derivatives bearing four different *meso*phenyl groups with *para* substitution (**3**, **6**, **7**, **9**, **12**−**14**, **17**, **18**) and according to the literature,[1e,20] the observation and the comparison of the *β* pyrrolic protons permits distinction between three classes of compounds. Indeed, *meso para* tetraphenylporphyrin derivatives **3**, **6**, **8b**, **9**, **12**,

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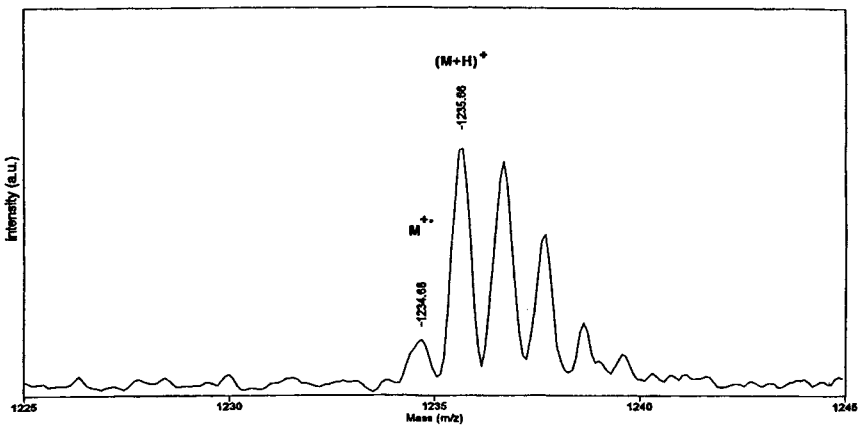

Figure 1. Example of MALDI mass spectra for compound **22b**.

13b, **14**, **17**, and **18b** whose *meso* positions were differently substituted (three identical *meso* phenyl groups) possess a symmetry plane. Thus, the pyrrolic proton resonance is split into two doublets ($J = 4.9$ Hz) and one singlet because protons H-12,18 and H-13,17, possessing a quasiequivalent electronic environment, are accidentally equivalent.[1d] When three *meso* positions are substituted by 4-nitrophenyl groups, which are electron-withdrawing, the resonance structures predict lower electron densities at H-3, H-7.[20] Thus, the doublet at δ 8.95 is assigned to these two pyrrolic protons, the doublet at δ 8.78 is assigned to H-2, H-8, and the H-12, H-13, H-17, H-18 resonance is assigned to the singlet at δ 8.80. When the three *meso*phenyl groups are electron-donating (as the 4-aminophenyl group **9b**, the 4-(*N*-Fmoc-L-alanyl)-aminophenyl group **14b**, and the 4-glucosylphenyl groups **6b**, **12b**, **17b**), they induce an upfield shift for protons H-2, H-8 (doublet) and for protons H-12, H-13, H-17, H-18 (singlet). We have observed the same behavior of β pyrrolic protons for tristolylporphyrin derivatives whose chemical shifts depend on the electronic effect of the 4-nitrophenyl **8b**, 4-aminophenyl **13b**, or 4-glucosylseryl-aminophenyl **18b** groups. The two other classes of porphyrins were substituted by two identical *meso* phenyl groups. The observation of their pyrrole protons permits us to distinguish between *cis* and *trans* isomers readily by ^{1}H NMR. Thus, pyrrole protons of *trans* compounds (**4**, **10**, **15**) (Scheme 2) which are the most symmetrical, give two doublets for any pair of adjacent protons. For the *cis* isomer (**5**, **11**, **16**) (Scheme 2), the four types of pyrroles protons give rise to two singlets (H-7(8), H-17-(18)) and two coupled doublets (H-2(13), H-3(12)).

For porphyrin derivatives which possess only one *meso* phenyl group with *ortho* substitution (**3a**, **6a**, **8a**, **9a**, **12a**, **13a**, **14a**, **17a**, **18a**), we have observed an obvious change in the chemical shift of the phenyl ring.[1f] Furthermore, compounds (**3a**, **9a**, **14a**, **18a**) which are characterized by *ortho* glucosyl, alanyl, and glucosylseryl substitutions, are subject to considerable changes in the ^{1}H NMR chemical shifts and/or in figures relative to most of the nuclei. Thus, for example, all the sugar protons experience a particularly pronounced shielding from -0.31 ppm (H-6_A) to -1.31 ppm (H-2), and two acetyl groups that would otherwise show a larger shift toward 2.0 ppm are also shifted downfield (δ 1.26 and δ -0.92). These nuclei are obviously located well within the range of the shielding current above the porphyrin macrocycle. Moreover, the β pyrrole proton signals of **3a** appeared as four doublets ($J = 4.9$ Hz) at 8.74, 8.77, 8.81, and 8.92 ppm and then as two singlets at δ 8.82 and 8.78 ppm for H-12, -13, -17, and -18. The signals of the nitrophenyl protons are broadened (Figure 2). These phenomena reflect a reduced symmetry induced by the orientation of the substituent that in turn leads to an unsymmetrical folded structure because of steric hindrance.

^{13}C NMR Analysis. ^{13}C NMR spectroscopy was also used to elucidate the structure by means of DEPT experiments and ^{1}H$-^{13}$C shift correlation. The observation and the comparison of the β pyrrolic carbons, in *meso para* phenyl-substituted compounds (**3b**, **4**, **5**, **6b**, **7**), permits the distinction of four differents signals. The appearance and the broadness of these signals are governed by the symmetry properties of the product, allowing us to differentiate molecules from each other. Figure 3 shows the spectra of mono-, bis-, or trisglucosylaryl tri-, di-, or mononitrophenylporphyrins **3b**, **4**, **5**, and **6b** and tetraglucosylarylporphyrin **7** for the β pyrrolic carbon. In the series of related compounds characterized by *ortho* glucosyl, alanyl, and glucosylseryl substitution (**3a**, **9a**, **14a**, **18a**), we found the same phenomenon as in ^{1}H NMR, that is, a shielding of *ortho* substituents and a modification of β pyrrolic carbons that reflect a diminished symmetry of the compounds and a distortion of the porphyrin macrocycle.

UV−visible Absorption. The porphyrins synthesized in this work show typical electronic spectra, with a Soret band near 420 nm and four less intense visible bands Q (I, II, III, and IV) in CH_2Cl_2.[21] Generally, these porphyrins give *etio* spectra ($\epsilon_{IV} > \epsilon_{III} > \epsilon_{II} > \epsilon_I$), but there are a few exceptions. The relative intensities of the Q (II) and Q (I) band of certain porphyrin derivatives **9a,b**, **10**, **11**, **12b**, **14b**, **15** show a nonstandard type ($\epsilon_I/\epsilon_{II} > 1$). In aqueous solutions, glucosylseryltristolylporphyrins **23a,b** exhibited an extremely broadened split Soret band (Figure 4). This result is due to the combination of cofacial and edge-to-edge interaction of self-assembled aggregates.[22] In contrast, the Soret band of compound **22b** is broadened and blue-shifted, whereas the Soret band of alanylphenylglucosylarylporphyrins **19**−**22a** are split into two bands that are also blue-shifted (Table 2). These blue-shift absorptions could be attributed to face-to-face orientation.[23]

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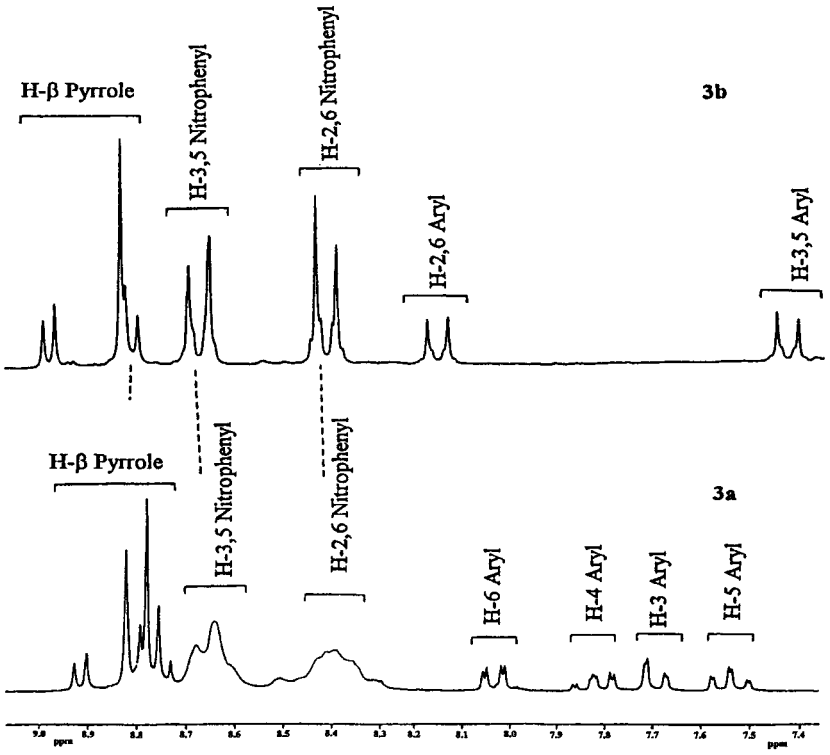

Figure 2. Behavior of β pyrrolic (δ 8.7−9.0 ppm) and *meso* glucosylaryl (7.4−8.7 ppm) protons for **3a,b** compounds.

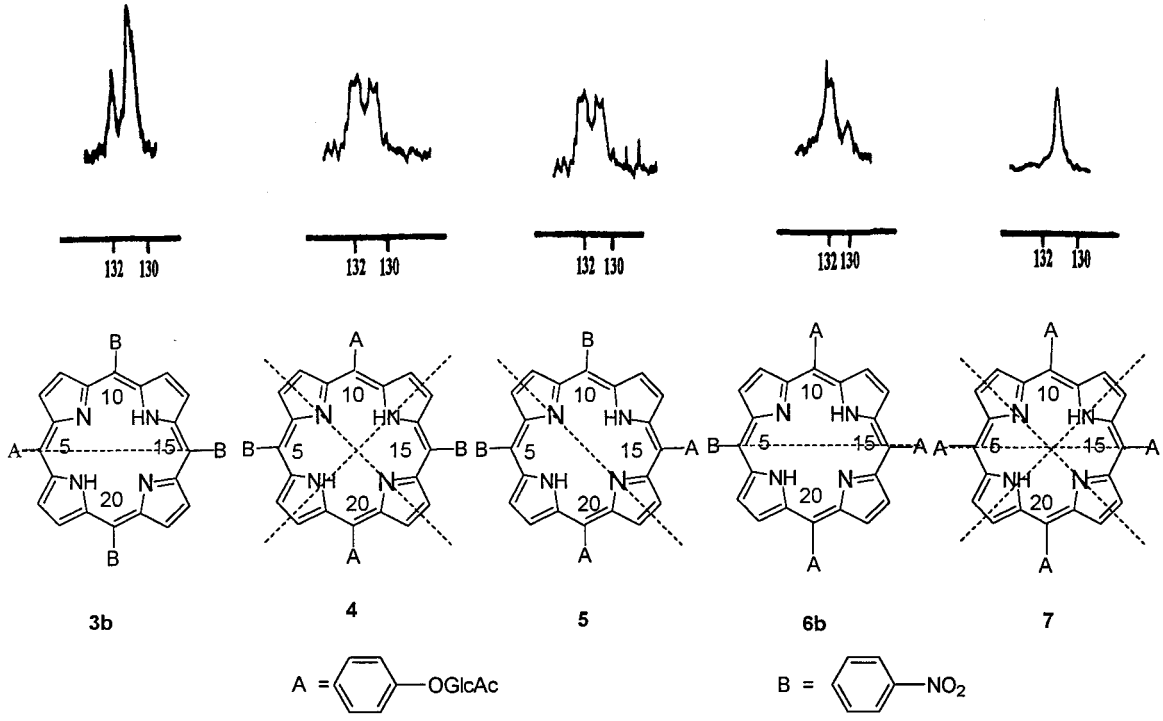

Figure 3. β pyrrole carbon part of ^{13}C NMR spectra of compounds **3**−**7**. The structures indicate the molecular symmetry.

Fluorescence Spectroscopy. All fluorescence spectra of compounds in CH_2Cl_2 were characterized by two emission bands.[1i] The only porphyrins (**6a**, **8a**) bearing an NO_2 group in the *ortho* position gave no fluorescence emission, most likely as a result of specific interaction of the NO_2 function with the porphyrin ring, whereas isomers **6b** and **8b** with the NO_2 group in the *para* position showed a significant fluorescence emission. The fluorescence emission wavelengths of **20**, **21**, and **22a,b** in aqueous solutions were identical to those obtained in THF, but the emission was strongly quenched. This decay of fluorescence can be explained by the formation of aggregates[22] and supports the results observed in the UV−visible spectra.

Singlet Oxygen Production. To determine the photosensitizing properties of porphyrins **19**−**23**, the trapping reactions of $^1O_2$ with ergosterol acetate were carried out.[24] Reference experiments with eosin and HP as

(24) Ohloff, G. *Pure Appl. Chem.* **1975**, *43*, 481.

