Porphyrin-Containing Glycodendrimers[‡]

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Two dendrimers, incorporating tetrasubstituted porphyrin units as their cores and, in one case, four perbenzoylated and, in the other case, twelve peracetylated β-D-glucopyranosyl residues at their peripheries, have been synthesized in yields of 39 and 16%, respectively. The deprotection of these dendrimers was achieved quantitatively under Zemplén conditions. The protected and deprotected dendrimers were characterized by liquid secondary-ion or matrix-assisted laser desorption ionization time-of-flight mass spectrometry and by a combination of one- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy. All the glycodendrimers were also characterized by absorption and emission spectroscopy, and lifetime measurements. The most relevant result is that both protected and deprotected dendrimers show two fluorescence lifetime values that are different from the porphyrin model compounds.

Introduction

Porphyrins play a fundamental role[1] in numerous biological processes as a result of their ability to coordinate with transition metals and because of their electrochemical, photophysical, and photochemical properties. As an example, proteins incorporating one or more porphyrin units embedded into their peptidic frameworks are well-known.[2] In these systems, the polypeptidic shells modulate the response of the porphyrin units to the external environment. Unnatural counterparts of these biologically occurring systems can be generated by embedding one or more porphyrins inside a dendritic framework. Indeed, several dendrimers[3,4] incorporating porphyrin cores have been designed and synthesized already.[5]

Recently, we have synthesized a series of carbohydrate dendrimers incorporating ferrocene cores.[6] A detailed analysis of the resulting molecular assemblies revealed that the β-D-glucopyranose branches surrounding the electroactive core have a profound influence on its redox response. In particular, the oxidation potential, the rate constant of heterogeneous electron transfer, and the rate constant for the energy-transfer reaction with luminescent species are all affected significantly by the carbohydrate shield around the ferrocene unit. In order to explore the potential influence of similar β-D-glucopyranose branches on the photophysical properties of photoactive cores, we have designed a synthetic procedure to construct a carbohydrate shell around a porphyrin chromophore. Our strategy is based on β-D-glucopyranose building blocks developed previously for the preparation of highly branched glycodendrimers.[6,7] Here, we report the synthesis, characterization and photophysical properties of two carbohydrate-containing dendrimers incorporating a porphyrin core in their protected and deprotected forms.

Results and Discussion

Synthesis and Characterization

Reaction of the tetrafunctionalized porphyrin **1**[8] with the β-D-glucopyranose-based compounds **2**[9] or **5**[9] in the presence of NEt_3 gave the dendrimers **3** and **6** in yields of 39 and 16%, respectively (Scheme 1 and 2). Removal of the

