Porphyrin-Cored 2,2-Bis(methylol)propionic Acid Dendrimers

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Received December 19, 2003. Revised Manuscript Received March 11, 2004

The synthesis and characterization of dendron-coated porphyrins up to the fifth generation are described. Both free base and zinc-cored tetraphenylporphyrin ($TPPH_2$ and TPPZn) were used, from which the dendrons were divergently grown using the anhydride of acetonide-protected bis-MPA (acetonide-2,2-bis(methoxy)propanoic anhydride). It is shown that a spacer must be attached to the porphyrin to increase the hydrolytic stability and allow synthesis of higher generations. Direct coupling of dendrons to the porphyrins was also investigated but failed to give full substitution of the porphyrin core. The absorption and fluorescence emission data for the TPPZn dendrimers indicate that the porphyrin configuration may change at higher generations. The hydrodynamic volume of the dendrimers is calculated from the polarization anisotropy decay data. It is shown that these bis-MPA dendrimers are significantly smaller than the same generation Fréchet-type benzyl ether TPP dendrimer.

Introduction

The use of dendritic macromolecules in different areas of research is steadily increasing.[1,2] The interest in these highly branched molecules lies in their many interesting properties, such as large number of end groups, good solubility, and the possibility to tailor their properties.

One very interesting property of the dendritic molecules is their ability to create a microenvironment inside.[3,4] This property has been extensively studied for a number of different applications. Some of the applications are as follows: shape-selective catalysts,[5−8] solubilization of insoluble molecules, and protection from the surrounding environment.[3] Site isolation could be used for protecting an active photocenter from de-excitation, hence to some extent controlling the lifetimes of the excited states. Controlled molecular photosystems could be for use for example in applications of nonlinear optics, such as optical power limiting[9−13] (OPL) or in sensing applications, such as measuring oxygen content.[14−16]

One such photocenter is provided by porphyrins. Porphyrin and porphyrin-like molecules are widespread in nature.[17] The porphyrins have been studied for a multitude of different applications.[18] They have shown to be useful in light-emitting diodes,[19,20] photodynamic therapy,[21,22] chemical sensors,[23] optical limiters,[10,24,25] and so forth. In past years, there has been a considerable increase in the number of reports dealing with

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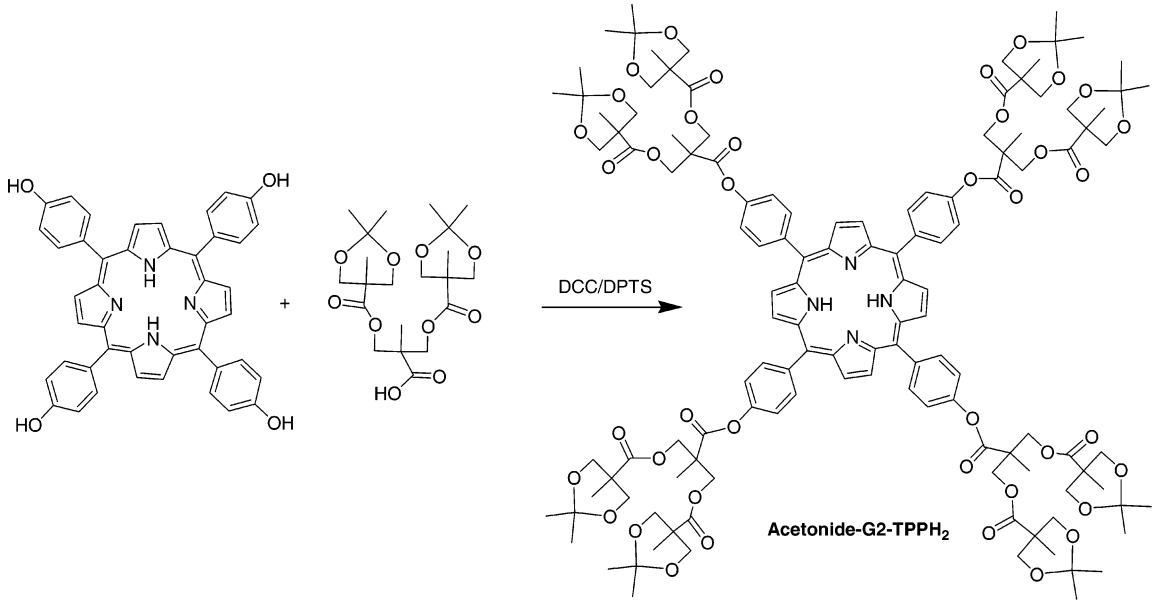
10.1021/cm035354e CCC: $27.50 © 2004 American Chemical Society
Published on Web 06/19/2004

Scheme 1. Direct Coupling of Dendrons to the Porphyrin Core



porphyrins decorated with dendrimers. The studies have dealt with for example light harvesting,[21,26,27] energy transfer,[8,28−31] and site isolation.[3,15,32−36] A large number of different dendrimers[26,28−30,37−39] have been utilized, ranging from Fréchet-type benzyl ether dendrimers[35,40−43] to glutamic dendrimers.[15,36,44]

Very little work has been conducted with the bis-MPA (2,2-bis(methylol)propionic acid) repeating unit. Fréchet et al.[3,33,34] have been growing poly(ϵ-caprolactone) stars from a bis-MPA functionalized porphyrin molecule. To date, there are no reports on bis-MPA dendron-decorated porphyrins. Therefore, we herein report the synthesis of porphyrins decorated with bis-MPA dendrons. Both free base and zinc-containing porphyrines are explored and some optical characterization is reported.

Results and Discussion

Synthesis. The chemistry of the anhydride of bis-MPA has proven to be a versatile way of synthesizing dendritic molecules.[45−48] Here, it is used as the building block in the synthesis of dendron-coated porphyrins. The porphyrin used was 5,10,15,20-tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphine. This porphyrin was chosen because of its commercial availability. It was used both as free base porphyrin ($TPPH_2$) and with a central zinc ion (TPPZn). Three different synthetic approaches have been utilized to achieve dendritic porphyrins of bis-MPA up to the fifth generation.

The first route that was employed was the direct addition of presynthesized bis-MPA dendrons to the free base as well as to the zinc-containing porphyrin (Scheme 1).

The addition was conducted with a DCC/DPTS (*N*,*N*′-dicyclohexylcarbodiimide)/(4-(dimethylamino)pyridinium *p*-toluenesulfonate) coupling[49,50] between the phenol of the porphyrin and the carboxylic focal point of the dendrons. For the second-generation dendrons this route yielded the desired dendritic porphyrin. However, a large excess (3 equiv per OH group) of dendrons had to be used and the separation of the not fully substituted dendritic porphyrins using medium pressure liquid chromatography (MPLC) was very tedious. For the third-generation dendrons this route did not lead to fully substituted porphyrins.