Table 2. UV−vis Spectra of Porphyrin Derivatives in Various Solvents

compd (solvent[a])	λ_{nm} ($\epsilon \times 10^{-3}$, cm^{-1} mol^{-1} L)						
	Soret 1	Soret 2	IV	III	II	I	ratio ϵ_I/ϵ_{II}
3a (a)		422 (380.3)	518 (10.6)	554 (5.9)	592 (3.5)	648 (2.5)	0.71
3b (a)		424 (152.0)	516 (12.7)	552 (6.8)	590 (4.2)	646 (2.5)	0.59
4 (a)		422 (279.5)	516 (16.6)	554 (9.5)	592 (5.3)	648 (4.2)	0.79
5 (a)		422 (380.3)	518 (10.6)	554 (5.9)	592 (3.5)	648 (2.5)	0.71
6a (a)		420 (233.3)	516 (13.3)	552 (8.2)	592 (5.0)	648 (4.2)	0.84
6b (a)		420 (335.9)	516 (13.9)	552 (6.8)	592 (4.3)	648 (2.9)	0.67
7 (a)		420 (458.0)	516 (17.6)	552 (9.8)	592 (5.5)	648 (4.4)	0.80
8a (a)		420 (365.4)	516 (16.7)	552 (7.8)	592 (5.0)	648 (3.8)	0.76
8b (a)		420 (325.4)	518 (12.3)	554 (9.2)	592 (4.3)	648 (3.0)	0.70
9a (a)		426 (205.9)	520 (10.9)	560 (9.0)	596 (4.0)	654 (5.1)	1.27
9b (a)		426 (434.7)	522 (11.0)	562 (10.4)	596 (4.0)	654 (5.5)	1.37
10 (a)		424 (384.2)	520 (16.3)	558 (13.3)	594 (5.5)	652 (7.1)	1.29
11 (a)		424 (376.5)	520 (14.9)	558 (12.2)	594 (5.2)	652 (6.5)	1.25
12a (a)		422 (344.8)	518 (11.7)	554 (7.5)	594 (4.9)	650 (4.5)	0.92
12b (a)		422 (312.0)	518 (13.4)	554 (9.1)	592 (4.3)	650 (4.5)	1.05
13a (a)		420 (435.7)	516 (19.3)	552 (10.1)	592 (6.0)	648 (4.0)	0.67
13b (a)		422 (335.7)	518 (16.5)	554 (5.4)	594 (2.6)	650 (2.1)	0.81
14a (a)		422 (309.1)	516 (11.5)	552 (6.1)	592 (3.5)	648 (3.2)	0.91
14b (a)		422 (240.9)	518 (11.4)	554 (7.7)	592 (3.9)	648 (3.8)	1.02
15 (a)		422 (319.6)	518 (8.8)	554 (5.5)	594 (2.7)	650 (2.8)	1.04
16 (a)		422 (352.7)	518 (9.5)	554 (7.0)	592 (4.9)	648 (4.8)	0.98
17a (a)		422 (240.6)	516 (10.9)	552 (6.3)	592 (3.7)	650 (3.6)	0.97
17b (a)		420 (348.6)	516 (11.8)	552 (6.8)	592 (3.6)	648 (3.5)	0.97
18a (a)		420 (473.4)	516 (17.2)	552 (9.0)	590 (5.3)	646 (4.1)	0.77
18b (a)		420 (379.0)	516 (9.3)	552 (5.3)	592 (2.2)	648 (2.0)	0.91
19a (b)	406 (75.6)	420 (46.3)	522 (7.9)	558 (6.4)	598 (3.3)	654 (3.3)	1.00
19b (b)	404 (79.4)	420[b] (65.4)	522 (8.1)	558 (6.5)	600 (3.6)	654 (3.5)	0.97
20 (b)	404 (73.1)	422 (44.1)	522 (7.1)	560 (6.0)	598 (3.1)	652 (3.0)	0.97
21 (b)	406 (82.1)	422[b] (60.1)	522 (8.9)	558 (6.8)	600 (3.8)	654 (3.6)	0.95
22a (b)	396 (70.4)	416 (40.1)	526 (8.1)	560 (6.5)	600 (3.7)	654 (3.6)	0.97
22b (b)		416 (79.6)	524 (8.0)	560 (6.3)	598 (3.7)	652 (3.5)	0.95
23a (b)	414[b] (17.1)	450 (50.3)	526 (12.4)	554 (6.3)	594 (3.8)	652 (3.5)	0.92
23b (b)	416[b] (16.6)	450 (42.9)	526 (10.1)	556 (5.6)	596 (3.2)	652 (3.1)	0.97

[a] The solvents used are as follows: (a) CH_2Cl_2, (b) aqueous solutions. [b] Soret band appears as a "shoulder".

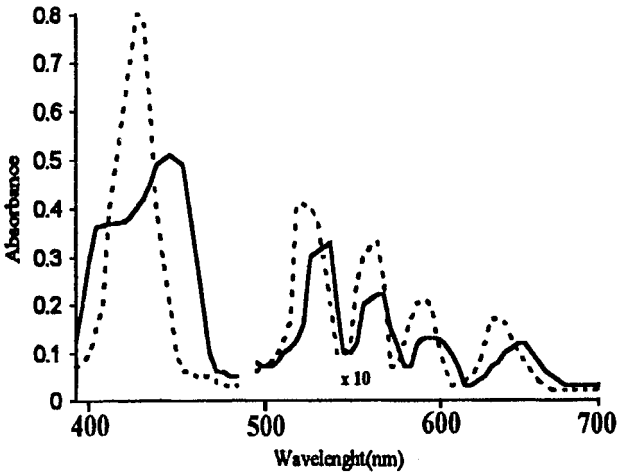

Figure 4. Absorption spectra of porphyrins **23b** (3.3×10^{-5} M) in THF (- - -) and in aqueous solution (—).

sensitizers gave ergosterol acetate endoperoxide with nearly quantitative yields. In the same experimental conditions, porphyrins **19**−**23** were almost as efficient as HP, which is known as a photosensitizer that produces singlet oxygen.

Biological Essays. The photocytotoxicity of glucosylated amino acid porphyrin derivatives **19a,b** and **22a,b** have been described in a previous paper.[1i] Using the same conditions, the photocytotoxicity of compounds **20**, **21**, and **23a,b** was tested against K562 human chronic myelogenous leukemia cells. Figure 5 displays dead cell counts as a function of irradiation time and the subsequent increase following a further 24 h incubation in the dark. HP was used as a control. For all synthetic porphyrins, the immediate dead cell counts were always lower than with HP, and did not increase with illumination times. Moreover, these dead cell counts were identical even if the irradiation time increased. Overall, the 24 h incubation in the dark resulted in an increase of dead cell counts. Although the immediate effects account for early necrotic death, the delayed postirradiation deaths are likely the result of photoirradiation-induced apoptosis followed by secondary necrosis. Although compounds **20**, **21**, and **22a** containing alanyl groups induced limited immediate cell death when compared to the immediate effect of HP, they lead to a large percentage of dead cells after 24 h postirradiation incubation in the dark, provided that the incubation is longer than 60 min. All other synthetic compounds showed a lower effect, especially compounds **23a,b** containing three tolyl groups and one glucosylseryl moiety, for which postirradiation dead cell count stalled as soon as they were irradiated for 40 min. Differences in activities of these glucosylated amino acid porphyrin derivatives may be attributed to the nature, number, and *meso* positions of amino acids and glucose.

In summary, this paper describes the synthesis and the characterization of glucosylaminoacylporphyrin derivatives that are obtained in best yield by condensation in different proportions of two benzaldehydes with pyrrole using Lindsey's conditions. To improve cell membrane recognitions, these tetrapyrrolic macrocycles are substituted on the *meso* positions by amino acids and glucose. Substitutions in the *ortho* and *para* positions lead to further insights into cell membrane interaction. The photocytotoxicity of these synthetic porphyrins against K562 indicated that the immediate dead cell counts were always lower than those observed with HP. However, for three porphyrin derivatives, the delayed effects (24 h

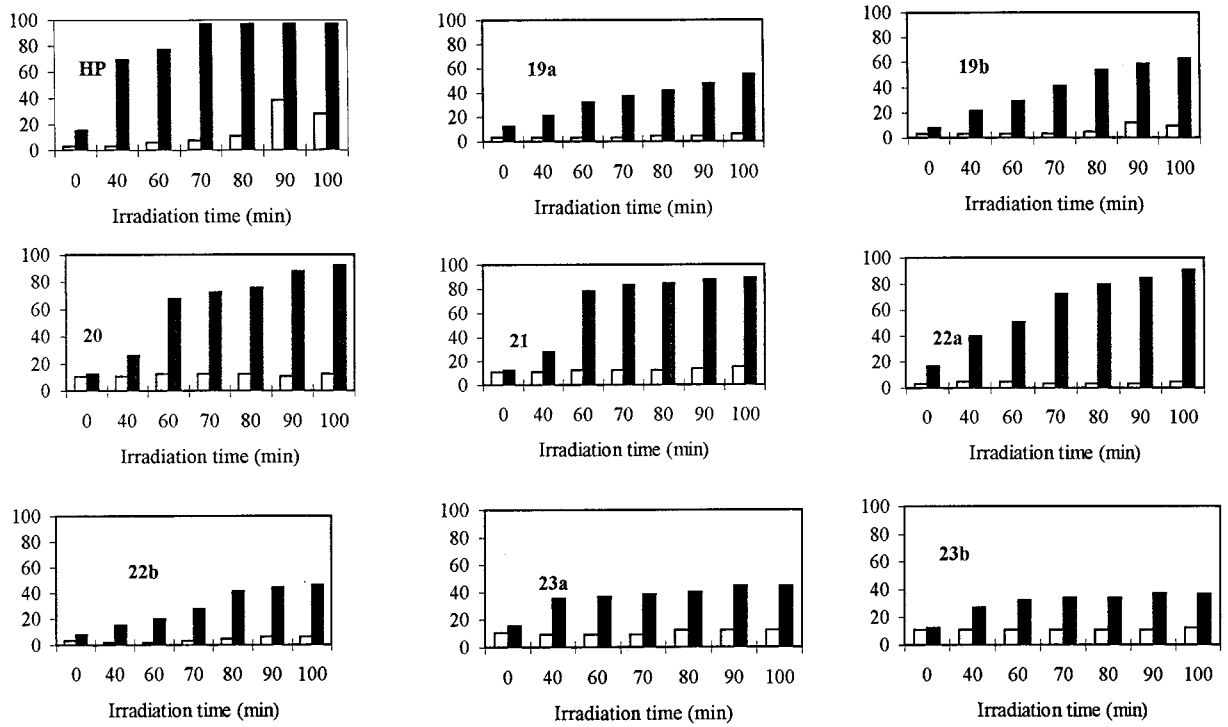

Figure 5. Percentage of PI stained cell vs time. Open bars: dead cell count after indicated irradiation time. Solid bars: dead cell count after a further 24 h incubation in the dark.

incubation in the dark at 37 °C) were always comparable to those observed with HP when irradiation was longer than 60 min. The present strategy may be easily used for preparation of glycosylated porphyrins substituted on the *meso* positions by small peptides (three or four amino acids).

Experimental Section

General. All solvents and reagents were purchased from Aldrich, Prolabo, or Janssen. Pyrrole was distilled over CaH_2 under reduced pressure immediately before use. Methylene chloride and chloroform were distilled over P_2O_5 and then CaH_2. Analytical thin-layer chromatography (TLC) was performed on silica gel (Merck, $60F_{254}$). Merck precoated plates (silica gel 60, 2 mm) were used for preparative thin-layer chromatography. Column chromatography was carried out with silica gel (60 ACC, 15−40 μm, Merck) or with Sephadex LH20 (Pharmacia). The UV−visible spectra were obtained on a spectrophotometer using 1 or 0.1 cm quartz cells, and emission spectra were recorded by using a Perkin-Elmer LS-5B spectrofluorimeter. Melting points were determined by capillary tube apparatus and were not corrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard. The chemical shifts are given in ppm, and coupling constants are in Hz. MALDI mass spectra were obtained on a Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. E.I. mass spectra were performed at the "Laboratoire Départemental d'Analyse de Limoges" and elemental analyses were carried by the "Service Régional de Microanalyse de l'Université Pierre et Marie Curie, Paris".

Synthesis. Benzaldehydes **1a,b** and glycosylated serine derivative **2** were synthesized according to the literature.[1f,10,11]

Synthesis of Nitrophenylporphyrins. Pyrrole (4 equiv), per-*O*-acetyl glucosylated benzaldehyde **1a,b** (1, 2, or 3 equiv) or *p*-tolualdehyde (3 equiv), and 2- or 4-nitrobenzaldehyde (1, 2, or 3 equiv) were added to methylene chloride (500 mL) purged with argon for 30 min. The mixture was stirred and purged with argon for a further 10 min, after which a BF_3/etherate solution (0.5 mL, 0.2 M) in methylene chloride was added. This reaction mixture was stirred overnight at room temperature. *p*-Chloranil (0.75 equiv/pyrrole) was then added, and the mixture was stirred under reflux for 1 h. The solvent was evaporated to dryness, and the porphyrin mixture was purified by column chromatography (toluene/acetone, 100/0 to 70/30) and thin-layer chromatography.