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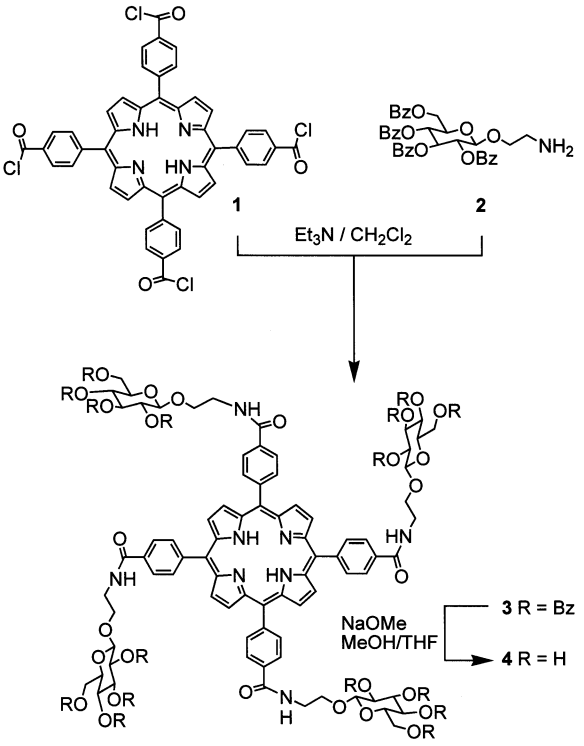
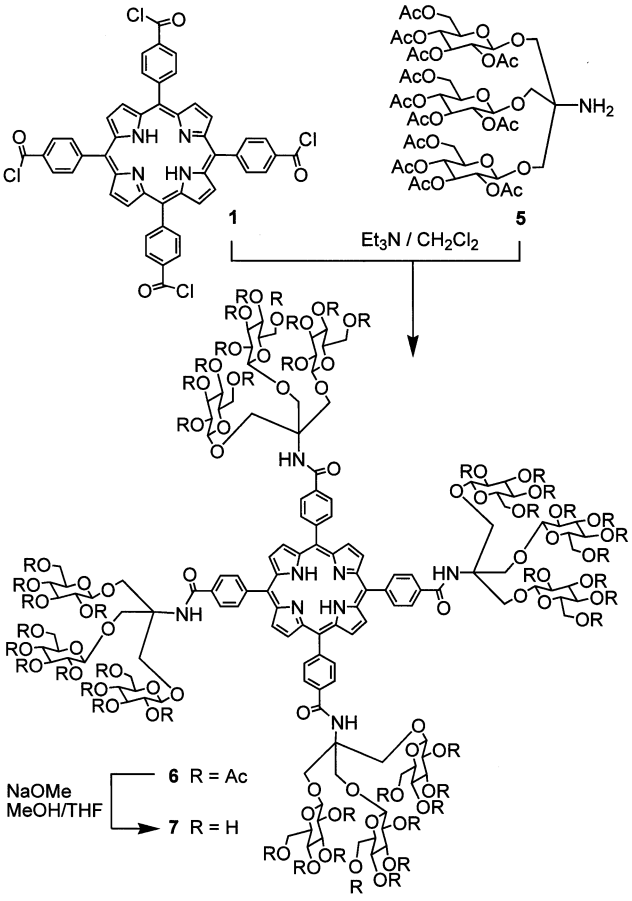
protecting groups of **3** and **6** with NaOMe in a mixture of MeOH and THF afforded respectively and quantitatively **4** and **7**.



Scheme 1. Synthesis of the porphyrin glycodendrimer **4**



Scheme 2. Synthesis of the porphyrin glycodendrimer **7**

All new compounds were characterized by high resolution liquid secondary ion mass spectrometry (HRLSIMS) or by high resolution matrix-assisted laser desorption ionization time-of-flight mass spectrometry (HRMALDI-TOFMS) which revealed peaks corresponding to $[M]^+$ ions (Table 1). A combination of one- and two-dimensional NMR techniques (dqf-COSY and HMQC) enabled the complete assignment of the resonances in the ^1H NMR and ^{13}C NMR spectra of the protected and the deprotected dendrimers. The resonances associated with the protons of the β-D-glucopyranose units and those corresponding to the protons of the porphyrin core have been assigned as summarized in Table 2.

In order to visualize the structures of the protected and the deprotected dendrimers in three-dimensions, their global minima were searched for by molecular dynamics calculations and are illustrated in Figure 1. Their approximate radii were determined as the distances between the center of the porphyrin and the surface of the β-D-glucopyranose units and range from 16 to 22 Å, increasing by ca. 2 Å on going from the smallest (**4**) to the largest (**6**) structure.

Photophysical Studies

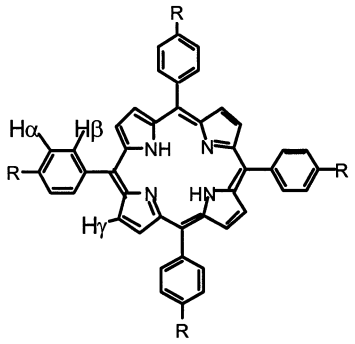
All the photophysical experiments were performed at room temperature in air-equilibrated solutions. It was not possible to find a common solvent for all the dendrimers and their reference compounds. The protected dendrimers **3** and **6**, the free-base *meso*-tetraphenylporphyrin **8**, the β-D-glucopyranose unit **9**, and the methyl benzoate model compound **10** were studied in $MeCN/CH_2Cl_2$ (85:15, v/v), while the deprotected dendrimers **4** and **7**, together with the free-base *meso*-tetra-4-carboxyphenylporphyrin **11** reference compound, were studied in H_2O/THF (80:20, v/v). The structural formulas of the compounds used as models of the chromophoric units are collected in Figure 2. All the relevant photophysical data are collected in Table 3.