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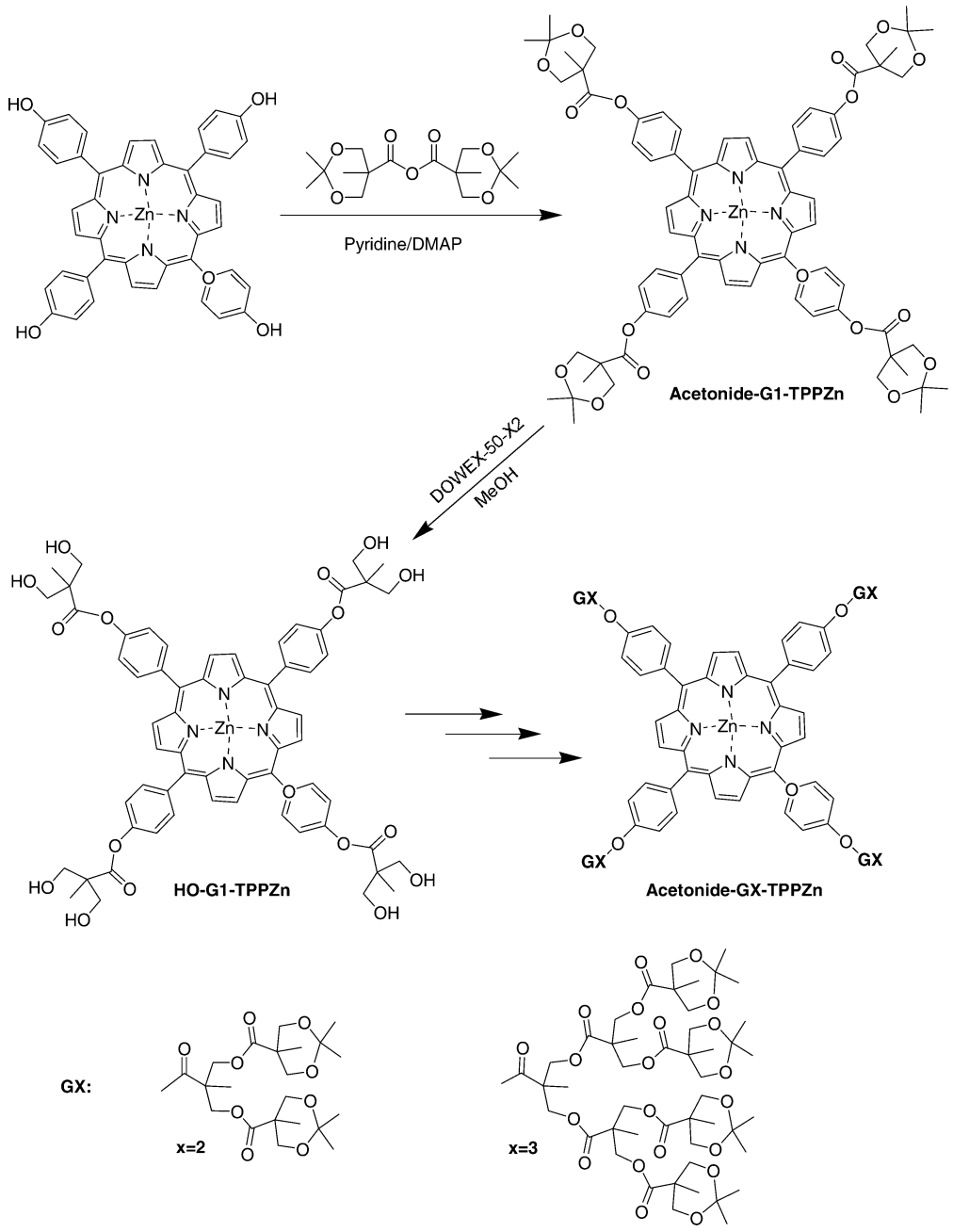
Scheme 2. Divergent Growth of Porphyrin-Cored Bis-MPA Dendrimers



The degree of substitution of the porphyrin core can be determined by ^{1}H NMR. The peaks corresponding to the hydrogens on the phenyl rings are shifted from 7.19 to 7.50 ppm and from 8.06 to 8.26 ppm, respectively, when substituted. Only approximately 3 qt of the phenolic groups were substituted with dendrons. It is believed that this is an effect of the crowding around the forth alcohol, when already three dendrons are added, prohibiting the last dendron from reacting.

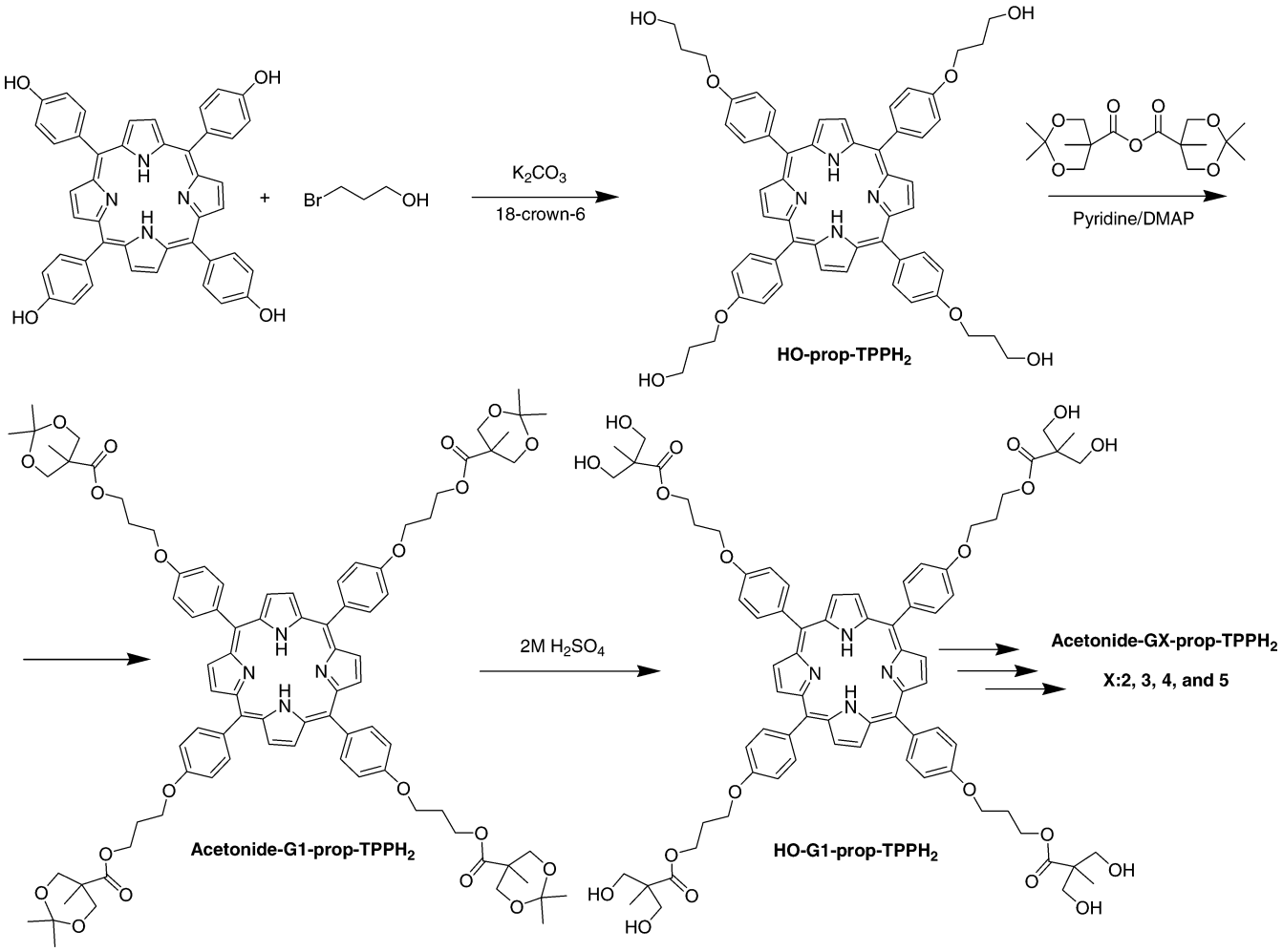
The next route for synthesizing these macromolecules was to grow the dendrons divergently direct from the phenol groups of the porphyrin (Scheme 2).