5-[2-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-phenyl]-10,15,20-tris(4-nitrophenyl) Porphyrin (3a). 1a (452 mg, 1 mmol, 1 equiv), 4-nitrobenzaldehyde (453 mg, 3 mmol, 3 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) afforded pure product **3a** 154 mg (14%). R_f 0.41 (toluene/acetone, 85/15). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.80(2H, br s, NH); −0.92(3H, s, OAc); 1.26(3H, s, OAc); 1.86(3H, s, OAc); 1.96(3H, s, OAc); 3.65(1H, ddd, J = 7.7, 5.1, 2.5 Hz, H-5′ose); 4.00(1H, dd, J = 12.1−2.6, H-6$_b$′ose); 4.12(1H, dd, J = 12.1−5.2 Hz, H-6$_a$′ose); 4.18(1H, dd, J = 7.7−2.2 Hz, H-2′); 4.64(1H, t, J = 9.2 Hz, H-3′ose); 4.92(1H, d, J = 7.7 Hz, H-1′ose); 7.52(1H, dt, J = 7.5−1.6 Hz, H-5 aryl); 7.70-(1H, dt, J = 7.5−1.6 Hz, H-3 aryl); 7.80(1H, dt, J = 7.5−1.6 Hz, H-4 aryl); 8.05(1H, dd, J = 7.5−1.6 Hz, H-6 aryl); 8.40-(6H, m, H-2,6 nitrophenyl); 8.65(6H, br d, J = 8.6 Hz, H-3,5 nitrophenyl); 8.74(1H, d, J = 4.9 Hz, H-2 or H-8 β pyrrole); 8.77(1H, d, J = 4.9 Hz, H-8 or H-2 β pyrrole); 8.78(2H, s, H-12,-18 or H13,17 β pyrrole); 8.81(1H, d, J = 4.9 Hz, H-3 or H-7 β pyrrole); 8.82(2H, s, H-12,18 or H-13,17 β pyrrole); 8.92(1H, d, J = 4.9 Hz, H-7 or H-3 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 17.5(1C, *C*H$_3$CO); 19.8(1C, *C*H$_3$CO); 20.3(1C, *C*H$_3$CO); 20.5-(1C, *C*H$_3$CO); 62.1(1C, C-6′ose); 68.4(1C, C-4′ose); 70.1(1C, C-2′ose); 72.0(1C, C-5′ose); 72.3(1C, C-3′ose); 99.7(1C, C-1′ose); 116.6(1C, C *meso*); 117.6(1C, C *meso*); 117.7(1C, C *meso*); 117.8-(1C, C-3 aryl); 118(1C, C *meso*); 121.9(6C, C-3,5 nitrophenyl); 122.7(1C, C-5 aryl); 130.4(C β pyrrole and C-4 aryl); 131.7(C β pyrrole); 132.2(1C, C-1 aryl); 135.0(6C, C-2,6 nitrophenyl); 135.9(1C, C-6 aryl); 146.2(8C, C-α pyrrole); 147.9(3C, C-4 nitrophenyl); 148.5(3C, C-1 nitrophenyl); 156.2(1C, C-2 aryl); 166.9(1C, CH$_3$*C*O); 169.0(1C, CH$_3$*C*O); 169.5(1C, CH$_3$*C*O); 170.3(1C, CH$_3$*C*O). MS (MALDI) *m/z*: 1096.2 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{58}H_{45}N_7O_{16}$: C, 63.55; H, 4.14; N, 8.94. Found: C, 63.35; H, 4.16; N, 8.92.

5-[4-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-phenyl]-10,15,20-tris(4-nitrophenyl) Porphyrin (3b). 1b (452 mg, 1 mmol, 1 equiv), 4-nitrobenzaldehyde (453 mg, 3

mmol, 3 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) gave **3b** 175 mg (16%); R_f 0.53 (toluene/acetone, 85/15). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.77(2H, br s, NH); 2.12(3H, s, OAc); 2.13(3H, s, OAc); 2.14(3H, s, OAc); 2.23(3H, s, OAc); 4.08(1H, ddd, J = 9.6−5.2−2.6 Hz, H-5′ ose); 4.32(1H, dd, J = 12.3−2.6 Hz, H-6_b′ose); 4.43(1H, dd, J = 12.3−5.2 Hz, H-6_a′ose); 5.35(1H, m, H-4′ose); 5.49(3H, m, H-1′,2′,3′ose); 7.43(2H, d, J = 8.6 Hz, H-3,5 aryl); 8.15(2H, d, J = 8.6 Hz, H-2,6 aryl); 8.38(6H, d, J = 8.9 Hz, H-2,6 nitrophenyl); 8.65-(6H, d, J = 8.6 Hz, H-3,5 nitrophenyl); 8.78(2H, d, J = 4.9 Hz, H-2,8 β pyrrole); 8.80(4H, s, H-12,13,17,18 β pyrrole); 8.95-(2H, d, J = 4.9 Hz, H-3,7 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6(2C, *C*H_3CO); 20.8(2C, *C*H_3CO); 62.1(1C, C-6′ose); 68.4-(1C, C-4′ose); 71.4(1C, C-2′ or 3′ose); 72.3(1C, C-5′ose); 72.8-(1C, C-2′ or 3′ ose); 99.1(1C, C1′ose); 115.6(2C, C-3,5 aryl); 117.7(1C, C *meso*); 118.0(2C, C *meso*); 121.1(2C, C *meso*); 122.0-(6C, C-3,5 nitrophenyl); 131.2(C β pyrrole); 132.3(C β pyrrole); 135.0(6C, C-2,6 nitrophenyl); 135.6(2C, C-2,6 aryl); 136.4(1C, C-1 aryl); 146.2(8C, C α pyrrole); 147.6(3C, C-4 nitrophenyl); 148.5(3C, C-1 nitrophenyl); 156.9(1C, C-4 aryl); 168.3(1C, CH_3*C*O); 169.4(1C, CH_3*C*O); 170.3(1C, CH_3*C*O); 170.5(1C, CH_3*C*O). MS (MALDI) *m*/*z*: 1096.2 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{58}H_{45}N_7O_{16}$: C, 63.55; H, 4.14; N, 8.94. Found: C, 63.48; H, 4.11; N, 8.91.

5,10,15,20-Bis(4-nitrophenyl)-bis[(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (4) and (5). 1b (904 mg, 2 mmol, 2 equiv), 4-nitrobenzaldehyde (302 mg, 2 mmol, 2 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) gave **4** 196 mg (14%) and **5** 140 mg (10%). **4**: R_f 0.42 (toluene/acetone, 75/25, two elutions). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200MH) δ −2.80(2H, br s, NH); 2.04(6H, s, OAc); 2.05(12H, s, OAc); 2.06(6H, s, OAc); 4.08(2H, ddd, J = 9.6−5.2−2.5 Hz, H-5′ose); 4.32(2H, J = 12.3−2.6 Hz, H-6_b′ose); 4.42(2H, J = 12.3−5.4 Hz, H-6_a′ose); 5.33(2H, m, H-4′ose); 5.47(6H, m, H-1′,2′,3′ose); 7.40(4H, d, J = 8.6 Hz, H-3,5aryl); 8.13(4H, d, J = 8.6 Hz, H-2,6 aryl); 8.37(4H, d, J = 8.7 Hz, H-2,6 nitrophenyl); 8.63(4H, d, J = 8.7 Hz, H-3,5 nitrophenyl); 8.75(4H, d, J = 4.8 Hz, H-3,7,13,17 β pyrrole); 8.91(4H, d, J = 4.8 Hz, H-2,8,12,18 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.5(8C, *C*H_3CO); 62.0(2C, C-6′ose); 68.3(2C, C-4′ose); 71.3(2C, C-2′ or C-3′ose); 72.5(2C, C-5′ose); 72.7(2C, C-2′ or C-3′ose); 99.0(2C, C-1′ose); 115.2(4C, C-3,5 aryl); 117.5-(2C, C *meso*); 120.2(2C, C *meso*); 121.6(4C, C-3,5 nitrophenyl); 131.7(8C, C β pyrrole); 135.0(4C, C-2,6 nitrophenyl); 136.5-(2C, C-1 aryl); 146.2(8C, C α pyrrole); 147.8(2C, C-4 nitrophenyl); 148.7(2C, C-1 nitrophenyl); 161.2(2C, C-4 aryl); 169.3(4C, CH_3*C*O); 170.2(2C, CH_3*C*O); 170.5(2C, CH_3*C*O). MS (MALDI) *m*/*z*: 1397.4 ([M + H]$^+$ monoisotopic); Anal. Calcd for $C_{72}H_{64}N_6O_{24}\cdot 2H_2O$: C, 60.43; H, 4.78; N, 5.87. Found: C, 60.25; H, 4.80; N, 5.83. **5**: R_f 0.44 (toluene/acetone,75/25, two elutions). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.77(2H, br s,NH); 2.12(6H, s, OAc); 2.13(6H, s, OAc); 2.14-(6H, s, OAc); 2.23(6H, s, OAc); 4.08(2H, ddd, J = 9.6−5.2−2.5 Hz, H-5′ose); 4.33(2H, dd, J = 12.5−2.5, H-6_b′ose); 4.45(2H, dd, J = 12.5−5.2 Hz, H-6_a′ose); 5.33(2H, m, H-4′ose); 5.48-(6H, m, H-1′,2′,3′ose); 7.14(4H, d, J = 8.6 Hz,H-3,5 aryl); 8.14-(4H,d, J = 8.6 Hz,H-2,6 aryl); 8.38(4H,d, J = 8.6 Hz,H-2,6 nitrophenyl); 8.64(4H,d,H-3,5 nitrophenyl); 8.76(2H,d, J = 4.9 Hz,H-3,12 β pyrrole); 8.78(2H,s,H-7,8 β pyrrole); 8.91(2H,s,H-17,18 β pyrrole); 8.93(2H, d, J = 4.9 Hz, H-2,13 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6(4C, *C*H_3CO); 20.8(4C, *C*H_3CO); 62.1(2C, C-6′ose); 68.4(2C, C-4′ose); 71.3(2C, C-2′ose or C-3′ose); 72.3(2C, C-5′ose); 72.6(2C, C-2′or C-3′ose); 99.1(2C, C-1′ose); 115.2(4C, C-3,5 aryl); 117.2(2C, C *meso*); 120.7(2C, C *meso*); 121.9(4C, C-3,5 nitrophenyl); 130.9(C-β pyrrole); 131.6(C-β pyrrole); 136.4(2C, C-1 aryl); 135.0(4C, C-2,6 nitrophenyl); 135.5(4C, C-2,6 aryl); 146.2(8C, C-α pyrrole); 147.6(2C, C-4 nitrophenyl); 148.7(2C, C-1 nitrophenyl); 156.8(2C, C-4 aryl); 169.4(4C, CH_3*C*O); 170.3(2C, CH_3*C*O); 170.6(2C, CH_3*C*O). MS (MALDI) *m*/*z*: 1397.4 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{72}H_{64}N_6O_{24}\cdot 3H_2O$: C, 59.67; H, 4.87; N, 5.80. Found: C, 59.87; H, 4.90; N, 5.84.

5-(2-Nitrophenyl)-10,15,20-tris[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (6a). 1a (1.35 g, 3 mmol, 3 equiv), 2-nitrobenzaldehyde (151 mg, 1 mmol, 1 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) gave **6a** 238 mg (14%). R_f 0.45 (toluene/acetone, 60/40). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.71(2H, br s, NH); 2.11(9H, s, −OAc); 2.12(9H, s, −OAc); 2.13(6H, s, OAc); 2.14-(3H, s, −OAc); 2.23(9H, s, −OAc); 4.08(3H, ddd, J = 9.7−5.3−2.8 Hz, H-5′ ose); 4.31(3H, dd, J = 12.2−2.2, H-6_b′ ose); 4.43(3H, dd, J = 12.2−5.3 Hz, H-6_a′ ose); 5.34(3H, br d, J = 9.7 Hz, H-4′ ose); 5.48(9H, m, H-1′,2′,3′ ose); 7.40(6H, br d, J = 7.3 Hz, H-3,5 aryl); 7.96 (2H, m, H-4,5 *o*-nitrophenyl); 8.14 (6H, brd, J = 7.5 Hz, H-2,6 aryl); 8.25(1H, dd, J = 7.1−2.1 Hz, H-6 *o*-nitrophenyl); 8.44(1H, dd, J = 7.3−2.1 Hz, H-3 *o*-nitrophenyl); 8.67(2H, d, J = 4.9 Hz, H-3,7 β pyrrole); 8.85-(2H, d, J = 4.8 Hz, H-2,8 β pyrrole); 8.86(4H, s, H-12,13,17,18 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6(6C, *C*H_3CO); 20.7-(6C, *C*H_3CO); 62.1(3C, C-6′ose); 68.4(3C, C-4′ose); 71.3(3C, C-2′ or C-3′ose); 72.3(3C, C-5′ose); 72.6(3C, C-2′ or C-3′ose); 99.1-(3C, C-1′ose); 113.9(1C, C *meso*); 115.1(6C, C-3,5 aryl); 119.6-(2C, C *meso*); 120,0(1C, C *meso*); 124,0(1C, C-3 nitrophenyl); 129.5(1C, C-4 nitrophenyl); 130.9(1C, C-5 nitrophenyl); 131.1-(C-β pyrrole); 131.5(C-β pyrrole); 135.5(6C, C-2,6 aryl); 136.5-(1C, C-6 nitrophenyl); 136.8(1C, C-1 nitrophenyl); 136.9(2C, C-1 aryl); 137.1(1C, C-1 aryl); 146.5(8C, C-α pyrrole); 169.4 (6C, CH_3*C*O); 170.2(4C, CH_3*C*O); 170.5(2C, CH_3*C*O). MS (MALDI) *m*/*z*: 1699.5 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{86}H_{83}N_5O_{32}\cdot 2H_2O$: C, 59.49; H, 5.13; N, 4.00. Found: C, 59.55; H, 5.15; N, 4.02.