In the solvents used, all the examined compounds were stable for days in the dark, as shown by the invariance of the absorption and emission spectra. Very small changes were observed after several hours of irradiation with light of wavelength greater than 400 nm, but the solutions were photochemically stable in the conditions of the photophysical experiments. The absorption spectra of compounds **3** and **6** are those expected on the basis of the component chromophores. As an example, the absorption spectra of **8** and **6** are shown in Figure 3. Compound **6** shows the same absorption bands as **8**, because the glycopyranoside branches do not absorb at wavelengths greater than 220 nm. In compound **3**, in addition to the Soret and Q absorption bands characteristic of the **8** core unit, an absorption band with λ_{max} = 230 nm is present, clearly attributable to the presence of benzoate groups in the glycopyranoside branch.[10] For both glycodendrimers, a quantitative com-

Table 1. High resolution mass spectrometric data for the compounds **3**, **4**, **6**, and **7**

Compound	Molecular Formula	Calculated *m*/*z* for M^+	Observed *m*/*z* for M^+	Technique
3	$C_{192}H_{154}N_8O_{44}$	3275.0059	3275.0055	LSI
4	$C_{80}H_{90}N_8O_{28}$	1611.5943	1611.6264	MALDITOF
6	$C_{232}H_{282}N_8O_{124}$	5164.6085	5164.7835	MALDITOF
7	$C_{136}H_{186}N_8O_{76}$	3148.1014	3148.0301	MALDITOF

Table 2. ^{1}H NMR spectroscopic data (δ values in ppm and *J* values in Hz) of compounds **3** and **4** in $CDCl_3$ and **6** and **7** in D_2O/[D_8]THF at 25 °C[a]



	β-D-Glucopyranosyl Protons							Porphyrin Core Protons		
	H−1 (*J*1,2)	H−2 (*J*2,3)	H−3 (*J*3,4)	H−4 (*J*4,5)	H−5	H−6a (*J*5,6a)	H−6b (*J*5,6b, *J*6a,6b)	Hα	Hβ	Hγ
3	5.02 [d, 4 H] (7.8)	5.64 [dd, 4 H] (9.7)	5.99 [pt, 4 H] (9.7)	5.75 [pt, 4 H] (9.7)	4.24−4.28 [m, 4 H]	4.55 [dd, 4 H] (5.3)	4.73 [dd, 4 H] (2.7,12.2)	8.07 [d, 8 H] (7.9)	7.85 [d, 8 H] (7.9)	8.79 [br. s, 8 H]
4	4.56 [d, 4 H] (7.9)	3.36 [dd, 4 H] (9.2)	3.55 [pt, 4 H] (9.2)	3.39 [pt, 4 H] (9.2)	3.45−3.49 [m, 4 H]	3.73 [dd, 4 H] (6.0)	3.93 [dd, 4 H] (3.4, 12.1)	8.37 [d, 8 H] (7.9)	8.25 [d, 8 H] (7.9)	8.85 [br. s, 8 H]
6	4.66 [d, 12 H] (7.9)	5.12 [dd, 12 H] (9.8)	5.65 [pt, 12 H] (9.8)	5.16 [pt, 12 H] (9.8)	3.80−3.84 [m, 12 H]	4.12−4.21 [m, 12 H]	4.37−4.43 [m, 12 H]	8.32 [d, 8 H] (7.9)	8.17 [d, 8 H] (7.9)	8.83 [br. s, 8 H]
7	4.62 [d, 12 H] (7.9)	3.39 [dd, 12 H] (9.3)	3.59 [pt, 12 H] (9.3)	3.42 [pt, 12 H] (9.3)	3.49−3.53 [m, 12 H]	3.75 [dd, 12 H] (5.9)	3.95 [dd, 12 H] (3.3,12.1)	8.38 [d, 8 H] (7.9)	8.30 [d, 8 H] (7.9)	9.02 [br. s, 8 H]

[a] The signals were assigned by two-dimensional homonuclear and heteronuclear correlation NMR spectroscopy.