The anhydride of acetonide-protected bis-MPA was used followed by deprotection of the acetonide, hence activating the dendron for subsequent addition of the next layer of acetonide-protected bis-MPA units. The addition reactions proved to be high yielding with fairly easy workups; however, here the problems arose in the deprotection steps.

Normally acidic DOWEX-50-X2[49] resin is used for deprotecting the acetonide groups but in this case the porphyrin attached irreversibly to the DOWEX-50-X2 resin, leading to very low yields. Only the zinc-cored porphyrins gave the desired product, and by going from methanol to a mixture of methanol (20%) and tetrahydrofurane (80%), the yields were slightly increased. However, the yields were still low and the reaction times very long, 1−2 weeks for full deprotection.

Therefore, a number of different dilute acids were explored for deprotecting the dendrons, sulfuric acid, hydrochloric acid, acetic acid, and *p*-toluenesulfonic acid. The results from these acidic deprotections showed that as soon as the acetonide groups start to deprotect, also the phenolic ester linkage, between the porphyrin and

Scheme 3. Spacer Addition Route to the Porphyrin-Cored Bis-MPA Dendrimers



the dendrons, start to hydrolyze. This was easily detected by ^{1}H NMR where, as discussed earlier, the peaks for the hydrogens on the phenolic ring shifts considerably compared to the ones on the ring with the phenolic ester. This route has earlier been investigated by Hecht,[51] where he also found hydrolyses of the phenolic esters.

To be able to deprotect the dendrons without hydrolyzing the ester linkage, a nonacidic cerium ammonium nitrate deprotecting agent was used. The reactions were carried out in a buffer solution, pH 8. This reagent was unsuccessful and yielded no deprotected product.

In the third and final route to synthesize the dendritic porphyrins a spacer molecule was used to avoid the problem with the hydrolytically unstable benzylic ester bonds (Scheme 3). The spacer was added through the reaction of the porphyrin with 1,3-bromopropanol.

The dendrimers were then grown by subsequent addition of acetonide-protected bis-MPA followed by deprotection with 2 M sulfuric acid in THF.[52] For the free base porphyrins these reactions worked well with good yields and dendrimers up to the fifth generation were synthesized (Figure 1). However, for the zinc-containing porphyrins the reactions only worked satisfactorily up to the second generation. For the third generation ^{1}H NMR spectroscopy showed that some of the zinc had detached from the porphyrin core and the peaks for the two hydrogen atoms could be seen in the spectra at −2.8 ppm. It could also be seen in the UV−Vis spectra since the absorption spectra shifts significantly between the free base and the zinc porphyrin.

Also, the yields were lower for the zinc-containing dendrimers, due to degradation of the porphyrin, and for the forth generation no product at all was obtained. It was seen that for the porphyrins with zinc in the core the porphyrin ring seems to degrade during the reactions. To obtain zinc-containing molecules, zinc was inserted again for the third generation and into the free base porphyrins of fourth and fifth generation by the reaction of zinc acetate. The reactions were carried out in pyridine so that the acetonide groups would not be deprotected, which was observed in early attempts to insert the zinc into dendritic free base porphyrins.

Characterization. The molecular weight measurements were conducted both with size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analyses. The SEC was performed in THF and the number average molecular weight (M_n) values obtained agreed well with the theoretical molecular weights. The polydispersity indices (PDI) were very low up to the forth generation, indicating virtually monodisperse molecules. However,