5-(4-Nitrophenyl)-10,15,20-tris[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (6b). 1b (1.35 g, 3 mmol, 3 equiv), 4-nitrobenzaldehyde (151 mg, 1 mmol, 1 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) gave **6b** 272 mg (16%). R_f 0.50 (toluene/acetone, 85/15). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.77(2H, br s, NH); 2.12(9H, s, −OAc); 2.13(18H, s, −OAc); 2.23(9H, s, −OAc); 4.08(3H, ddd, J = 9.8−5.3−2.6 Hz, H-5′ ose); 4.32(3H, dd, J = 12.1−2.1 Hz, H-6′$_b$ ose); 4.42(3H, dd, J = 12.1−5.1 Hz, H-6′$_a$ ose); 5.35(3H, m, H-4′ ose); 5.49(9H, m, H-1′,2′,3′ ose); 7.39-(6H, d, J = 8.5 Hz, H-3,5 aryl); 8.14(6H, d, J = 8.4 Hz, H-2,6 aryl); 8.39(2H, d, J = 8.6 Hz, H-2,6 nitrophenyl); 8.64(2H, d, J = 8.6 Hz, H-3,5 nitrophenyl); 8.75(2H, d, J = 4.9 Hz, H-3,7 β pyrrole); 8.88(4H, s, H-12,13,17,18 β pyrrole); 8.90(2H, d, J = 4.9 Hz, H-2,8 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6-(8C, *C*H_3CO); 20.8(4C, *C*H_3CO); 62.1(3C, C-6′ ose); 68.4(3C, C-4′ ose); 71.4(3C, C-2′ or C-3′ ose); 72.3(3C, C-5′ ose); 72.8-(3C, C-3′ or C-2′ ose); 99.1(3C, C-1′ ose); 115.2(6C, C-3,5 aryl); 116.8(1C, C *meso*); 119.2(2C, C *meso*); 120.2(1C, C *meso*); 121.7-(2C, C-3,5 nitrophenyl); 130.3(C-β pyrrole); 131.7(C-β pyrrole) 135.1(2C, C-2,6 nitrophenyl); 135.5(6C, C-2,6 aryl); 136.7(3C, C-1 aryl); 146.2(8C, C-α pyrrole); 147.8(1C, C-4 nitrophenyl); 149.1(1C, C-1 nitrophenyl); 156.7(3C, C-4 aryl); 168.4(6C, CH_3*C*O); 170.3(3C, CH_3*C*O); 170.6(3C, CH_3*C*O). MS (MALDI) *m*/*z*: 1699.5 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{86}H_{83}N_5O_{32}$: C, 60.81; H, 4.92; N, 4.12. Found: C, 60.67; H, 4.89; N, 4.09.

5,10,15,20-Tetra[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (7).[1d] This compound was isolated as a byproduct from the synthesis of **6b**. 220 mg were obtained (11%). R_f 0.49(toluene/acetone/methanol, 80/10/10). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) −2.78-(2H, br s, NH); 2.11(3H, s, OAc); 2.12(3H, s, OAc); 2.13(3H, s, OAc); 4.08(4H, ddd, J = 2.4−5.3−9.6 Hz, H-5′ ose); 4.32(4H, dd, J = 2.4−5.3−9.6 Hz, H-6_b′ose); 4.44(4H, dd, J = 5.3−12.3 Hz, H-6′a ose); 5.35(4H, m, H-4′ ose); 5.49(12H, m, H-1′,2′,3′ ose); 7.40(8H, d, J = 8.6 Hz, H-3,5 aryl); 8.14(8H, d, J = 8.5 Hz, H-2,6 aryl); 8.90(8H, s, H-β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 26.6(3C, *C*H_3CO); 20.8(1C, *C*H_3CO); 62.1(4C, c-6′ ose); 68.4(4C, C-4′ ose); 71.4(4C, C-2′ ose or C-3′ ose); 72.3(4C, C-5′ ose); 72.8(4C, C-3′ ose or C-2′ ose); 99.2(4C, C-1′ ose); 115.1-(8C, C-3,5 aryl); 119.3(4C, C *meso*); 131.1(8C, C-β pyrrole); 135.5(8C, C-2,6 aryl); 137.5(4C, C-1 aryl); 146.2(8C, C-α pyrrole); 156.6(4C, C-4 aryl); 169.4(2C, CH_3*C*O); 170.3(1C, CH_3*C*O); 170.5(1C, CH_3*C*O). MS (MALDI) *m*/*z*: 1999.9 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{100}H_{102}N_4O_{40}$: C, 60.06; H, 5.14; N, 2.80. Found: C, 60.04; H, 5.17; N, 2.82.

5-(2-Nitrophenyl)-10,15,20-tristolylporphyrin (8a). 2-Nitrobenzaldehyde (151 mg, 1 mmol, 1 equiv), *p*-tolualdehyde

(0.35 mL, 3 mmol, 3 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) gave **8a** 105 mg (15%). R_f 0.75 ($CHCl_3$). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.70 (2H, s, NH); 2.71 (9H, s, Me tolyl); 7.56 (6H, d, J = 7.9 Hz, H-3−5 tolyl); 7.94 (2H, m, H-4,5 nitrophenyl); 8.11 (6H, br d, H-2,6 tolyl); 8.28 (1H, dd, J = 7.1−2.0, H-6 nitrophenyl); 8.43 (1H, dd, J = 7.0−2.5 Hz, H-3 nitrophenyl); 8.78 (2H, dd, J = 4.8 Hz, H-3−7 pyr); 8.86 (4H, s, H-12,13,17,18 pyr); 8.87 (2H, d, J = 5.1 Hz, H-2,8 pyr). ^{13}C NMR (50 MHz) 21.5 (3C, Me tolyl); 113.9 (1C, C-5 *meso*); 120.5 (2C, C-10,20 *meso*); 121.0 (1C, C-15 *meso*); 123.9 (1C, C-3 nitrophenyl); 127.4 (6C, C-3,5 tolyl); 129.4 (1C, C-4 nitrophenyl); 130.8 (1C, C-5 nitrophenyl); 131.3 (Cβ pyrrole); 131.9 (Cβ pyrrole); 134.5 (6C, C-2,6 tolyl); 136.8 (1C, C-1 nitrophenyl); 136.5 (1C, C-6 nitrophenyl); 137.4 (3C, C-4 tolyl); 139.0 (2C, C-1 tolyl); 139.2 (1C, C-1 tolyl); 146.2 (8C, Cα pyr); 152.0 (1C, C-2 nitrophenyl). MS (MALDI) *m/z*: 702.3 ([M + H]$^+$monoisotopic) . Anal. Calcd for $C_{47}H_{35}N_5O_2 \cdot H_2O$: C, 78.40; H, 5.18; N, 9.72. Found: C, 78.16; H, 5.15; N, 9.67.

5-(4-Nitrophenyl)-10,15,20-tristolylporphyrin (8b). 4-Nitrobenzaldehyde (151 mg, 1 mmol, 1 equiv), *p*-tolualdehyde (0.35 mL, 3 mmol, 3 equiv), and pyrrole (0.28 mL, 4 mmol, 4 equiv) gave **8b** 99 mg (14%). R_f 0.53 (methylene chloride/petroleum ether, 60/40). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.73(2H, s, NH); 2.72(9H, s, Me tolyl); 7.56(6H, d, J = 7.8 Hz, H-3,5 tolyl); 8.10(6H, d, J = 7.9 Hz, H-2,6 tolyl); 8.38 (2H, d, J = 8.7 Hz, H-2,6 nitrophenyl); 8.62 (2H, d, J = 9.0 Hz, H-3,5 nitrophenyl); 8.72(2H, d, J = 4.8 Hz, H-3,7 β pyrrole); 8.89 (4H, s, H-12-13-17-18 β pyrrole); 8.92 (2H, d, J = 4.8 Hz, H-2−8 β pyrrole). MS (MALDI) *m/z*: 703 (M+H)$^+$. ^{13}C NMR (50 MHz) δ 149.4 (1C, C-1 nitrophenyl); 147.7 (1C, C-4 nitrophenyl); 146.2 (8C, Cα pyrrole); 139.1 (3C, C-1 tolyl); 137.5 (3C, C-4 tolyl); 135.1 (2C, C-2,6 nitrophenyl); 134.5 (6C, C-2,6 tolyl); 131.4 (Cβ pyrrole); 130.9 (Cβ pyrrole); 127.5 (6C, C-3,5 tolyl); 121.8 (2C, C-3,5 nitrophenyl); 121.0 (1C, C-15 *meso*); 120.7 (2C, C-10,20 *meso*); 116.8 (1C, C-15 *meso*); 21.5 (3C, Me tolyl). MS (MALDI) *m/z*: 702.3 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{47}H_{35}N_5O_2 \cdot 3H_2O$: C, 74.68; H, 5.45; N, 9.26. Found: C, 74.86; H, 5.49; N, 9.20.

General Procedure for Reduction of Glucosylated Nitrophenylporphyrins 3−6. Porphyrins **3a,b**, **4**, **5**, and **6a,b** were dissolved in THF and 10% palladium on carbon was added.[13] The mixture was stirred under H_2 for 5 h, and then the reaction was filtered through Celite. The solvent was removed in vacuo, and the pure product was obtained after purification on thin-layer chromatography.

5-[2-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-phenyl]-10,15,20-tris(4-aminophenyl) Porphyrin (9a). 3a (52 mg, 0.048 mmol) and 10% Pd/C (300 mg) gave 28 mg of **9a** (60%). R_f 0.26 (toluene/acetone, 60/40). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.74(2H, br s, NH); 0.92-(3H, s, OAc); 1.26(3H, s, OAc); 1.86(3H, OAc); 1.96(3H, OAc); 3.65(1H, ddd, J = 7.7−5.1−2.5 Hz, H-5′ ose); 4.00(1H, dd, J = 12.1−2.6 Hz, H-6$_b$′ose); 4.03(2H, br s, NH_2); 4.12(1H, dd, J = 12.1−5.2 Hz, H-6$_a$′ose); 4.18(1H, dd, J = 7.7−2.2 Hz, H-2′ose); 4.64(1H, t, J = 9.2 Hz, H-3′ose); 4.70(1H, t, J = 9.2 Hz, H-4′ose); 4.92(1H, d, J = 7.7 Hz, H-1′ose); 7.04(6H, d, J = 8.3 Hz, H-3,5 aminophenyl); 7.52(1H, dt, J = 7.5−1.6 Hz, H-5 aryl); 7.70(1H, dt, J = 7.5−1.6 Hz, H-3 aryl); 7.80(1H, dt, J = 7.5−1.6 Hz, H-4 aryl); 7.98(6H, d, J = 8.4 Hz, H-2,6 aminophenyl); 8.85(2H, d, J = 4.9 Hz, H-3,7 β pyrrole); 8.90(4H, s, H-12,13,17,18 β pyrrole); 8.92(2H, d, J = 4.9 Hz, H-2,8 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 17.5(1C, *C*H_3CO); 20.3-(1C, *C*H_3CO); 20.5(2C, *C*H_3CO); 62.1(1C, C-6′ ose); 68.4(1C, C-4′ ose); 70.1(1C, C-2′ ose); 72.0(1C, C-5′ose); 72.3(1C, C-3′ose); 99.7(1C, C-1′ose); 113.4(6C, C-3,5 aminophenyl); 116.4(1C, C *meso*); 117.8(1C, C-2 aryl); 119.7(2C, C *meso*); 120.1(1C, C *meso*); 122.7(1C, C-5 aryl); 130.4(1C, C-4 aryl); 131.0(8C, C-β pyrrole); 132.2(1C, C-1 aryl); 132.6(3C, C-4 aminophenyl); 135.7(6C, C-2,6 aminophenyl); 135.9(1C, C-6 aryl); 146.0(3C, C-1 aminophenyl); 146.5(8C, C-α aminophenyl); 156.2(1C, C-2 aryl); 166.9(1C, CH$_3$*C*O); 169.0(1C, CH$_3$*C*O); 169.5(1C, CH$_3$*C*O); 170.3(1C, CH$_3$*C*O). MS (MALDI) *m/z*: 1006.4 ([M + H]$^+$ monoisotopic). Anal. Calcd for $C_{58}H_{51}N_7O_{10}$: C, 69.24; H, 5.11; N, 9.75. Found: C, 69.04; H, 5.08; N, 9.72.

5-[4-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-phenyl]-10,15,20-tris(4-aminophenyl) Porphyrin (9b). 3b (30 mg, 0.027 mmol) and 10% Pd/C (172 mg) gave 15 mg of **9b** (56%). R_f 0.47 (methylene chloride/ethanol, 95/5). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.74(2H, br s, NH); 2.10(3H, s, OAc); 2.11(3H, s, OAc); 2.12(3H, br s, OAc); 2.22(3H, br s, OAc); 4.03(2H, br s, NH_2); 4.05(1H, ddd, J = 9.6−5.5−2.4 Hz, H-5′ose); 4.30(1H, dd, J = 12.3−2.3 Hz, H-6$_b$′ose); 4.41(1H, dd, J = 12.2−5.5 Hz, H-6$_a$′ose); 5.31(1H, m, H-4′ose); 5.46(3H, m, H-1′,2′,3′ose); 7.04(6H, d, J = 8.3 Hz, H-3,5 aminophenyl); 7.36(2H, d, J = 8.6 Hz, H-3,5 aryl); 7.98-(6H, d, J = 8.4 Hz, H-2,6 aminophenyl); 8.13(2H, d, J = 8.5 Hz, H-2,6 aryl); 8.80(2H, d, J = 4.8 Hz, H-3,7 β pyrrole); 8.90-(4H, s, H-12,13,17,18 β pyrrole); 8.91(2H, d, J = 4.7 Hz, H-2,8 pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.7(2C, *C*H_3CO); 20.8-(2C, *C*H_3CO); 62.1(1C, C-6′ose); 68.4(1C, C-4′ose); 71.3(1C, C-2′ or C-3′ose); 72.3(1C, C-5′ose); 72.9(1C, C-2′ or C-3′ose); 99.2-(1C, C-1′ose); 113.4(6C, C-3,5 aminophenyl); 114.9(2C, C-3,5 aminophenyl); 118.7(1C, C *meso*); 119.1(2C, C *meso*); 120.0-(1C, C *meso*); 130.9(8C, C-β pyrrole); 132.6(3C, C-4 aminophenyl); 135.5(2C, C-2,6 aryl); 135.7(6C, C-2,6 aminophenyl); 137.6(1C, C-1 aryl); 146.2(3C, C-1 aminophenyl); 146.5(8C, C-α pyrrole); 156.5(1C, C-4 aryl); 168.3(1C, CH$_3$*C*O); 169.5(1C, CH$_3$*C*O); 170.4(1C, CH$_3$*C*O); 170.7(1C, CH$_3$*C*O). MS (MALDI) *m/z*: 1006.4 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{58}H_{51}N_7O_{10}$: C, 69.24; H, 5.11; N, 9.75. Found: C, 69.13; H, 5.15; N, 9.76.