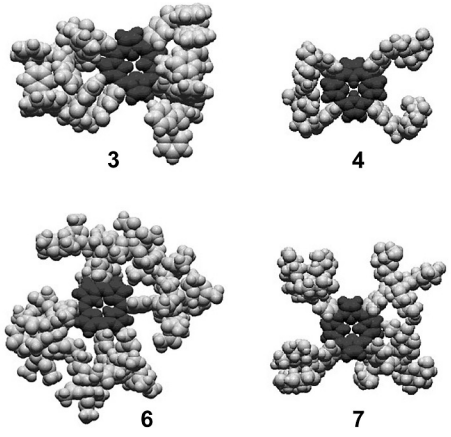


Figure 1. Space-filling representations of the global minima found for **3**, **4**, **6**, and **7**; in each structure, the porphyrin core is represented in dark shading and the four substituents in light shading

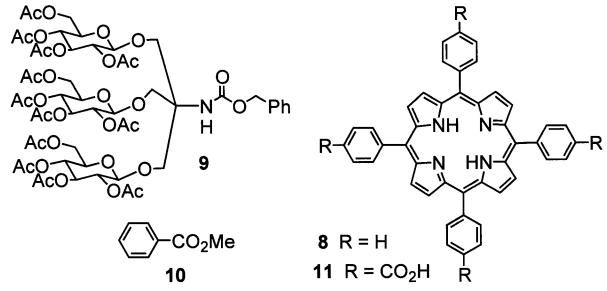


Figure 2. Model compounds for the photophysical measurements

parison with **8** shows only a very small red shift (2−3 nm) of the absorption maxima, accompanied by a decrease in the molar absorption coefficients (see Table 3). This decrease cannot be attributed to the association processes that are often observed in porphyrins and their derivatives;[11] indeed, for **8** and both compounds **3** and **6** no effect of

Table 3. Photophysical data of the porphyrin glycodendrimers and reference compounds (room temperature, air equilibrated solutions)

Compound	Solvent	Absorption[a]		Emission			
		λ_{max} (nm)	ε_{max} ($M^{-1}\cdot cm^{-1}$)	λ_{max} (nm)	Φ	τ (ns)	R[b] (%)
3	$MeCN/CH_2Cl_2$	417	270000	650, 715[c]	0.10	3.7	38
	(85:15, v/v)	516	11200			10.0	62
6	$MeCN/CH_2Cl_2$	416	248000	650, 715[c]	0.14	4.6	47
	(85:15, (v/v)	514	12700			10.8	53
8	$MeCN/CH_2Cl_2$	414	350000	650, 715[c]	0.12	9.4	
	(85:15, v/v)	512	14800				
9	$MeCN/CH_2Cl_2$	227	1000	300[d]	0.02	1.7	
	(85:15, v/v)						
10	$MeCN/CH_2Cl_2$	230	10000				
	(85:15, v/v)						
4	H_2O/THF	418	300000[e]	652, 716[c]	0.12	3.5	46
	(80:20, v/v)	515	15400			13.0	54
7	H_2O/THF	418	113000[e][f]	652, 716[c]	0.14	4.7	35
	(80:20, v/v)	515	7700			13.0	65
11	H_2O/THF	418	328000[e]	652, 716[c]	0.13	12.0	
	(80:20, v/v)	515	16000				

[a] The first value refers to the Soret band, the second to the highest energy Q band. [b] Relative population of the two emissive excited states, calculated from the preexponential factors, assuming the same nonradiative deactivation constant. [c] Structured band. [d] Very broad band. [e] $c = 10^{-4}$ to 10^{-6} M. At $c = 1.0 \times 10^{-4}$ M the ε value decreases by 20%, indicating a small effect of aggregation. [f] Molar extinction coefficient value lower than expected; different solutions of **7** always give the same ε value. This could be attributed to the presence in the sample of a nonabsorbing impurity.

dilution on the ε value is observed and the emission quantum yield is independent of the concentration, at least in the concentration range explored (10^{-4} to 10^{-6} M).