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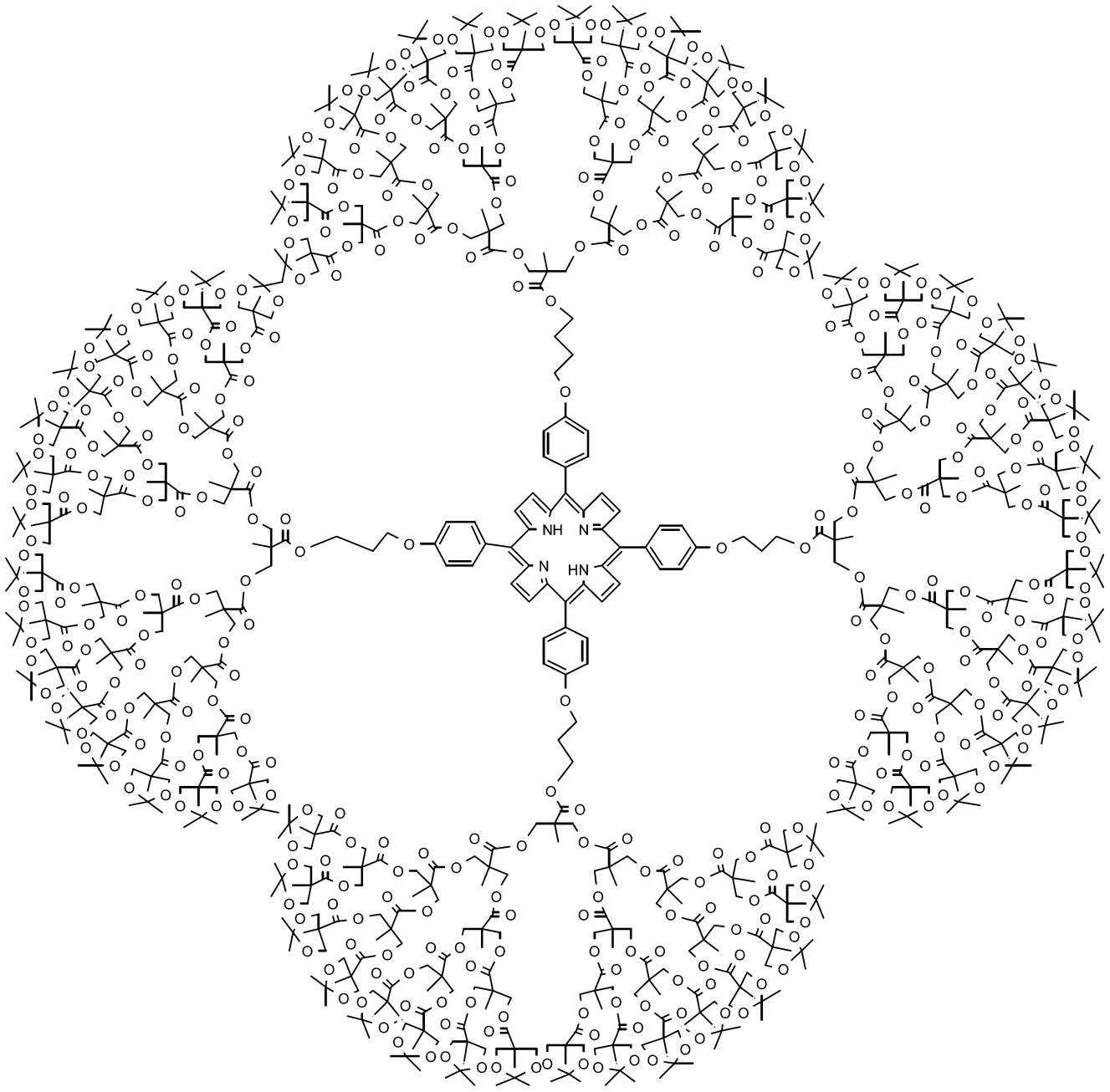

Figure 1. Fifth-generation free base porphyrin-cored dendrimer (acetonide-G5-prop-TPPH$_2$).

for the fifth-generation dendrimers a somewhat broader molecular weight distribution was observed, indicating that not all of the molecules are perfect generation five dendrimers. The reason for this is unknown but it could be imperfections from the synthesis or a result of some minor degradation. Degradation in the form of transesterification and acid-catalyzed hydrolysis will be statistically more likely to occur at higher generations. The SEC data are presented in Table 1.

The MALDI-TOF was performed with different matrixes and sometimes with the addition of metal salts. The analysis worked well for the small dendrimers (up to second generation), giving a single peak in good agreement with the theoretical values. For the third generations the peak corresponding to the theoretical molecular weight was still there but minor fragmentation was also observed. Primarily, several fragments with a mass decrease of 40 Da are observed. These

Table 1. Characterization of the Porphyrin-Cored Bis-MPA Dendrimers

compound	M_w[a] (g/mol)	M_n[b] (g/mol)	PDI[b]	θ[c] (ns)	V (Å^3)	r[d] (Å)
acetonide-G0-prop-TPPH$_2$	911	700	1.04	0.41	3400	11
acetonide-G1-prop-TPPH$_2$	1536	1100	1.03	0.57	4700	13
acetonide-G2-prop-TPPH$_2$	2625	2600	1.02	0.9	7400	15
acetonide-G3-prop-TPPH$_2$	4571	5500	1.01	1.53	12600	18
acetonide-G4-prop-TPPH$_2$	9160	9800	1.00	2.33	19200	20
acetonide-G5-prop-TPPH$_2$	17871	17100	1.07	4.16	34300	24
acetonide-G0-prop-TPPZn	974	500	1.05	0.42	3500	11
acetonide-G1-prop-TPPZn	1599	1400	1.03	0.57	4700	13
acetonide-G2-prop-TPPZn	2688	3200	1.02	0.84	6900	14
acetonide-G3-prop-TPPZn	4634	5600	1.01	1.23	10200	16
acetonide-G4-prop-TPPZn	9223	11100	1.00	1.96	16200	19
acetonide-G5-prop-TPPZn	17935	19400	1.11	3.47	28700	23

[a] Theoretical molecular weight. [b] SEC with universal calibration. [c] Rotational correlation time from polarization anisotropy decay data. [d] Radius calculated assuming spherical symmetry.

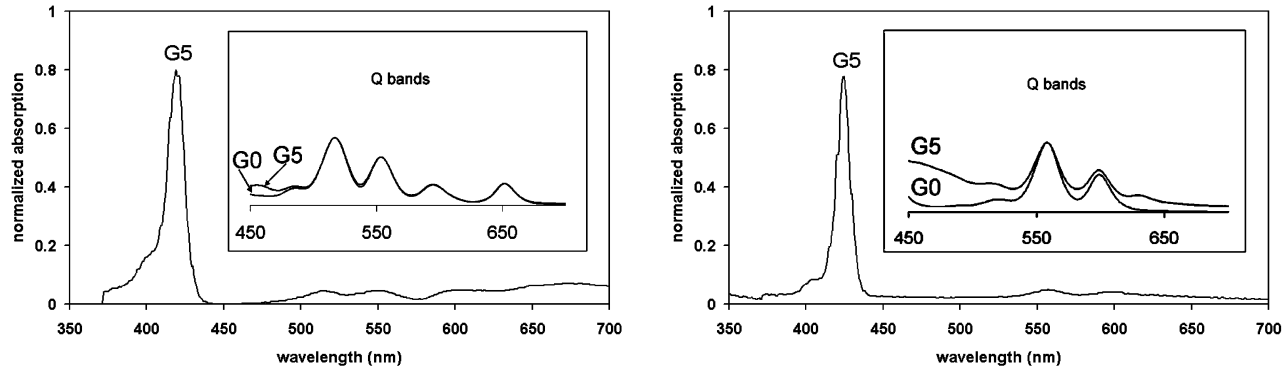

Figure 2. Absorption spectra for acetonide-G0/G5-prop-TPPH$_2$ (left) and acetonide-G0/G5-prop-TPPZn (right).