5,15-Bis(4-aminophenyl)-10,20-bis[-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)phenyl] Porphyrin (10). 4 (30 mg, 0.021 mmol) and 10% Pd/C (89 mg) gave 17 mg of **10** (62%). R_f 0.50 (methylene chloride/ethanol, 95/5). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.72(2H, br s, NH); 2.11(6H, s, OAc); 2.12(6H, s, OAc); 2.13(6H, s, OAc); 2.23-(6H, s, OAc); 3.97(4H, br s, NH_2); 4.06(2H, ddd, J = 9.6−5.3−2.5, H-5′ose); 4.31(2H, dd, J = 12.3−2.0, H-6$_b$′ose); 4.43(2H, dd, J = 12.3−5.4 Hz, H-6$_a$′ose); 5.32(2H, m, H-4′ose); 5.48-(6H, m, H-1′,2′,3′ose); 7.03(4H, d, J = 8.4 Hz, H-3,5 aminophenyl); 7.38(4H, d, J = 8.6 Hz, H-3,5 aryl); 7.98(4H, d, J = 8.3 Hz, H-2,6 aminophenyl); 8.14(4H, d, J = 8.6 Hz, H-2,6 aryl); 8.83(4H, d, J = 4.8 Hz, H-2,8,12,18 β pyrrole); 8.93(4H, d, J = 4.8 Hz, H-3,7,13,17 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6-(2C, *C*H_3CO); 20.8(2C, *C*H_3CO); 62.1(2C, C-6′ose); 68.5(2C, C-5′ose); 71.4(2C, C-2′ or C-3′ose); 72.3(2C, C-2′ or C-3′ose);72.9-(2C, C-2′ or C-3′ose); 99.2(2C, C-1′ose); 113.4(4C, C-3,5 aminophenyl); 115.0(4C, C-3,5 aryl); 118.7(2C, C *meso*); 120.5(2C, C *meso*); 130.7(C-β pyrrole); 131.2(C-β pyrrole); 132.3(2C, C-4 aminophenyl); 135.5(4C, C-2,6 aryl); 135.6(4C, C-2,6 aminophenyl); 137.4(2C, C-1 aryl); 146.0(2C, C-1 aminophenyl); 146.5(8C, C-α pyrrole); 156.6(2C, C-4 aryl); 169.4(4C, CH$_3$*C*O); 170.3(2C, CH$_3$*C*O); 170.6(2C, CH$_3$*C*O). MS (MALDI) *m/z*: 1337.6 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{72}H_{68}N_6O_{20}$: C, 64.67; H, 5.12; N, 6.28. Found: C, 64.91; H, 5.14; N, 6.31.

5,10-Bis(4-aminophenyl)-15,20-bis[-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)phenyl] Porphyrin (11). 5 (30 mg, 0.021 mmol) and 10% Pd/C (89 mg) gave 18 mg of **11** (64%). R_f 0.55 (methylene chloride/ethanol, 95/5). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) −2.71(2H, br s, NH); 2.11(6H, s, OAc); 2.12(6H, s, OAc); 2.13(6H, s, OAc); 2.23(6H, s, OAc); 3.97(4H, br s, NH_2); 4.06(2H, ddd, J = 9.6−5.3−2.4, H-5′ose); 4.31(2H, dd, J = 12.2−2.4, H-6$_b$′ose); 4.44(2H, dd, J = 12.3−5.4, H-6$_a$′ose); 5.33(2H, m, H-4′ose); 5.48(6H, m, H-1′,2′,3′ose); 7.02(4H, d, J = 8.3 Hz, H-3.5 aminophenyl); 7.39-(4H, d, J = 8.6 Hz, H-3.5 aryl); 7.98(4H, d, J = 8.3 Hz, H-2,6 aminophenyl); 8.15(4H, d, J = 8.6 Hz, H-2,6 aryl); 8.83(2H, d, J = 4.9 Hz, H-2,13 β pyrrole); 8.84(2H, s, H-17,18 β pyrrole); 8.93(2H, s, H-7,8 β pyrrole); 8.94(2H, d, J = 4.7 Hz, H-3,12 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6(2C, *C*H_3CO); 20.7-(2C, *C*H_3CO); 62.1(2C, C-6′ose); 68.5(2C, C-5′ose); 71.4(2C, C-2′ or C-3′ose); 72.3(2C, C-2′ or C-3′ose); 72.9(2C, C-2′ or C-3′ose); 99.2(2C, C-1′ose); 113.4(4C, C-3,5 aminophenyl); 115.1(4C, C-3,5 aryl); 118.6(2C, C *meso*); 120.8(2C, C *meso*); 130.7(C-β pyrrole); 131.2(C-β pyrrole); 132.4(2C, C-4 aminophenyl); 135.5(4C, C-2,6 aryl); 135.6(4C, C-2,6 aminophenyl); 137.4-(2C, C-1 aryl); 146.0(2C, C-1 aminophenyl); 146.5(8C, C-α pyrrole); 156.6(2c, C-4 aryl); 169.4(4C, CH$_3$*C*O); 170.3(2C,

CH_3CO); 170.6(2C, CH_3CO). MS (MALDI) *m/z*: 1337.6 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{72}H_{68}N_6O_{20}$: C, 64.67; H, 5.12; N, 6.28. Found: C, 64.82; H, 5.15; N, 6.30.

5-(2-Aminophenyl)-10,15,20-tris[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (12a). **6a** (67 mg, 0.04 mmol) and 10% Pd/C (85 mg) gave 40 mg of **12a** (60%). R_f 0.40 (toluene/acetone, 70/30). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.75(2H, br s, NH); 2.11(18H, s, OAc); 2.12(12H, s, OAc); 2.22(6H, s, OAC); 3.55-(2H, br s, NH_2); 4.07(3H, ddd, J = 9.6−5.4−2.5 Hz, H-5′ose); 4.31(3H, dd, J = 12.3−2.0 Hz, H-6$_b$′ose); 4.43(3H, dd, J = 12.3−5.3 Hz, H-6$_a$′ose); 5.31(3H, m, H-4′ose); 5.47(9H, m, H-1′,2′,3′ose); 7.15(2H, m, H-5,6 *o*-aminophenyl); 7.39(6H, d, J = 8.6 Hz, H-3,5 aryl); 7.60(1H, m, H-4 *o*-aminophenyl); 7.87-(1H, d, J = 7.6−1.3 Hz, H-3 *o*-aminophenyl); 8.13(6H, d, J = 8.5 Hz, H-2,6 aryl); 8.85(4H, s,H-12,13,17,18 β pyrrole); 8.86-(2H, d, J = 4.7 Hz, H-2,8 β pyrrole); 8.91(2H, d, J = 8.91 Hz, H-3,7 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6(6C, CH_3CO); 20.8(6C, CH_3CO), 62.1(3C, C-6′ose); 68.5(3C, C-4′ose); 71.4-(3C, C-2′ or C-3′ose); 72.3(3C, C-5′ose); 72.9(3C, C-2′ or C-3′ose); 99.2(3C, C-1′ose); 115.1(6C, C-3,5 aryl); 115.1(1C, C *meso*); 115.7(1C, C-2 aminophenyl); 117.6(1C, C-6 aminophenyl); 119.2(3C, C *meso*); 127.1(1C, C-5 aminophenyl); 129.7(1C, C-3 aminophenyl); 130.9(C-β pyrrole); 134.8(1C, C-4 aminophenyl); 135.5(6C, C-2,6 aryl); 137.0(4C, C-1 aryl); 137.2(2C, C-1 aryl); 146.5(8C, C-α pyrrole); 146.9(1C, C-1 aminophenyl); 156.7(3C, C-4 aryl); 169.4(6C, CH_3CO); 170.3(3C, CH_3CO); 170.6(3C, CH_3CO). MS (MALDI) *m/z*: 1668.5 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{86}H_{85}N_5O_{30}$: C, 61.90; H,5.13; N, 4.20. Found: C, 61.87; H, 5.15; N, 4.18.

5-(4-Aminophenyl)-10,15,20-tris[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (12b). **6b** (25 mg, 0.015 mmol) and 10% Pd/C (32 mg) gave 19 mg of **12b** (76%). R_f 0.44 (methylene chloride/ethanol, 90/10). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.75(2H, br s, NH); 2.11(9H, s, OAc); 2.12(9H, s, OAc); 2.13(9H, s, OAc); 2.23(9H, s, OAc); 4.00(2H, br s, NH_2); 4.07(3H, ddd, J = 9.6−5.4−2.5 Hz, H-5′ose); 4.31(3H, dd, J = 12.2−2.5 Hz, H-6$_b$′ose); 4.44(3H, dd, J = 12.2−5.3 Hz, H-6$_a$′ose); 5.35(3H, m, H-4′ose); 5.49(9H, m, H-1′,2′,3′ ose); 7.05(2h, d, J = 8.4 Hz, H-3,5 aminophenyl); 7.39(6H, d, J = 8.5 Hz, H-3,5 aryl); 7.98(2H, d, J = 8.3 Hz, H-2,6 aminophenyl); 8.14(6H, d, J = 8.6 Hz, H-2,6 aminophenyl); 8.83(2H, d, J = 4.9 Hz, H-2,8 β pyrrole); 8.85-(4H, s, H-12,13,17,18 β pyrrole); 8.95(2H, d, J = 4.9 Hz, H-3,7 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 20.6(6C, CH_3CO); 20.7-(6C, CH_3CO), 62.1(3C, C-6′ose); 68.4(3C, C-4′ose); 71.4(3C, C-2′ or C-3′ose); 72.3(3C, C-5′ose); 72.9(3C, C-2′ or C-3′ose); 99.2-(3C, C-1′ose); 113.2(2C, C-3,5 aminophenyl); 115.1(6C, C-3,5 aryl); 118.8(1C, C *meso*); 119.1(2C, C *meso*); 119.3(1C, C *meso*); 130.9(C-β pyrrole); 132.2(1C, C-4 aminophenyl); 135.0(2C, C-2,6 aminophenyl); 135.5(6C, C-2,6 aryl); 137.2(3C, C-1 aryl); 146.1(1C, C-1 aminophenyl); 146.5(8C, C-α pyrrole); 156.6(3C, C-4 aryl); 169.4(6C, CH_3CO); 170.3(3C, CH_3CO); 170.5(3C, CH_3CO), MS (MALDI) *m/z*: 1668.5 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{86}H_{85}N_5O_{30}$: C, 61.90; H, 5.13; N, 4.20. Found: C, 61.86; H, 5.10; N, 4.22.

General Procedure for Reduction of Mononitrophenyltristolylporphyrin. Reductions were performed according to methods already described in the literature.[14] Mononitrophenyltristolylporphyrin **8a,b** was dissolved in 9 mL of chloroform/acetic acid (1/2), and then a solution (3 mL) of $SnCl_2$ (3 equiv/NO_2) in concentrated HCl was added. The mixture was stirred, refluxed overnight, and then neutralized with 1 M sodium hydroxide to pH 8−9, an ice-bath being used for cooling. Chloroform (250 mL) was added, and the organic layer was washed with water (3 × 75 mL), followed by drying over magnesium sulfate. The solvent was evaporated in a vacuum. The crude product was purified on TLC (CH_2Cl_2).

5-(2-Aminophenyl)-10,15,20-tristolylporphyrin (13a):[15] 43 mg (92%). R_f 0.52 (CH_2Cl_2). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.70(2H, s, NH); 2.72(9H, s, Me tolyl); 3.50(2H, br s, NH_2); 7.07(1H, dd, J = 8.0−0.9 Hz, H-6 aminophenyl); 7.18(1H, dt, J = 7.4−1.0 Hz, H-5 aminophenyl); 7.56(6H, d, J = 8.0 Hz, H-3,5 tolyl); 7.61(1H, m, H-4 aminophenyl); 7.91(1H, dd, J = 7.5−1.5 Hz, H-3 aminophenyl); 8.11(6H, d, J = 8.0 Hz, H-2,6 tolyl); 8.88(2H, d, J = 4.7 Hz, H-2,8 β pyrrole); 8.89(4H, s, H-12,13,17,18 β pyrrole); 8.90-(2H, d, J = 4.7 Hz, H-3,7 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 146.7 (1C, C-1 aminophenyl); 146.2 (8C, Cα pyr); 139.3 (1C, C-1 tolyl); 139.1 (2C, C-1 tolyl); 137.4 (3C, C-4 tolyl); 134.8 (1C, C-1 aminophenyl); 134.5 (6C, C-2,6 tolyl); 131.7(Cβ pyr); 130.9 (Cβ pyr); 129.5 (1C, C-3 aminophenyl); 127.4 (6C, C-3,5 tolyl); 120.7 (1C, C-20 *meso*); 120.1 (2C, C-10,15 *meso*); 117.5 (1C, C-6 aminophenyl); 115.5 (1C, C-2 aminophenyl); 115.1 (1C, C-5 *meso*); 21.5 (3C, Me tolyl). MS (MALDI) *m/z*: 672.3 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{47}H_{37}N_5 \cdot 2H_2O$: C, 79.75; H, 5.84; N, 9.89. Found: C, 79.49; H, 5.87; N, 9.93.