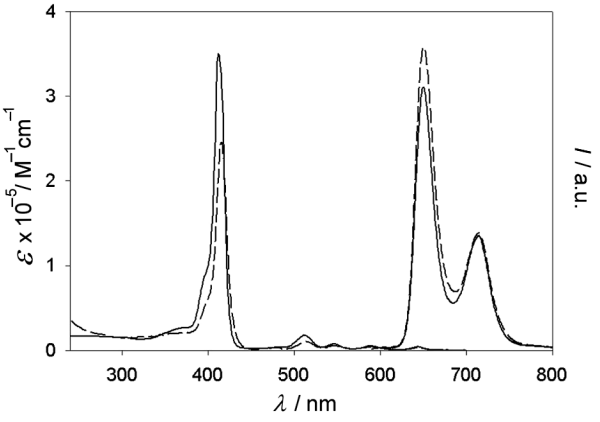


Figure 3. Absorption and emission spectra of the porphyrin glycodendrimer **6** and of the reference compound **8** [$MeCN/CH_2Cl_2$ (85:15, v/v), room temperature]

The fluorescence spectra of glycodendrimers **3** and **6** and of the reference compound **8** are identical (see, for example, Figure 3); glycodendrimer **6** and the reference compound **8** show almost the same emission quantum yield value (Table 3), independent of the excitation wavelength. This means that the acetate substituents in the β-D-glucopyranose branch do not show any electronic interaction with the porphyrin core. For glycodendrimer **3** almost complete quenching of the fluorescence emission of the porphyrin core is observed when exciting at 230 nm, where more than 90% of the exciting light is absorbed by the benzoate groups of the β-D-glucopyranose; this quenching is confirmed by the excitation spectrum of **3** (Figure 4), in which the band attributable to the benzoate groups is completely absent. These results can be interpreted by assuming that upon exciting the peripheral benzoate units, an energy-transfer process to the lowest excited states of the porphyrin core does not occur, while a very fast radiationless deactivation process of the excited benzoate moieties or an electron-transfer process can be responsible for the lack of luminescence of the porphyrin core ($E_{1/2}$ for reduction of **10** is −2.29 V in DMF vs. SCE,[12] E_{ox} for **8** is −1.19 V vs. NHE in organic solvents,[13] and an E^{0-0} value greater than 4 eV can be estimated from the tail of the absorption band of **10**).

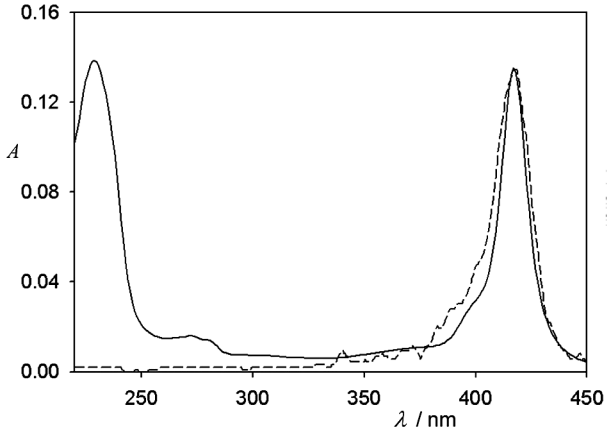


Figure 4. Comparison between the absorption and excitation spectrum of the porphyrin glycodendrimer **3** [$MeCN/CH_2Cl_2$ (85:15, v/v), room temperature]

The absorption spectra in H_2O/THF (80:20, v/v) of glycodendrimers **4** and **7** show the same Soret and Q bands with the same maximum wavelengths as the reference compound **11** (see Table 3). In contrast with the protected glycodendrimers **3** and **6** examined in MeCN/CH_2Cl_2 (85:15, v/v), the molar absorption coefficients at λ_{max} of the Soret band of compounds **4** and **7** show an increase of about 20% upon decreasing the concentration from 10^{-4} to 10^{-6} M. This result may be attributed to an aggregation effect in this different solvent.[11]

As far as the emission properties are concerned, the glycodendrimers **4** and **7** exhibit the same emission spectrum shown by the reference compound **11**, with the same quantum yield (see Table 3). Quite surprising results have been obtained from the lifetime measurements. While the reference compounds **8** and **11** exhibit a monoexponential decay (τ = 9.4 and 12 ns, respectively), all the studied glycodendrimers are characterized by a double exponential decay (see Table 3): one of the lifetime values is quite similar to that of the corresponding reference compound, while the other lifetime value is shorter; the two decays are characterized by comparable preexponential factors. Recently, similar results were obtained in substituted zinc porphyrins with dendritic architectures.[14] In that case, the authors attribute the shorter lived component to aggregate species, as indicated by the blue shift in the Soret band. This explanation cannot be invoked in our case, since our lifetime measurements were performed in very dilute solutions, where aggregation phenomena (observed only in more concentrated solutions in H_2O/THF, see above) were completely absent. One possible explanation could be the presence in solution of two different conformations on account of the bulky β-D-glucopyranoside substituents.