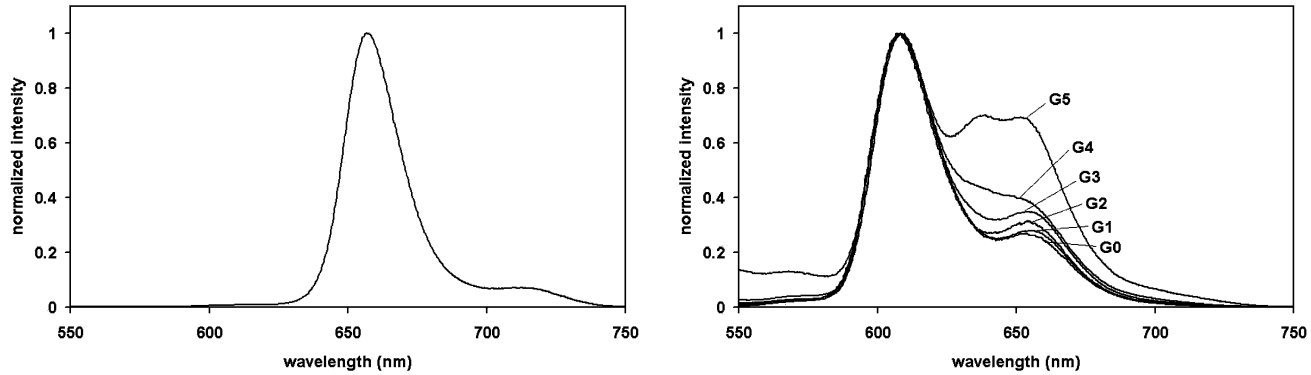

Figure 3. Emission spectra for acetonide-G3-prop-TPPH$_2$ (left) and acetonide-G*n*-prop-TPPZn ($n = 0-5$) (right).

correspond to the loss of some of the acetonide protection groups. This agrees well with earlier MALDI-TOF analyzes performed in our group on acetonide-protected bis-MPA dendrimers where sometimes the loss of acetonide groups during MALDI-TOF has been observed. Also some minor fragmentation with the mass decrease of 272 Da is observed. This is assumed to be caused by fragmentation during MALDI-TOF analyzes because not fully substituted product would have the molecular weight decrease of 156 Da (weight of acetonide-protected bis-MPA fragment), or multiples thereof. Fragmentation, and especially loss of acetonides, are likely to occur during the MALDI-TOF analysis since it is performed with acidic matrixes. For the fourth generation much more fragmentation was observed and the fifth generation showed only a broad peak with no single peaks visible. This is in good agreement with results reported by Vinogradov et al.[16] where substantial fragmentation of their higher generation glutamic dendrimers during MALDI-TOF analysis was observed.

All the spectroscopic measurements were performed in THF and the spectra for both free base and zinc porphyrin are shown in Figure 2.

The sensitivity and poor baseline calibration for the full spectra explain the differences with the insets; the latter were recorded at higher dye concentrations. The spectra show the typical absorption bands of porphyrins (Soret-band and Q-bands) and the difference in the Q-bands between free base and zinc-containing porphyrin can clearly be seen. No shift of the absorption spectra between the generations was observed. This agrees with earlier findings for tetraphenyl porphyrins (TPP)[42] where no red shift was observed. However, some differences between different generations can be observed. In the free base porphyrins, increased absorption just above 450 nm is observed for the fifth generation. This absorption is also present for the fifth-generation zinc-cored porphyrin, and here it is much more pronounced. The reason for this is unclear, but one possible explanation could be that the dendrons interact with the porphyrins or changes the conformation of the porphyrin. For example, absorption to vibrational levels giving the substructure could be modified by the heavy dendron substitution. Similar results were observed in fluorescence emission spectra (more below). Another explanation could be that the fifth-generation dendrimer is not perfect, as indicated by the SEC and MALDI-TOF measurements discussed above, leading to unsymmetrical substitution of the porphyrin. Another interesting feature of the absorption spectra for the zinc-containing porphyrins is the appearance of a shoulder at around 630 nm. This absorption is first observed for the second generation and becomes more prononced for higher generations. This may also be the result of conformational changes of the porphyrin core; however, further investigation of this absorption, and the absorption above 450 nm, is currently conducted.

The emission spectra (in THF) were obtained after excitation at 403 nm (Figure 3). The emission for the free base porphyrin shows two peaks, one strong peak at 658 nm and a weaker peak at 714 nm. There is no difference in the emission for different generations of the free base. However, for the zinc-cored porphyrins the spectra show a different behavior. The spectrum (for Acetonide-G0-prop-TPPZn) shows a strong peak at 610 nm and a smaller one around 650 nm. As can be seen in Figure 3, the emission around 650 nm increases with increasing generation and the difference is largest between the fourth and the fifth generation. The explanation for this could be interactions between the por-

phyrin and the dendrons changing the porphyrin conformation and vibrational substructure. Similar changes upon dendron substitution were observed in the absorption spectra as discussed above. Again, another reason could be contamination of free base porphyrin in the zinc porphyrin samples since the growing peek occurs in the region of the free base porphyrin. However, no free base porphyrin was detected in the NMR and UV spectra obtained for the zinc porphyrins. Preliminary lifetime decay results of the ZnG1 type showed a short decay for the 610-nm emission (ca 1.3−1.4 ns) and a longer decay for the 650-nm emission (ca. 7−8 ns). The longer decay was more prominent for the larger dendrimers, in qualitative agreement with the emission spectra. The unsubstituted porphyrin did not show any trace of the emission at 650 nm, nor any contribution from a decay of the longer lifetime.

Since the measurements have been performed in THF solutions where oxygen was present, we also considered oxygen quenching of the excited lifetimes.[53,54] Upon degassing of the sample with several freeze and thaw cycles, there was a minor change in the longer emission decay (it increased ca. 1 ns); however, there was no or very minor differences observed in the emission spectra. This is reasonable since emission decays on the nanosecond scale should be fairly insensitive to oxygen quenching. The reason for the differences between the free base and the zinc porphyrin are not fully understood and more systematic photophysical studies are currently underway.

Polarization anisotropy decay data were also obtained assuming a "spherical tumbling model" (one component). The data are presented in Table 1. From the rotational correlation time, θ, the size of the molecules can be calculated using the Stokes−Einstein−Debye relation

$$\theta = V_h \eta / kT$$

where V_h is the hydrodynamic volume of the molecule, η is the viscosity of the solvent (THF, 0.49 mPa·s),[55,56] T is the absolute temperature, and k is the Boltzmann constant.

From the calculated sizes it is seen that the hydrodynamic size increased with increasing generation as expected. It can also be seen that the zinc-containing dendrimers are slightly smaller than the corresponding free base porphyrins. This is probably due to the fact that the measuring of the rotational correlation time for the zinc-cored molecules is much more difficult since it has more components. If the size of these TPP molecules are compared to earlier results obtained by De Schryver and Fréchet et al.,[42] it can be seen that these porphyrins occupy less volume than the Fréchet-type dendrons they used in their experiments. A comparison between their third-generation dendrimer (V = 18890 Å^3) to our fourth-generation dendrimer (V = 19200 Å^3) shows that their third generation is approximately the same size as our fourth generation. The reason for this smaller hydrodynamic volume of the bis-MPA dendrimers could be many. The repeating units are smaller and they could have a more flexible structure, improving the ability to pack; they have a propyloxy-spacer unit between the porphyrin and the dendrons, leading to a more flexible structure around the porphyrin. Fréchet et al.[42] also concluded that enhanced flexibility leads to a less extended structure. It can also be a solvent effect, where the solvent swells the benzyl ether dendrons more than the bis-MPA ones.