5-(4-Aminophenyl)-10,15,20-tristolylporphyrin (13b): 43.2 mg (90%); R_f 0.34 (CH_2Cl_2). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.87(d, J = 4.9 Hz, 2H, H-3,7 pyr); 8.85(s, 4H, H-12,13,17,18 pyr); 8.83(d, J = 4.9 Hz, 2H, H-2,8); 8.10(d, J = 7.9 Hz, 6H, H-2,6 tolyl); 7.90(d, J = 8.3 Hz, 2H, H-2,6 aminophenyl); 7.56(d, J = 7.9 Hz, 6H, H-3,5 tolyl); 6.72-(d, J = 8.3 Hz, 2H, H-3,5 aminophenyl); 3.45(bs, 2H, NH_2); 2.71(s, 9H, Me tolyl); −2.73(s, 2H, NH). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 146.2 (8C, Cα pyr); 146.1 (1C, C-1 aminophenyl); 139.4 (3C, C-1 tolyl); 137.2 (3C, C-4 tolyl); 135.4 (2C, C-2,6 aminophenyl); 134.5 (6C, C-2,6 tolyl); 132.7 (1C, C-4 aminophenyl); 131.7(C-β pyr); 130.8 (C-β pyr); 127.4 (6C, C-3,5 tolyl); 119.9 (3C, C-10,15,20 *meso*); 119.1 (1C, C-5 *meso*); 113.4 (2C, C-3,5 aminophenyl); 21.5 (3C, Me tolyl). MS (MALDI) *m/z*: 672.3 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{47}H_{37}N_5 \cdot 3H_2O$: C, 77.76; H, 5.96; N, 9.65; Found: C, 77.54; H, 5.97; N, 9.69.

General Procedure for Binding Amino Acids on Porphyrins Amino Function. Porphyrins **9a,b**, **10**, **11**, **12a,b**, and **13a,b** were reacted with Fmoc amino acid (3 equiv/NH_2) in the presence of dicyclohexylcarbodiimide (DCC) (3 equiv/NH_2) in CH_2Cl_2 (10 mL). The mixture was stirred in darkness at room temperature for 15 h. The solution was concentrated in vacuo, and ethyl acetate was added to the residue in order to remove insoluble dicyclohexylurea by filtration. The solvent was evaporated, and the residue was purified on TLC.

5-[2-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)-phenyl]-10,15,20-tris[4-(*N*-(9-fluorenylmethoxycarbonyl)-L-alanylamino)phenyl] Porphyrin (14a). 9a (30 mg, 0.03 mmol), Fmoc-L-alanine (84 mg, 0.27 mmol), and dicyclohexylcarbodiimide (54 mg, 0.27 mmol) gave 51 mg of **14a** (90%). R_f 0.50 (toluene/acetone, 70/30). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −2.81(2H, br s, NH); −1.11(3H, s, OAc); 1.28(3H, s, OAc); 1.64(9H, d, J = 6.9 Hz, CH_3 alanine); 1.84(3H, OAc); 2.02(3H, OAc); 3.65(1H, ddd, J = 7.7−5.1−2.5 Hz, H-5′ose); 4.01(1H, br d, J = 10.1 Hz, H-6$_b$′ose); 4.12(1H, dd, J = 12.1−5.1 Hz, H-6$_a$′ose); 4.20(1H, dd, J = 7.9−1.5 Hz, H-2′ose); 4.29(3H, t, J = 7.2 Hz, H-9 Fmoc); 4.54(9H, m, CH_2 Fmoc); 4.56(1H, t, J = 9.4 Hz, H-3′ose); 4.67(3H, C*H* alanine); 4.71(1H, t, J = 9.5 Hz, H-4′ose); 4.83(1H, d, J = 7.8 Hz, H-1′ose); 5.96(3H, m, N*H* alanine); 7.32(6H, t, J = 7.5 Hz, H−Fmoc); 7.37(6H, t, J = 7.7 Hz, H−Fmoc); 7.64(7H, m, H−Fmoc and H-3 aryl); 7.71(7H, m, H-5 aryl and H−Fmoc); 7.87(6H, br d, J = 8.1 Hz, H-3,5 amidophenyl); 7.91(1H, br d, J = 6.4 Hz, H-4 aryl); 8.05(6H, br d, J = 8.3 Hz, H-2,6 amidophenyl); 8.16(1H, br d, J = 7.37 Hz, H-6 aryl); 8.65(2H, d, J = 4.8 Hz, H-2,8 β pyrrole); 8.74(2H, d, J = 4.8 Hz, H-3,7 β pyrrole); 8.79(4H, s, H-12,13,17,18 β pyrrole); 8.91(3H, br s, N*H* amidophenyl). ^{13}C NMR ($CDCl_3$, 100 MHz) 17.4(1C, CH_3-CO); 18.6(3C, CH_3 alanine); 19.9(1C, CH_3CO); 20.4(1C, CH_3-CO), 20.7(1C, CH_3CO); 47.2(3C, *C*H-9 Fmoc); 49.2(3C, *C*H alanine); 61.9(1C, C-6′ ose); 67.5(3C, CH_2 Fmoc); 68.1(1C, C-4′ ose); 70.1(1C, C-2′ ose); 71.8(1C, C-5′ose); 72.1(1C, C-3′ose); 99.6(1C, C-1′ose); 114.7(1C, C *meso*); 118.2(7C, C-3 aryl and C-3,5 amidophenyl); 119.2(1C, C *meso*); 119.6(1C, C *meso*); 119.8(1C, C *meso*); 120.1(6C, C−Fmoc); 122.5(1C, C-5 aryl); 125.0(6C, C−Fmoc); 127.2(6C, C−Fmoc); 127.6(6C, C−Fmoc); 130.7(1C, C-4 aryl); 131.0(8C, C-β pyrrole); 133.0(1C, C-1 aryl); 135.1(6C, C-2,6 amidophenyl); 136.1(1C, C-6 aryl); 137.5(3C, C-1 amidophenyl); 138.2(3C, C-4 amidophenyl); 141.3(6C, C^{IV} Fmoc); 143.6(6C, C^{IV} Fmoc); 146.0(4C, C-α Pyrrole); 156.2(1C, C-2 aryl); 156.6(3C, *C*O Fmoc); 167.0(1C, CH_3CO); 169.1(1C, CH_3CO); 169.5(1C, CH_3CO); 170.5(1C, CH_3CO); 171.1(3C, *C*O

alanine). MS (MALDI) *m/z*: 1885.7 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{112}H_{96}N_{10}O_{19}$·$2H_2O$: C, 69.98; H, 5.24; N, 7.29. Found: C, 70.08; H, 5.27; N, 7.34.

5-[4-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)-phenyl]-10,15,20-tris[4-(*N*-(9-fluorenylmethoxycarbonyl)-L-alanylamino)phenyl] Porphyrin (14b). 9b (15 mg, 0.015 mmol), Fmoc-L-alanine (42 mg, 0.14 mmol), and dicyclohexylcarbodiimide (28 mg, 0.14 mmol) gave 51 mg of **14b** (89%). R_f 0.42 (methylene chloride/ethanol, 95/5). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ −2.84(2H, br s, NH); 1.65-(9H, d, J = 7.1 Hz, CH_3 alanine); 2.10(3H, s, OAc); 2.11(3H, s, OAc); 2.11(3H, br s, OAc); 2.21(3H, br s, OAc); 4.06(1H, ddd, J = 9.6−5.2−2.5 Hz, H-5′ose); 4.30(1H, dd, J = 12.1−2.6 Hz, H-6$_b$′ose); 4.42(1H, dd, J = 12.1−5.2 Hz, H-6$_a$′ose); 4.18(1H, dd, J = 7.7−2.2 Hz, H-2′ose); 4.28(3H, m, H-9 Fmoc); 4.56-(3H, d, J = 6.8 Hz, CH_2 Fmoc); 4.58(3H, d, J = 6.8 Hz, C*H* alanine); 5.31(1H, m, H-4′ose); 5.48(3H, m, H-1′,2′,3′ose); 5.65-(3H, m, N*H* alanine); 7.29(3H, dt, J = 7.5−2.4 Hz, H−Fmoc); 7.35(2H, d, J = 8.6 Hz, H-3,5 aryl); 7.38(3H, dt, J = 7.5−2.4 Hz, H−Fmoc); 7.66(3H, dt, J = 7.5−2.4 Hz, H−Fmoc); 7.70-(1H, dt, J = 7.5−1.6 Hz, H-3 aryl); 7.75(3H, d, J = 7.5 Hz, H−Fmoc); 7.80(1H, dt, J = 7.5−1.6 Hz, H-4 aryl); 7.91(6H, br d, J = 8.6 Hz, H-3,5 amidophenyl); 8.11(2H, br d, J = 8.6 Hz, H-2,6 aryl); 8.15(6H, br d, J = 8.6 Hz, H-2,6 amidophenyl); 8.70(3H, br s, N*H* amidophenyl); 8.80(2H, d, J = 4.8 Hz, H-3,7 β pyrrole); 8.84(4H, s, H-12,13,17,18 β pyrrole); 8.87(2H, d, J = 4.8 Hz, H-2,8 β pyrrole). ^{13}C NMR ($CDCl_3$, 100 MHz) 18.3-(3C, *C*H$_3$ alanine); 20.6(1C, *C*H$_3$CO); 20.7(1C, *C*H$_3$CO); 47.2-(3C, *C*H-9 Fmoc); 51.4(3C, *C*H alanine); 62.1(1C, C-6′ ose); 67.4(3C, *C*H$_2$ Fmoc); 68.5(1C, C-4′ ose); 71.4(1C, C-2′ or C-3′ ose); 72.3(1C, C-5′ose); 72.9(1C, C-3′ or C-2′ ose); 99.1(1C, C-1′ose); 115.1(2C, C-3,5 aryl); 118.2(6C, C-3,5 amidophenyl); 119.4(1C, C *meso*); 119.7(3C, C *meso*); 120.1(6C, C−Fmoc); 124.9(6C, C−Fmoc); 127.2(6C, C−Fmoc); 127.7(6C, C−Fmoc); 131.0(8C, C-β pyrrole); 135.0(6C, C-2,6 amidophenyl); 135.5-(2C, C-2,6 aryl); 137.1(1C, C-1 aryl); 137.4(3C, C-1 amidophenyl); 138.2(3C, C-4 amidophenyl); 141.3(6C, C^{IV} Fmoc); 143.7(6C, C^{IV} Fmoc); 146.2(4C, C-α pyrrole); 156.7(4C, *C*O Fmoc and C-4 aryl); 169.5(2C, CH$_3$*C*O); 170.4(2C, CH$_3$*C*O); 170.7(3C, *C*O alanine). MS (MALDI) *m/z*: 1885.7 ([M + H]$^+$monoistopic). Anal. Calcd for $C_{112}H_{96}N_{10}O_{19}$: C, 71.32; H, 5.13; N, 7.43. Found: C, 71.46; H, 5.15; N, 7.47.

5,15-Bis[4-(*N*-(9-fluorenylmethoxycarbonyl)-L-alanylamino)phenyl]-10,20-bis[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (15). 10 (50 mg, 0.037 mmol), Fmoc-L-alanine (69 mg, 0.22 mmol), and dicyclohexylcarbodiimide (46 mg, 0.22 mmol) gave 63 mg of **15** (88%). R_f 0.47 (toluene/acetone, 60/40). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −2.80(2H, br s, NH); 1.64(6H, d, J = 6.9 Hz, CH_3 alanine); 2.11(6H, s, OAc); 2.12(12H, s, OAc); 2.23(6H, s, OAc); 4.07(2H, ddd, J = 9.6−5.2−2.5, H-5′ose); 4.29(2H, m, H-9 Fmoc and H-6$_b$′ose); 4.43(2H, dd, J = 12.2−5.2, H-6$_a$′ose); 4.58(4H, m, CH_2 alanine); 4.62(2H, br s, C*H* alanine); 5.31(2H, m, H-4′ose); 5.49(6H, m, H-1′,2′,3′ose); 5.61-(2H, m, NH-alanine); 7.30(4H, dt, J = 7.0−3.1 Hz, H−Fmoc); 7.40(4H, dt, J = 7.0−3.0 Hz, H−Fmoc); 7.38(4H,br d, J = 8.6 Hz, H-3.5 aryl); 7.65(4H, dd, J = 8.2−3.0 Hz, H−Fmoc); 7.77-(4H, m, H−Fmoc); 7.95(4H,br d, J = 8.5 Hz, H-3,5 amidophenyl); 8.15(8H,br d, J = 8.6 Hz, H-2,6 aryl and H-2,6 amidophenyl); 8.63(2H, br s, NH amidophenyl); 8.84(4H, d, J = 4.8 Hz, H-3,7,13,17 β pyrrole); 8.87(4H, d, J = 4.8 Hz, H-2,8,-12,18 β pyrrole). ^{13}C NMR ($CDCl_3$, 100 MHz) 18.3(2C, *C*H$_3$ alanine); 20.6(4C, *C*H$_3$CO); 20.8(4C, *C*H$_3$CO); 47.2(2C, *C*H-9 Fmoc); 51.6(2C, *C*H alanine); 62.1(2C, C-6′ ose); 67.5(2C, *C*H$_2$ Fmoc); 68.5(2C, C-4′ ose); 71.4(2C, C-2′ or C-3′ ose); 72.3(2C, C-5′ose); 72.9(2C,C-2 or C-3′ose); 99.2(2C, C-1′ose); 115.1(4C, C-3,5 aryl); 118.2(4C, C-3,5 amidophenyl); 119.1(2C, C *meso*); 119.5(2C, C *meso*); 120.1(4C, C−Fmoc); 124.9(4C, C−Fmoc); 127.1(4C, C−Fmoc); 127.8(4C, C−Fmoc); 131.0(8C, C-β pyrrole); 135.0(4C, C-2,6 amidophenyl); 135.5(4C, C-2,6 aryl); 137.2(2C, C-1 aryl); 137.5(2C, C-1 amidophenyl); 138.2(2C, C-4 amidophenyl); 141.3(4C, C^{IV} Fmoc); 143.7(4C, C^{IV} Fmoc); 146.2-(4C, C-α Pyrrole); 156.7(4C, *C*O Fmoc and C-4 aryl); 169.4-(2C, CH$_3$*C*O); 170.3(2C, CH$_3$*C*O); 170.6(4C, CH$_3$*C*O); 170.7(2C, *C*O alanine). MS (MALDI) *m/z*: 1923.7 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{108}H_{98}N_8O_{26}$·$2H_2O$: C, 66.18; H, 5.24; N, 5.71. Found: C, 66.10; H, 5.21; N, 5.67.