Conclusions

The covalent attachment of four β-D-glucopyranose-based wedges to a tetrafurcated porphyrin core has been realized by amide bond formation. The resulting two dendrimers have molecular weights of 3277 and 5167 and approximate radii of 18 and 22 Å, respectively. Removal of the protecting groups attached to the carbohydrate units located at the surface of these dendrimers afforded two water-soluble porphyrin-containing dendrimers with molecular weights of 1612 and 3149 and approximate radii of 16 and 20 Å, respectively. Liquid secondary ion mass spectrometry, and one- and two-dimensional ^1H and ^{13}C NMR spectroscopy were employed to characterize these highly-branched molecules. All the glycodendrimers were also characterized by electronic absorption and emission spectroscopy, and lifetime measurements. The most relevant result is that each glycodendrimer shows two distinct fluorescence lifetime values, while the porphyrin model compounds have only one. In the case of compound **3** no energy transfer occurs from the benzoate groups of the glycopyranoside branch to the porphyrin core.

Experimental Section

General Methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to literature procedures.[15] The compounds **1**,[8] **2**,[9] **5**,[9] and **9**[9] were prepared according to literature procedures. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with silica-gel 60 (Merck 5554). Column chromatography was performed on silica-gel 60 (Merck, 40−63 nm). Gel permeation chromatography (GPC) was carried out on a Phenogel semi-preparative column (500 Å, 300 × 7.80 mm, Phenomenex, England) operated by a Gilson 714 high-performance liquid chromatographic system equipped with a UV detector set at a wavelength of 260 nm using THF as the mobile phase. High resolution liquid secondary ion mass spectra (HRLSIMS) were recorded on a VG ZabSpec mass spectrometer, equipped with a cesium ion source, with *m*-nitrobenzyl alcohol containing a trace amount of NaOAc as matrix. High resolution matrix-assisted laser desorption ionization time-of-flight mass spectrometry (HRMALDITOFMS) was performed on a Voyager-DE STR with an α-cyano-4-hydroxycinnamic acid matrix. ^1H NMR Spectra were recorded on a Bruker ARX400 (400 MHz), or a Bruker ARX500 (500 MHz) spectrometer. ^{13}C NMR Spectra were recorded on either a Bruker ARX400 (100 MHz), or a Bruker ARX500 (125 MHz) spectrometer. The chemical shift values are expressed as δ values in ppm and the coupling constant values (*J*) are in Hertz.

***meso*-Tetrakis[{4-[2-*O*-(2,3,4,6-*O*-benzoyl-β-D-glucopyranosyl)-ethyl]aminocarbonyl}phenyl]porphyrin (3):** A solution of **2** (320 mg, 0.5 mmol) and NEt_3 (0.2 mL, 1.4 mmol) in dry CH_2Cl_2 (2 mL) was added to a stirred solution of **1** (95 mg, 0.1 mmol) in dry CH_2Cl_2 (10 mL) maintained under an atmosphere of N_2. The mixture was stirred for 12 h at ambient temperature and the solvent was then distilled off under reduced pressure. Purification of the residue by column chromatography (SiO_2: $CHCl_3$/MeOH 95:5) afforded **3** (140 mg, 39%) as a purple glass. HRLSIMS: *m*/*z* calcd. for $[M]^+$ ($C_{192}H_{154}N_8O_{44}$): 3275.0059; found 3275.0055. ^1H NMR ($CDCl_3$): δ = −2.77 (s, 2 H), 3.75−3.79 (m, 4 H), 3.92−3.96 (m, 4 H), 3.99−4.03 (m, 4 H), 4.18−4.22 (m, 4 H), 4.24−4.28 (m, 4 H), 4.55 (dd, *J* = 5.3, 12.2 Hz, 4 H), 4.73 (dd, *J* = 2.7, 12.2 Hz, 4 H), 5.02 (d, *J* = 7.8 Hz, 4 H), 5.64 (dd, *J* = 7.8, 9.7 Hz, 4 H), 5.75 (pseudo t, *J* = 9.7 Hz, 4 H), 5.99 (pseudo t, *J* = 9.7 Hz, 4 H), 6.93 (br. s, 4 H), 7.24−8.04 (m, 88 H), 8.07 (d, *J* = 7.9 Hz, 8 H), 8.79 (s, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 39.9, 62.9, 69.4, 72.0, 72.5, 72.6, 101.3, 119.0, 125.3, 128.3−129.7, 133.1, 133.4, 137.3, 165.1, 165.3, 165.7 ppm.