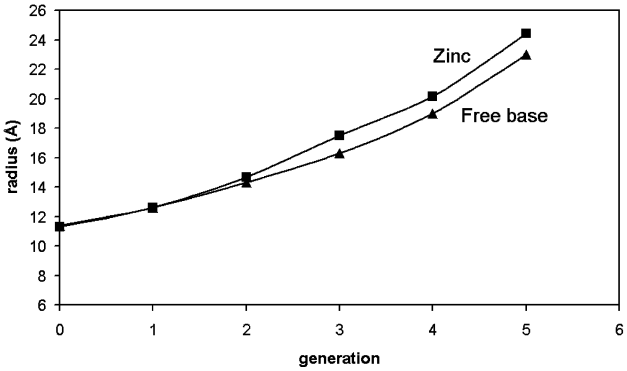

Figure 4. Hydrodynamic radius as a function of generation.

If the hydrodynamic radius (Table 1) is plotted as a function of generation, Figure 4, it can be seen that the radii increases with the generation and that no structural collapse is observed. Also Fréchet et al.[42] did not find any structural collapse for the benzyl ether $TPPH_2$ dendrimers. They observed structural collapse only for the ones with *meso*-3,5-substituted tetraarylporphyrin benzyl ether dendrimers.

As discussed above, the porphyrin-cored bis-MPA dendrimers pack closer than the Fréchet-type[42] porphyrins. The effect of this closer packing of the dendrons around the porphyrin core could be a denser shell around the porphyrin core, but it could also lead to insufficient shielding due to the fact that the more densely packed dendrons occupy less space.

Conclusions

We have shown that it is possible to build large (up to fifth generation) porphyrin bis-MPA dendrimers both with a free base core and with a zinc ion in the core. We have also shown that to achieve the large dendrons, a spacer had to be attached between the dendrons and the porphyrin to increase the hydrolytical stability. It was not possible to attach large dendrons with direct addition of dendrons through DCC coupling reactions since full substitution was not obtained. The preliminary spectroscopic measurements showed differences in both the absorption and the emission spectra between different generations, especially for the zinc-cored porphyrins. The results indicate changes in the porphyrin conformation, probably due to perturbations of vibrational levels. Comparing to Fréchet-type porphyrins (TPP), we conclude that the bis-MPA dendrimers have a lower hydronamic volume in THF. The size of the bis-MPA type dendrimers is approximately one generation smaller than the Fréchet-type dendrimers (i.e., their third generation is about the same size as our fourth generation). It could also lead to more stresses in the

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molecule, resulting in a change of the porphyrin configuration. More detailed photophysical studies are currently being performed to understand the influence of the dendrons on the porphyrin.

Experimentals

Methods. ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AM 400 using $CDCl_3$. The solvent signal was used as the internal standard. Size exclusion chromatography (SEC) was performed using a TDA Model 301 equipped with one or two GMH_{HR}-M columns with TSK-gel (Tosoh Biosep), a VE 5200 GPC Autosampler, a VE 1121 GPC Solvent pump, and a VE 5710 GPC Degasser, all of which were made by Viscotek Corp. THF (1.0 mL min^{-1}) was used as the mobile phase. The SEC apparatus was calibrated with linear polystyrenes (PS), 11 narrow standards (M_p 0.580 to 185 kg mol^{-1}), and one broad standard. Corrections for flow rate fluctuations were made by using the DRI signal of the injected THF as an internal standard. The right-angle laser light scattering (RALLS) was calibrated with linear PS standards (M_w = 90.1 kg mol^{-1}, PDI = 1.04, concentration = 1.00 mg/mL; M_w = 250 kg mol^{-1}, PDI = 2.5, concentration = 1.00 mg/mL). The columns and all detectors were thermostated to 35 °C. Viscotek Trisec 2000 version 1.0.2 software was used to process data. Absorption measurements were performed at room temperature with a WPA S2000 Lightwave UV/Vis diode-array spectrophotometer. MALDI analysis was performed using a Bruker Reflex III MALDI-MS instrument, equipped with a N_2 laser, 337 nm (Bruker Daltonik GmbH, Bremen, Germany). All mass spectra have been obtained in reflectron mode. The ion optics were optimized to give good resolution for the molecular weight region of interest. Calibration was performed to secure good mass accuracy. As for the samples, solutions of 2−5 mM in THF were prepared. The matrixes utilized were either *trans*-3-indoleacrylic acid (t3iA) or 2,5-dihydroxybenzoic acid (DHB). Matrix solutions were prepared as 0.1 M solutions in THF. The samples were prepared both as sample−matrix solutions and as sample−matrix−NaTFA− or LiTFA solutions, employing a 0.1 M of either NaTFA− or LiTFA solution in THF. The preparation protocol included mixing of 0.5−1.0 μL of sample with 10 μL of matrix and/or 0.5−1.0 μL of the cat ionization agent. Then 0.2−0.4 μL of the mixture was spotted on the MALDI target and was left to crystallize in room temperature. Normally 50 pulses were acquired for each sample. To achieve good mass accuracy and resolution, the analysis was performed at the laser threshold of each individual matrix/sample combination. The sample molecules were also analyzed with the above-stated instrumental parameters in laser desorption mode (without any matrix being present in the preparation). Continuous wave fluorescense spectra were recorded using an Hitachi F-4500 spectrometer equipped with a Xe lamp. Time-resolved measurements at selected emission wavelengths were recorded using an IBH 5000 spectrometer equipped with an emission monochromator (5000M) and the TBX-04 picosecond photon detection module. A laser diode (NanoLed 07) operating at 403 nm was used as an excitation source (ca. 100-ps width, operating at 1 MHz). The lifetime decays were measured using time-correlated single-photon counting along with the Data Station v 2.1 software for running the spectrometer and deconvolution and analysis of decays. The system also allowed variation of excitation and emission polarization, thus enabling the determination of time-resolved anisotropy decays.

Materials. The synthesis of the dendrons (acetonide-G2-CH_2−COOH) used in the direct coupling route is described elsewhere.[49] Also the synthesis of acetonide-2,2-bis(methoxy)-propanoic anhydride, which is used as a generic building block for divergent dendrimer growth, is described elsewhere.[45]

TPPZn. Prepared similar to previously reported synthesis[43] in 94% yield. ^{1}H NMR (DMSO-d_6): δ 7.38 (d, 8 H, *o*-Ar-*H*, J = 6.8 Hz), 8.19 (d, 8 H, *m*-Ar-*H*, J = 6.8 Hz), 9.09 (s, 8 H, β-pyrrole-*H*), and 10.06 (s, 4 H, Ar−O*H*). ^{13}C NMR (DMSO-d_6): δ 113.69 (*o*-Ar*C*), 120.42 (*meso*-porphyrin *C*), 131.60 (β-pyrrole *C*), 133.63 (*m*-Ar*C*), 135.44 (*p*-Ar*C*), 149.77 (α-pyrrole *C*), and 156.96 (Ar*C*−OH).