5,10-Bis[4-(*N*-(9-fluorenylmethoxycarbonyl)-L-alanylamino)phenyl]-15,20-bis[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (16). 11 (41 mg, 0.03 mmol), Fmoc-L-alanine (56 mg, 0.18 mmol), and dicyclohexylcarbodiimide (37 mg, 0.18 mmol) gave 48 mg of **16** (85%). R_f 0.45 (toluene/acetone, 60/40). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.87(2H, br s, NH); 1.64(6H, d, J = 6.9 Hz, CH_3 alanine); 2.08(6H, s, OAc); 2.10(6H, s, OAc); 2.11(6H, s, OAc); 2.21(6H, s, OAc); 4.06(2H, ddd, J = 9.6−5.2−2.5, H-5′ose); 4.29(2H, m, H-9 Fmoc); 4.31(2H, br dd, J = 10.2−2.6, H-6$_b$′ose); 4.43(2H, dd, J = 12.1−5.3 Hz, H-6$_a$′ose); 4.58(6H, br d, J = 6.8 Hz, CH_2 Fmoc and C*H* alanine); 5.30-(2H, br t, J = 9.6 Hz, H-4′ose); 5.49(6H, m, H-1′,2′,3′ose); 5.60-(2H, m, NH alanine); 7.26−7.35(8H, m, H−Fmoc); 7.38(4H,br d, J = 8.6 Hz, H-3,5 aryl); 7.65(4H, br dd, J = 6.8−2.7 Hz, H−Fmoc); 7.76(4H, d, J = 6.8 Hz, H−Fmoc); 7.90(4H, d, J = 8.6 Hz, H-3,5 amidophenyl); 8.15(8H, d, J = 8.6 Hz, H-2,6 amidophenyl and H-2,6 aryl); 8.70(2H, br s, NH−Fmoc); 8.81-(2H, d, J = 4.8 Hz, H-3,12 β pyrrole); 8.83(4H, s, H-7,8,17,18 β pyrrole); 8.84(2H, d, J = 4.8 Hz, H-2,13 β pyrrole). ^{13}C NMR ($CDCl_3$, 50 MHz) 18.4(2C, *C*H$_3$ alanine); 20.7(4C, *C*H$_3$CO); 20.8(4C, *C*H$_3$CO); 47.2(2C, *C*H-9 Fmoc); 49.2(2C, *C*H alanine); 62.1(2C, C-6′ ose); 67.4(2C, *C*H$_2$ Fmoc); 68.4(2C, C-4′ ose); 71.3-(2C, C-2′ or C-3′ ose); 72.3(2C, C-5′ose); 72.9(2C,C-2 or C-3′ose); 99.1(2C, C-1′ose); 114.9(4C, C-3,5 aryl); 118.2(4C, C-3,5 amidophenyl); 119.2(2C, C *meso*); 119.5(2C, C *meso*); 120.1(4C, C−Fmoc); 125.0(4C, C−Fmoc); 127.2(4C, C−Fmoc); 127.9(4C, C−Fmoc); 130.9(8C, C-β pyrrole); 135.1(4C, C-2,6 amidophenyl); 135.4(4C, C-2,6 aryl); 137.1(2C, C-1 aryl); 137.4(2C, C-1 amidophenyl); 138.2(2C, C-4 amidophenyl); 141.4(4C, C^{IV} Fmoc); 143.7(4C, C^{IV} Fmoc); 146.2(4C, C-α Pyrrole); 156.6(2C, C-4 aryl); 156.7(2C, *C*O Fmoc); 169.5(4C, CH$_3$*C*O); 170.4(2C, CH$_3$*C*O); 170.7(2C, CH$_3$*C*O); 170.8(2C, *C*O alanine). MS (MALDI) *m/z*: 1923.7 ([M + H]$^+$monoisotopic). Anal. Calcd for $C_{108}H_{98}N_8O_{26}$·$3H_2O$: C, 65.58; H, 5.30; N, 5.66. Found: C, 65.82; H, 5.31; N, 5.65.

5-[2-(*N*-9-Fluorenylmethoxycarbonyl)-L-alanylamino)-phenyl]-10,15,20-tris[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (17a). 12a (15 mg, 0.009 mmol), Fmoc-L-alanine (9 mg, 0.027 mmol), and dicyclohexylcarbodiimide (6 mg, 0.0027 mmol) gave 15 mg of **17a** (85%). R_f 0.34 (toluene/acetone, 70/30). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ −2.73(2H, br s, NH); 0.51-(3H, br s, CH_3 alanine); 2.11(12H, s, OAc); 2.12(12H, s, OAc); 2.22(12H, s, OAC); 3.22(1H, m, H-9 Fmoc); 3.38(2H, br s, NH$_2$); 3.50(2H, m, CH_2 Fmoc); 4.06(3H, ddd, J = 9.6−5.1−2.5 Hz, H-5′ose); 4.31(4H, m, H-6$_b$′ose and NH alanine); 4.44(3H, dd, J = 12.3−5.3 Hz, H-6$_a$′ose); 5.32(3H, m, H-4′ose); 5.48(9H, m, H-1′,2′,3′ose); 6.21(2H, dt, J = 7.6−1.2 Hz, H−Fmoc); 6.30-(2H, dt, J = 7.6−1.2 Hz, H−Fmoc); 6.41(2H, br d, J = 7.4 Hz, H−Fmoc); 6.68(2H, br t, J = 7.3 Hz, H−Fmoc); 7.37(6H, d, J = 8.1 Hz, H-3,5 aryl); 7.55(1H, dt, J = 7.6−1.1 Hz, H-5 *o*-aminophenyl); 7.86(1H, dt, J = 7.6−1.2 Hz, H-4 *o*-aminophenyl); 8.02(1H, dd, J = 7.6−1.2 Hz, H-6 *o*-aminophenyl); 8.11(6H, d, J = 8.2 Hz, H-2,6 aryl); 8.68(1H, d, J = 8.1 Hz, H-3 *o*-aminophenyl); 8.77(2H, d, J = 4.7 Hz, H-2,8 or H-3,7 β pyrrole); 8.82(4H, s,H-12,13,17,18 β pyrrole); 8.87(2H, d, J = 8.91 Hz, H-3,7 or H-2,8 β pyrrole); 8.87(1H, br s, NH amidophenyl). ^{13}C NMR ($CDCl_3$, 50 MHz) 17.8(1C, *C*H$_3$ alanine); 20.6(6C, *C*H$_3$CO); 20.7(6C, *C*H$_3$CO); 45.7(1C, *C*H-9 Fmoc); 50.1(1C, *C*H alanine); 62.1(3C, C-6′ ose); 65.5(1C, *C*H$_2$ Fmoc); 68.4(3C, C-4′ ose); 71.4(3C, C-2′ or C-3′ ose); 72.3(3C, C-5′ose); 72.8(3C,C-2 or C-3′ose); 99.1(3C, C-1′ose); 112.9(1C, C *meso*); 115.1(6C, C-3,5 aryl); 119.3(2C, C−Fmoc); 119.7(2C, C *meso*); 120.2(1C, C *meso*); 121.2(1C, C-3 amidophenyl); 123.4(1C, C-5 amidophenyl); 124.0(1C, C−Fmoc); 124.1(1C, C−Fmoc); 126.3-(1C, C−Fmoc); 126.5(1C, C−Fmoc); 127.0(1C, C−Fmoc); 127.1-(1C, C−Fmoc); 129.6(1C, C-4 amidophenyl); 131.2(8C, C-β pyrrole); 132.0(1C, C-1 amidophenyl); 134.6(1C, C-6 amidophenyl); 135.5(6C, C-2,6 aryl); 136.7(2C, C-1 aryl); 136.9(1C, C-1 aryl); 138.1(1C, C-2 amidophenyl); 140.5(1C, C^{IV} Fmoc); 140.6(1C, C^{IV} Fmoc); 142.7(1C, C^{IV} Fmoc); 142.9(1C, C^{IV} Fmoc); 146.2(4C, C-α Pyrrole); 156.4(1C, *C*O Fmoc); 156.7(3C, C-4

aryl); 170.1(1C, *C*O alanine); 169.4(6C, CH_3CO); 170.3(3C, CH_3CO); 170.5(3C, CH_3CO). MS (MALDI) *m/z*: 1961.6 ($[M + H]^+$monoisotopic). Anal. Calcd for $C_{104}H_{100}N_6O_{33}\cdot H_2O$: C, 63.66; H, 5.24; N, 4.28. Found: C, 63.49; H, 5.20; N, 4.29.

5-[4-(*N*-9-Fluorenylmethoxycarbonyl)-L-alanylamino)-phenyl]-10,15,20-tris[4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyloxy)phenyl] Porphyrin (17b). 12b (17 mg, 0.01 mmol), Fmoc-L-alanine (13 mg, 0.03 mmol), and dicyclohexylcarbodiimide (9 mg, 0.03 mmol) gave 18 mg of **17b** (90%). R_f 0.49 (toluene/acetone, 70/30). UV−visible (see Table 2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −2.87(2H, br s, NH); 2.03(6H, s, OAc); 1.55(3H, d, J = 6.8 Hz, CH_3 alanine); 2.12(12H, s, OAc); 2.13(6H, s, OAc); 2.23(12H, s, OAc); 3.98(3H, ddd, J = 9.6−5.4−2.6 Hz, H-5′ose); 4.22(4H, m, H-9 Fmoc and H-6$_b$′ose); 4.34(3H, dd, J = 12.4−5.6 Hz, H-6$_a$′ose); 4.50(3H, m, C*H* alanine and CH_2 Fmoc); 5.23(3H, m, H-4′ose); 5.39(10H, m, H-1′,2′,3′ ose and NH alanine); 7.24(2H, dt, J = 7.5−1.2 Hz, H−Fmoc); 7.28(6H, d, J = 8.8 Hz, H-3,5 aryl); 7.33(2H, dt, J = 7.5−1.1 Hz, H−Fmoc); 7.58(2H, dd, J = 7.3−1.0 Hz, H−Fmoc); 7.69(2H, br d, J = 7.5 Hz, H−Fmoc); 7.84(2H, d, J = 8.6 Hz, H-3,5 amidophenyl); 8.06(6H, d, J = 8.8 Hz, H-2,6 aryl); 8.08(2H, d, J = 8.5 Hz, H-2,6 amidophenyl); 8.51(1H, br s, NH-amidophenyl); 8.75(2H, d, J = 4.9 Hz, H-3,7 β pyrrole); 8.77(4H, s, H-12,13,17,18 β pyrrole); 8.79(2H, d, J = 4.9 Hz, H-2,8 β pyrrole). ^{13}C NMR ($CDCl_3$, 100 MHz) 18.2(1C, *C*H_3 alanine); 20.6(12C, *C*H_3CO); 20.7(3C, *C*H_3CO); 20.8(3C, *C*H_3-CO); 47.2(1C, *C*H-9 Fmoc); 51.4(1C, *C*H alanine); 62.1(3C, C-6′ ose); 67.6(1C, CH_2 Fmoc); 68.5(3C, C-4′ ose); 71.4(3C, C-2′ or C-3′ ose); 72.3(3C, C-5′ose); 72.9(3C,C-2 or C-3′ose); 99.2(3C, C-1′ose); 115.1(6C, C-3,5 aryl); 118.0(2C, C-3,5 amidophenyl); 119.3(3C, C *meso*); 119.5(1C, C *meso*); 120.1(2C, C−Fmoc); 124.9(2C, C−Fmoc); 127.2(2C, C−Fmoc); 127.8(2C, C−Fmoc); 131.0(8C, C-β pyrrole); 135.1(2C, C-2,6 amidophenyl); 135.5-(6C, C-2,6 aryl); 137.2(3C, C-1 aryl); 137.5(1C, C-1 amidophenyl); 138.2(1C, C-4 amidophenyl); 141.4(2C, C^{IV} Fmoc); 143.8(2C, C^{IV} Fmoc); 146.5(4C, C-α Pyrrole); 156.7(4C, C-4 aryl and *C*O Fmoc); 169.4(6C, CH_3CO); 170.3(4C, CH_3CO and *C*O alanine); 170.5(3C, CH_3CO). MS (MALDI) *m/z*: 1961.6 ($[M + H]^+$monoisotopic). Anal. Calcd for $C_{104}H_{100}N_6O_{33}\cdot 3H_2O$: C, 61.96; H, 5.30; N, 4.16. Found: C, 62.09; H, 5.33; N, 4.19.