***meso*-Tetrakis[{4-[2-*O*-(β-D-glucopyranosyl)ethyl]amino-carbonyl}phenyl]porphyrin (4):** A solution of NaOMe (0.5 M) in MeOH (2.15 mL), was added to a stirred solution of **3** (235 mg, 0.1 mmol) in anhydrous MeOH (30 mL) and THF (10 mL) maintained under an atmosphere of N_2. After 16 h, the mixture was brought to neutrality with 0.1 M HCl. The solvent was then distilled off under reduced pressure and the residue was washed with CH_2Cl_2 (3 × 30 mL), cold H_2O (2 × 30 mL), and dried to afford **4** (116 mg, 100%) as a purple glass. HRMALDITOFMS: *m*/*z* calcd. for $[M]^+$ ($C_{80}H_{90}N_8O_{28}$): 1611.5943; found 1611.6264. ^1H NMR (D_2O/[D_8]THF): δ = 3.36 (dd, *J* = 7.9, 9.2 Hz, 4 H), 3.39 (pseudo t, 4 H, *J* = 9.2 Hz), 3.45−3.49 (m, 4 H), 3.55 (pseudo t, 4 H, *J* = 9.2 Hz), 3.73 (dd, *J* = 6.0, 12.1 Hz, 4 H), 3.79−3.83 (m, 4 H), 3.86−3.90 (m, 4 H), 3.93 (dd, *J* = 3.4, 12.1 Hz, 4 H), 3.97−4.01 (m, 4 H), 4.20−4.24 (m, 4 H), 4.56 (d, *J* = 7.9 Hz, 4 H), 8.25 (d, *J* = 7.9 Hz, 8 H), 8.37 (d, *J* = 7.9 Hz, 8 H), 8.85 (br. s, 8 H) ppm. ^{13}C NMR (D_2O/[D_8]THF): δ = 40.0, 61.0, 68.5, 69.9, 73.3, 76.1,

76.3, 102.8, 107.54, 118.7, 125.9, 128.7, 133.8, 134.2, 144.3, 167.5 ppm.

***meso*-Tetrakis{4-[tris-{*O*-[2,3,4,6-tetra-(*O*-acetyl)-β-D-glucopyranosyl]methyl}methylaminocarbonyl]phenyl}porphyrin (6):** A solution of **5** (424 mg, 0.4 mmol) and NEt_3 (0.8 mL, 5.8 mmol) in dry CH_2Cl_2 (10 mL) was added to a stirred solution of **1** (76 mg, 0.1 mmol) in dry CH_2Cl_2 (10 mL) maintained under an atmosphere of N_2. The reaction was stirred for three days and the solvent was then distilled off under reduced pressure. Purification of the residue by column chromatography (SiO_2: $CHCl_3$/MeOH 99:1−95:5) followed by GPC afforded **6** (76 mg, 16%) as a purple glass. HRMALDI-TOFMS: *m/z* calcd. for $[M]^+$ ($C_{232}H_{282}N_8O_{124}$): 5164.6085; found 5164.7835. ^1H NMR ($CDCl_3$): δ = −2.92 (s, 2 H), 2.09 (m, 144 H), 3.80−3.84 (m, 12 H), 4.12−4.21 (m, 24 H), 4.37−4.43 (m, 24 H), 4.66 (d, *J* = 7.9 Hz, 12 H), 5.12 (dd, *J* = 7.9, 9.8 Hz, 12 H), 5.16 (pseudo t, *J* = 9.8 Hz, 12 H), 5.65 (pseudo t, *J* = 9.8 Hz, 12 H), 6.82 (br. s, 4 H), 8.17 (d, *J* = 7.9 Hz, 8 H), 8.32 (d, *J* = 7.9 Hz, 8 H), 8.83 (s, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.6, 59.5, 62.7, 68.2, 68.5, 71.3, 71.9, 72.5, 101.1, 119.1, 125.4, 128.3, 129.9, 132.1, 134.5, 145. 5, 167.4, 169.2, 169.3, 170.0, 170.5 ppm.