Synthesis of Acetonide-G2-TPPH$_2$ and Acetonide-G2-TPPZn: General Procedure Direct Addition Route. 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphine (100 mg, 0.147 mmol) was dissolved in a mixture of 5 mL of tetrahydrofuran (THF) and 5 mL of dichloromethane. To the solution was added acetonide-G2-CH_2−COOH (788 mg, 1.76 mmol, 12 equiv), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS)[50] (69 mg, 0.24 mmol) followed by *N,N*′-dicyclohexylcarbodiimide (363 mg, 1.74 mmol, 12 equiv). The reaction was carried out at room temperature for 48 h. The crude reaction mixture was then filtered, concentrated, and purified by medium pressure liquid chromatography (MPLC) on silica using 20/80 ethyl acetate (EtOAc)/hexane, gradually increasing to 80/20 EtOAc/hexane.

Acetonide-G2-TPPH$_2$ was prepared according to the general procedures above, yielding (48%) a purple solid. ^{1}H NMR ($CDCl_3$): δ −2.91 (s broad, 2H, N*H*), 1.25 (s, 24H, −CH_3), 1.43 (s, 24H, −O−C−CH_3), 1.45 (s, 24H, −O−C−CH_3), 1.63 (s, 12H, −CH_3), 3.72 (d, 16H, J = 16.0 Hz, second generation −CH_2−O−), 4.82 (d, 16H, J = 16.0 Hz, second generation −CH_2−O−), 4.65 (s, 16H, first generation −CH_2−O−), 7.52 (d, 8H, J = 8 Hz, −*o*-Ar-*H*), 8.23 (d, 8H, J = 8 Hz, *m*-Ar−*H*), and 8.85 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.92 (first generation *C*H_3), 18.63 (second generation *C*H_3), 21.75 (O−C−*C*H_3), 25.57 (O−C−*C*H_3), 42.28 (second generation *C*), 47.45 (first generation *C*), 66.09 (second generation *C*H_2), 98.23 (O−*C*−CH_3), 119.13 (*o*-Ar*C*), 119.78 (*meso*-porphyrin *C*), 135.32 (*m*-Ar*C*), 139.90 (*p*-Ar*C*), 150.40 (Ar*C*−O), 171.48 (first generation *C*═O), and 173.73 (second generation *C*═O).

Acetonide-G2-TPPZn was prepared according to the general procedures above, yielding (44%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.18 (s, 24H, CH_3), 1.36 (s, 24H, O−C−CH_3), 1.38 (s, 24H, O−C−CH_3), 1.59 (s, 12H, CH_3), 3.62 (d, 16H, J = 12.0 Hz, second generation −CH_2−O−), 4.19 (d, 16H, J = 12.0 Hz, second generation −CH_2−O−), 4.57 (s, 16H, first generation −CH_2−O−), 7.49 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.20 (d, 8H, J = 8.4 Hz, *m*-Ar−H), and 8.96 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.76 (first generation *C*H_3), 18.41 (second generation −*C*H_3), 21.57 (−O−C−*C*H_3), 25.37 (O−C−*C*H_3), 42.05 (second generation −*C*−), 47.25 (first generation −*C*−), 65.32 (first generation −*C*H_2−), 65.86 (second generation −*C*H_2−), 98.04 (−O−*C*−CH_3), 119.43 (*o*-Ar*C*), 119.83 (*meso*-porphyrin *C*), 131.93 (β-pyrrole *C*), 135.12 (α-pyrrole *C*), 135.19 (*m*-Ar*C*), 140.66 (*p*-Ar*C*), 150.03 (Ar*C*−O), 171.34 (first generation *C*═O), and 173.52 (second generation *C*═O).

Synthesis of Acetonide-G*n*-TPPZn (*n* = 1, 2, 3): General Procedure Anhydride Addition Exemplified by Acetonide-G1-TPPZn. 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphine (100 mg, 0.147 mmol) and 4-(dimethylamino)pyridine DMAP, (20 mg, 0.13 mmol) were dissolved in 5 mL of pyridine. Acetonide-2,2-bis(methoxy)propanoic anhydride (0.29 g, 0.88 mmol, 6 equic) was dissolved in approximately 3 mL of dichloromethane and then added to the solution. The reaction was monitored by ^{13}C NMR. Full substitution was achieved when the peak at around 49 ppm (corresponding to the quaternary carbon) disappeared while maintaining the peak at 169 ppm to ascertain an excess of anhydride. The residual anhydride was quenched by reaction with approximately 2 mL of water under rigorous stirring for a couple of hours. The reaction mixture was then taken up into approximately 150 mL of dichloromethane and extracted three times with 50 mL of $NaHSO_4$, three times with 50 mL of $NaHCO_3$, and finally one time with 50 mL of brine. The organic layer was dried with $MgSO_4$, the solvent was evaporated, and the crude product was purified by MPLC.

Synthesis of HO-G*n*-TPPZn (*n* = 1, 2): General Deprotection Procedure. The acetonide functional porphyrin (acetonide-G*n*-TPPZn**)** was deprotected in approximately 15 mL of MeOH:THF with DOWEX-50-X2 resin at 50 °C as described previously.[49] The reaction was easily monitored by TLC. The reaction time varied from 3 days to 2 weeks. The DOWEX-50-X2 resin was filtered off and the solvents were evaporated. The crude product was dissolved in THF, precipitated into cold diethyl ether, filtered, and dried. The yields are very low and the samples impure, which is why no NMR spectra are

available. Instead, the crude product was used directly in the coupling reactions.

Acetonide-G1-TPPZn. MPLC was performed by eluting with hexane and increasing the polarity to 40/60 EtOAc/Hex, yielding (94%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 12H, $-CH_3$), 1.38 (s, 12H, $-O-C-CH_3$), 1.41 (s, 12H, $-O-C-CH_3$), 3.70 (d, 8H, J = 12.0 Hz, $-CH_2-O-$), 4.33 (d, 8H, J = 12.0 Hz, $-CH_2-O-$), 7.50 (d, 8H, J = 8 Hz, *o*-Ar$-H$), 8.26 (d, 8H, J = 8 Hz, *m*-Ar$-H$), and 9.02 (s, 8H, β-pyrrole$-H$). ^{13}C NMR ($CDCl_3$): δ 18.48 ($-CH_3$), 22.07 ($-O-C-CH_3$), 24.87 ($-O-C-CH_3$), 42.35 ($-C-$), 65.93 ($-CH_2-$), 98.18 ($-O-C-CH_3$), 119.56 (*o*-Ar*C*), 120.05 (*meso*-porphyrin *C*), 132.05 (β-pyrrole *C*), 135.12 (α-pyrrole *C*), 135.19 (*m*-Ar*C*), 140.44 (*p*-Ar*C*), 150.18 (Ar*C*$-$O), and 173.03 (*C*=O).