5-[2-(*N*-(9-Fluorenylmethoxycarbonyl)-3-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-L-serylamino)phenyl]-10,15,20-tristolylporphyrin (18a). 13a (20 mg, 0.03 mmol), **2** (59 mg, 0.09 mmol), and dicyclohexylcarbodiimide (19 mg, 0.09 mmol) gave 23 mg of **18a** (60%). R_f 0.70 (CH_2Cl_2). UV−visible (see Table 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75(2H, br s, NH); −1.11(3H, s, OAc); 1.24(3H, s, OAc); 1.84(3H, s, OAc); 2.00(3H, s, OAc); 2.70(9H, s, Me tolyl); 3.20−3.38(3H, m, H-9 Fmoc, H-α and H-β serine); 3.52(2H, m, CH_2 Fmoc); 3.65(1H, ddd, J = 2.5−5.1−9.7 Hz, H-5′ ose); 3.78(1H, m, H-β serine); 4.00(1H, dd, J = 2.6−12.1 Hz, H-6$_b$′ose); 4.12(1H, dd, J = 5.2−12.1 Hz, H-6$_a$′ ose); 4.18(1H, dd, J = 2.2−7.8 Hz, H-2′ ose); 4.30(1H, m, NH serine); 4.64(1H, t, J = 9.2 Hz, H3′ ose); 4.70(1H, t, J = 9.2 Hz, H-4′ ose); 4.91(1H, d, J = 7.8 Hz, H-1′ ose); 6.20(2H, dt, J = 1.2−7.6 Hz, H Fmoc); 6.31(2H, m, H Fmoc); 6.40(2H, br d, J = 7.4 Hz, H Fmoc); 6.70(2H, m, H Fmoc); 7.54(1H, m, H-4 amidophenyl); 7.56(6H, d, J = 7.9 Hz, H-3,5 tolyl); 7.85(1h, dt, J = 1.3−7.9 Hz, H-3 amidophenyl); 8.03(1H, dd, J = 1.2−7.6 Hz, H-5 amidophenyl); 8.10(6H, J = 7.9 Hz, H-2,6 tolyl); 8.68(1H, d, J = 8.1 Hz, H-2 amidophenyl); 8.86(1H, br s, H-6 amidophenyl); 8.75(1H, d, J = 4.9 Hz, H-3 or H-7 β pyrrole); 8.77(1H, d, J = 4.9 Hz, H-3 or H-7 β pyrrole); 8.82(1H, d, J = 4.9 Hz, H-2 or H-8 β pyrrole); 8.86(1H, d, J = 4.9 Hz, H-2 or H-8 β pyrrole); 8.91(4H, s, H-12,13,17,18 β pyrrole). ^{13}C NMR (100 MHz) 17.3(1C, *C*H_3CO); 19.8(1C, *C*H_3-CO); 20.4(1C, *C*H_3CO); 20.7(1C, *C*H_3CO); 21.5(3C, Me tolyl); 45.7(1C, C-9 Fmoc); 51.3(1C, *C*H serine); 61.3(1C, C-6′ ose); 65.5(1C, *C*H_2 Fmoc); 66.5(1C, *C*H_2 serine); 67.8(1C, C-4′ ose); 70.1(C-2′ ose); 71.2(C-5′ ose); 72.1(1C, C-3′ ose); 102.4(1C, C-1′ose); 114.1(1C, C *meso*); 119.5(2C, C−Fmoc); 120.5(2C, C *meso*); 121.0(1C, C *meso*); 121.3(1C, C-3 amidophenyl); 12.3.4-(1C, C-5 amidopheyl); 124.0(2C, C−Fmoc); 126.6(2C, C−Fmoc); 127.1(2C, C−Fmoc); 127.4(6C, C-3,5 tolyl); 129.6(1C, c-4 amidophenyl); 130.9(8C, C-β pyrrole); 132.0(1C, C-1 amidophenyl); 134.4(6C, C-2,6 tolyl); 134.7(1C, C-6 amidophenyl); 137.3(3C, C-4 tolyl); 138.1(1C, C-2 amidophenyl); 139.2(3C, C-1 tolyl); 142.6(2C, C^{IV} Fmoc); 142.8(2C, C^{IV} Fmoc); 146.2(8C, C-α pyrrole); 156.7(1C, *C*O Fmoc); 167.0(1C, CH_3CO); 169.1(1C, CH_3CO); 169.5(1C, CH_3CO); 170.1(1C, *C*O serine); 170.5(1C, CH_3CO). MS (MALDI) *m/z*: 1311.5 ($[M + H]^+$monoisotopic). Anal. Calcd for $C_{79}H_{70}N_6O_{13}$: C, 72.38; H, 5.34; N, 6.41. Found: C, 72.17; H, 5.31; N, 6.40.

5-[4-(*N*-(9-Fluorenylmethoxycarbonyl)-3-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-L-serylamino)phenyl]-10,15,20-tristolylporphyrin (18b). 13b (7 mg, 0.01 mmol), **2** (20 mg, 0.03 mmol), and dicyclohexylcarbodiimide (6 mg, 0.03 mmol) gave 11 mg of **18b** (84%). R_f 0.54 (toluene/acetone/methanol, 85/10/5). UV−visible (see Table 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.75(2H, br s, NH); 2.07(12H, s, OAc); 2.70-(9H, s, Me tolyl); 3.88(1H, m, H-5′ ose); 4.0(1H, br t, J = 8.2 Hz, H-β serine); 4.1(1H, dd, J = 2.5−12.2 Hz, H-6$_b$′ ose); 4.18−4.32(4H, m, H-6$_a$′ose, H-9 Fmoc, H-α and H-β serine); 4.53-(3H, m, H-1′ ose and CH_2 Fmoc); 5.10(1H, m, H-2′ ose); 5.18(1H, br t, J = 9.3 Hz, H-4′ ose); 5.29(1H, br t, J = 9.2 Hz, H-3′ ose); 5.91(1H, br s, NH serine); 7.36(2H, br t, J = 7.3 Hz, H−Fmoc); 7.43(2H, br t, J = 7.0 Hz, H−Fmoc); 7.55(6H, d, J = 7.8 Hz, H-3,5 tolyl); 7.66(2H, br d, J = 7.1 Hz, H−Fmoc); 7.79(2H, br d, J = 7.1 Hz, H−Fmoc); 7.96(2H, d, J = 7.9 Hz, H-3,5 amidophenyl); 8.09(6H, d, J = 7.8 Hz, H-2,6 tolyl); 8.20-(2H, d, J = 8.2 Hz, H-2,6 amidophenyl); 8.70(1H, br s, NH amidophenyl); 8.86(8H, br s, H-β pyrrole). ^{13}C NMR (100 MHz) 20.6(2C, *C*H_3CO); 20.7(1C, *C*H_3CO); 20.8(1C, *C*H_3CO); 21.5-(3C, Me tolyl); 47.2(1C, C-9 Fmoc); 54.7(1C, *C*H serine); 61.7-(1C, *C*H_2 Fmoc); 61.8(1C, C-6′ ose); 67.0(1C, *C*H_2 serine); 68.0(1C, C-4′ ose); 71.2(1C, C-2′ ose); 71.9(1C, C65′ ose); 72.5-(1C, C-3′ ose); 102.2(C-1′ ose); 118.1(2C, C-3,5 amidophenyl); 119.0(1C, C *meso*); 120.1(2C, C Fmoc); 120.2(2C, C *meso*); 120.3(1C, C *meso*); 125.0(2C, C Fmoc); 127.2(2C, C Fmoc); 127.4(6C, C63,5 tolyl); 127.9(2C, C−Fmoc); 131.0(8C, C-β pyrrole); 134.5(6C, C-2,6 tolyl); 135.1(2C, C-2,6 amidophenyl); 137.3(4C, C-4 tolyl and C-1 amidophenyl); 138.7(1C, C-4 amidophenyl); 139.2(3C, C-1 tolyl); 141.4(2C, C_{IV} Fmoc); 143.6-(2C, C_{IV} Fmoc); 146.2(8C, Cα-pyrrole); 156.7(1C, *C*O Fmoc); 169.5(2C, CH_3CO); 169.6(1C, CH_3CO); 170.2(1C, CH_3CO); 170.7(1C, *C*O serine). MS (MALDI) *m/z*: 1311.6 ($[M + H]^+$monoisotopic). Anal. Calcd for $C_{79}H_{70}N_6O_{13}$: C, 72.38; H, 5.34; N, 6.41. Found: C, 72.21; H, 5.31; N, 6.42.

General Procedure for Synthesis of Compounds 19a,b, 20, 21, and 22a,b. A 20 mg portion of the porphyrin was dissolved in 2 mL of CH_2Cl_2/morpholine (1/1), and the mixture was stirred for 60 min at room temperature. After evaporation under vacuum, the crude product was dissolved in 2 mL of CH_2Cl_2/MeOH (80/20). Sodium methanolate in dry methanol (1.5 equiv/OAc, 1 M) was added, and the mixture was stirred for 60 min at room temperature. Then porphyrin was precipitated by addition of petroleum ether.

5-[2-(*β*-D-glucopyranosyloxy)phenyl]-10,15,20-tris[4-(L-alanylamino)phenyl]porphyrin (19a). The title compound was purified by gel filtration on a Sephadex LH20 column eluted with THF/H_2O (8/2), (8 mg, 71%). R_f 0.45 (CH_2Cl_2/MeOH, 70/30). UV−visible (see Table 2). MS (MALDI) *m/z*: 1051.5 ($[M + H]^+$ monoisotopic). Anal. Calcd for $C_{59}H_{58}N_{10}O_9$: C, 67.44; H, 5.52; N, 13.33. Found: C, 67.36; H, 5.50, N, 13.30.

5-[4-(*β*-D-glucopyranosyloxy)phenyl]-10,15,20-tris[4-(L-alanylamino)phenyl]porphyrin (19b). The title compound was purified by gel filtration on a Sephadex LH20 column eluted with THF/H_2O (8/2), (8 mg, 71%). R_f 0.43 (CH_2Cl_2/MeOH, 70/30). UV−visible (see Table 2). MS (MALDI) *m/z*: 1051.5 ($[M+H)^+$ monoisotopic). Anal. Calcd for $C_{59}H_{58}N_{10}O_9$: C, 67.44; H, 5.52; N, 13.33. Found: C, 67.39, H, 5.53, N, 13.29.

5,15-Bis[4-(L-alanylamino)phenyl]-10,20-bis[4-(*β*-D-glucopyranosyloxy)phenyl]porphyrin (20). The title compound was purified by gel filtration on a Sephadex LH20 column eluted with THF/H_2O (9/1), (9 mg, 75%). R_f 0.57 (CH_2Cl_2/EtOH/H_2O, 4/6/2). UV−visible (see Table 2). MS (MALDI) *m/z*: 1143.6 ($[M + H]^+$monoisotopic). Anal. Calcd for $C_{62}H_{62}N_8O_{14}$: C, 65.17; H, 5.42; N, 9.80. Found: C, 65.02; H, 5.40; N, 9.81.

5,10-Bis[4-(L-alanylamino)phenyl]-15,20-bis[4-(*β*-D-glucopyranosyloxy)phenyl]porphyrin (21). The title com-

pound was purified by gel filtration on a Sephadex LH20 column eluted with THF/H_2O (9/1), (8 mg, 67%). R_f 0.54 (CH_2Cl_2/EtOH/H_2O, 4/6/2). UV−visible (see Table 2). MS (MALDI) *m*/*z*: 1143.6 ([M + H]$^+$ monoisotopic). Anal. Calcd for $C_{62}H_{62}N_8O_{14}$: C, 65.17; H, 5.42; N, 9.80. Found: C, 65.07; H, 5.39; N, 9.78.

5-[2-(L-Alanylamino)phenyl]-10,15,20-tris[4-(β-D-glucopyranosyloxy)phenyl]porphyrin (22a). The title compound was purified by gel filtration on a Sephadex LH20 column eluted with MeOH/H_2O (9/1), (9 mg, 71%). R_f 0.52 (CH_2Cl_2/EtOH/H_2O, 4/6/2). UV−visible (see Table 2). MS (MALDI) *m*/*z*: 1235.5 ([M + H]$^+$ monoisotopic). Anal. Calcd for $C_{65}H_{66}N_6O_{19}$: C, 63.23; H, 5.35; N, 6.81. Found: C, 63.18; H, 5.31; N, 6.78.

5-[4-(L-Alanylamino)phenyl]-10,15,20-tris[4-(β-D-glucopyranosyloxy)phenyl]porphyrin (22b). The title compound was purified by gel filtration on a Sephadex LH20 column eluted with MeOH/H_2O (9/1), (8 mg, 64%). R_f 049 (CH_2Cl_2/EtOH/H_2O, 4/6/2). UV−visible (see Table 2). MS (MALDI) *m*/*z*: 1235.7 ([M + H]$^+$ monoisotopic). Anal. Calcd for $C_{65}H_{66}N_6O_{19}$: C, 63.23; H, 5.35; N, 6.81. Found: C, 63.14; H, 5.37; N, 6.81.

Procedure for Deprotection of Monoglucosylseryltristolylporphyrins 23a,b. A 20 mg portion of porphyrin **18a,b** was dissolved in 2 mL of CH_2Cl_2/morpholine (1/1). The mixture was stirred for 60 min at room temperature. After evaporation under vacuum, the acetate groups of the carbohydrate moieties were removed according to the literature.[18] The crude product was dissolved in 2 mL of hydrazine/MeOH/CH_2Cl_2 (4/3/3), and the mixture was stirred for 2 h. Afterward, acetone (2 mL) was added to the solution to remove excess hydrazine. The porphyrin was precipitated by addition of petroleum ether, filtered, and then purified by gel filtration on a Sephadex LH20 column, eluted with THF/H_2O (9/1).

5-[2-(3-*O*-(β-D-glucopyranosyl)-L-serylamino)phenyl]-10,15,20-tristolylporphyrin (23a): 10 mg (71%). R_f 0.48 (CH_2Cl_2/MeOH,80/20). UV−visible (see Table 2). MS (MALDI) *m*/*z*: 920.4 ([M + H]$^+$ monoisotopic). Anal. Calcd for $C_{56}H_{51}N_6O_7$: C, 73.14; H, 5.55; N, 9.14. Found: C, 73.07; H, 5.56; N, 9.10.

5-[4-(3-*O*-(β-D-glucopyranosyl)-L-serylamino)phenyl]-10,15,20-tristolylporphyrin (23b): 8 mg (57%). R_f 0.42 (CH_2Cl_2/MeOH,80/20). UV−visible (see Table 2). MS (MALDI) *m*/*z*: 920.4 ([M + H]$^+$ monoisotopic). Anal. Calcd for $C_{56}H_{51}N_6O_7$: C, 73.14; H, 5.55; N, 9.14. Found: C, 73.04; H, 5.53; N, 9.15.

JO982499+