***meso*-Tetrakis{4-[tris-(*O*-β-D-glucopyranosylmethyl)methylaminocarbonyl]phenyl}porphyrin (7):** A solution of NaOMe (0.5 M) in MeOH (560 μL) was added to a stirred solution of **6** (25 mg, 0.004 mmol) in anhydrous MeOH (15 mL) and THF (5 mL) maintained under an atmosphere of N_2. After 16 h, the mixture was brought to neutrality with 0.1 M HCl. The solvent was distilled off under reduced pressure and the residue was washed with CH_2Cl_2 (3 × 30 mL) and cold H_2O (2 × 20 mL) to afford **7** (15 mg, 100%) as a purple solid. HRMALDITOFMS: *m/z* calcd. for $[M]^+$ ($C_{136}H_{186}N_8O_{76}$): 3148.1014; found 3148.0301. ^1H NMR (D_2O/[D_8]THF): δ = 3.39 (dd, *J* = 7.9, 9.3 Hz, 12 H), 3.42 (d, *J* = 9.3 Hz, 12 H), 3.49−3.53 (m, 12 H), 3.59 (d, *J* = 9.3 Hz, 12 H), 3.75 (dd, *J* = 5.9, 12.1 Hz, 12 H), 3.95 (dd, *J* = 3.3, 12.1 Hz, 12 H), 4.24 (d, *J* = 10.2 Hz, 12 H), 4.62 (d, *J* = 7.9 Hz, 12 H), 4.68 (d, *J* = 10.2 Hz, 12 H), 8.30 (d, *J* = 7.9 Hz, 8 H), 8.38 (d, *J* = 7.9 Hz, 8 H), 9.02 (br. s, 8 H) ppm. ^{13}C NMR (D_2O/[D_8]THF): δ = 60.8, 68.1, 69.9, 73.8, 76.2, 76.3, 102.8, 107.5, 117.7, 126.0, 128.6, 133.2, 134.0, 144.9, 168.3 ppm.

Molecular Modeling: The compounds **3**, **4**, **6**, and **7** were constructed within the input mode of Macromodel 5.0.[16] The geometries were optimized by employing the Polak−Ribiere conjugate gradient (PRCG) algorithm[17] in conjunction with the AMBER* force field[18] and the generalized-Born surface area (GB/SA) solvation model[19] for $CHCl_3$ (**3** and **4**) or for H_2O (**6** and **7**) as implemented in Macromodel 5.0. The minimized geometries were subjected to an equilibration molecular dynamics run of 20 ps (simulated temperature = 500 K, time-step = 1.5 fs), followed by a molecular dynamics run of 200 ps (simulated temperature = 500 K, time-step = 1.5 fs) using the AMBER* force field and the GB/SA solvation model for $CHCl_3$ (**3** and **4**) or for H_2O (**6** and **7**). In all cases, 200 randomly selected geometries were minimized using the PRCG algorithm, the AMBER* force field, and the GB/SA solvation model for $CHCl_3$ (**3** and **4**) or for H_2O (**6** and **7**).

Photophysical Measurements: The solvents used were Merck Uvasol, used without purification. All the experiments were performed at room temperature on air equilibrated solutions. The concentration range was 10^{-4} to 10^{-6} M. The absorption spectra were recorded with a Perkin−Elmer Lambda 40 spectrophotometer. Uncorrected emission spectra were recorded with a Perkin−Elmer LS 50 spectrofluorimeter. Emission quantum yields were calculated using as standards *para*-dimethoxybenzene (Φ = 0.11 in MeCN)[20] for compound **9** and the free base *meso*-tetraphenylporphyrin **8** (φ = 0.13 in methylcycloexane)[21] for all the studied porphyrins derivatives. The estimated experimental error on quantum yield values is ±20%. An Edinburgh 199 single-photon counting apparatus was used for lifetime measurements. In some cases control experiments were performed with a Jobin−Yvon Fluorolog Tau-3 apparatus. In all cases the experimental error of the lifetime values is estimated to be ±10%. Irradiation experiments were performed using a Helios−Italquartz Polymer 125 medium pressure mercury lamp.

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