Acetonide-G2-TPPZn. MPLC was performed by eluting with hexane and increasing the polarity to 40/60 EtOAc/Hex, yielding (38%) a purple solid. See above for spectral data.

Acetonide-G3-TPPZn. MPLC was performed by eluting with hexane and increasing the polarity to 40/60 EtOAc/Hex, yielding (9%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.16 (s, 48H, $-CH_3$), 1.24 (s, 24H, $-CH_3$), 1.33 (s, 48H, $-O-C-CH_3$), 1.40 (s, 48H, $-O-C-CH_3$), 1.60 (s, 12H, $-CH_3$), 3.62 (d, 32H, J = 12.0 Hz, third generation $-CH_2-O-$), 4.16 (d, 32H, J = 12.0 Hz, third generation $-CH_2-O-$), 4.44 (s, 32H, second generation $-CH_2-O-$), 4.58 (s, 16H, first generation $-CH_2-O-$), 7.47 (d, 8H, J = 8 Hz, *o*-Ar$-H$), 8.22 (d, 8H, J = 8 Hz, *m*-Ar$-H$), and 8.94 (s, 8H, β-pyrrole$-H$). ^{13}C NMR ($CDCl_3$): δ 17.79 (second generation $-CH_3$), 17.85 (first generation $-CH_3$), 18.48 (third generation $-CH_3$), 21.86 ($-O-C-CH_3$), 25.35 ($-O-C-CH_3$), 42.06 (first generation $-C-$), 42.11 (second generation $-C-$), 46.98 (third generation $-C-$), 65.00 (first generation $-CH_2$), 65.07 (second generation $-CH_2-$), 65.92 (third generation $-CH_2-$), 98.09 ($-O-C-CH_3$), 119.16 (*o*-Ar*C*), 119.46 (*meso*-porphyrin *C*), 132.87 (β-pyrrole *C*), 135.32 (α-pyrrole *C*), 135.34 (*m*-Ar*C*), 140.42 (*p*-Ar*C*), 150.11 (Ar*C*$-$O), 171.05 (first generation *C*=O), 172.00 (second generation *C*=O), and 173.52 (third generation *C*=O).

HO-prop-TPPH$_2$. 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphine (177 mg, 0.261 mmol), K_2CO_3 (453 mg, 3.13 mmol, 12 equiv), and 18-crown-6 (10 mg) were added to 30 mL of dimethylformamide (DMF). 1,3-Bromopropanol (291 mg, 2.09 mmol, 8 equiv) was added and the reaction was vigorously stirred under reflux overnight followed by TLC. The DMF was evaporated and the c reaction mixture was dissolved in 200 mL of THF and extracted three times with water (100 mL) with the addition of brine to obtain phase separation. The solvents were evaporated, and the crude product was dissolved in a small amount of THF, precipitated in cold diethyl ether, filtered, and dried to yield (80%) a purple solid. ^{1}H NMR (DMSO-d_6): δ $-$2.82 (s broad, 2H, N*H*), 2.06 (m, 8H, J = 6.4 Hz, $-CH_2-CH_2-CH_2-$), 3.72 (t, 8H, J = 5.8 Hz, $-CH_2-OH$), 4.35 (t, 8H, J = 5.8 Hz, $-O-CH_2-CH_2$), 4.68 (s, 4H, $-OH$), 7.37 (d, 8H, J = 8.6 Hz, *o*-Ar$-H$), 8.11 (d, 8H, J = 8.6 Hz, *m*-Ar$-H$), and 8.86 (s, 8H, β-pyrrole$-H$). ^{13}C NMR: δ 31.62 ($-CH_2-CH_2-CH_2-$), 54.01 ($-CH_2-OH$), 56.87 ($-O-CH_2-CH_2$), 112.00 (*o*-Ar*C*), 119.52 (*meso*-porphyrin *C*), 134.60 (β-pyrrole *C*), 135.41 (*m*-Ar*C*), 135.47 (*p*-Ar*C*, and 158.40 (Ar*C*$-$O).

HO-prop-TPPZn. HO-prop-TPPZn was prepared in the same way as HO-prop-TPPH$_2$. ^{1}H NMR (DMSO-d_6): δ 2.05 (m, 8H, J = 5.6 Hz, $-CH_2-CH_2-CH_2-$), 3.73 (t, 8H, J = 5.8 Hz, $-CH_2-OH$), 4.28 (t, 8H, J = 5.6 Hz, $-O-CH_2-CH_2$), 4.70 (s, 4H, $-OH$), 7.28 (d, 8H, J = 7.4 Hz, *o*-Ar$-H$), 8.04 (d, 8H, J = 7.4 Hz, *m*-Ar$-H$), and 8.81 (s, 8H, β-pyrrole$-H$). ^{13}C NMR: δ 31.87 ($-CH_2-CH_2-CH_2-$), 54.23 ($-CH_2-OH$), 56.98 ($-O-CH_2-CH_2$), 112.00 (*o*-Ar*C*), 119.47 (*meso*-porphyrin *C*), 131.96 (β-pyrrole *C*), 134.38 (*m*-Ar*C*), 134.67 (*p*-Ar*C*), 149.09 (α-pyrrole *C*), and 157.70 (Ar*C*$-$O).

Synthesis of Acetonide-G*n*-prop-TPPH$_2$ (*n* = 1, 2, 3, 4, 5) and Acetonide-G*n*-prop-TPPZn (*n* = 1, 2, 3): General Procedure Anhydride Addition. The anhydride addition follows the same procedure as described above for the addition directly to the porphyrin without spacer using 2 equiv of anhydride per hydroxyl group.

Synthesis of HO-G*n*-prop-TPPH$_2$ (*n* = 1, 2, 3, 4,) and HO-G*n*-prop-TPPZn (*n* = 1, 2): General Deprotection Procedure Exemplified with HO-G1-prop-TPPZn. The reaction is carried out according to previously reported procedures[52] where HO-G1-prop-TPPZn (0.63 g, 0,39 mmol) was dissolved in 50 mL of THF. H_2SO_4 (16 mL, 1 mL per 0.1 mmol of acetonide groups) was added and the reaction was monitored by TLC. The reaction was stopped by the addition of 16 mL of ammonium in ethanol (50/50), extracted three times with brine, and dried with magnesium sulfate, and the solvents were evaporated.

Acetonide-G1-prop-TPPZn. MPLC was performed by eluting with 20/80 EtOAc/Hex and increasing the polarity to 60/40 EtOAc/Hex, yielding (54%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 12H, $-CH_3$), 1.38 (s, 12H, $-O-C-CH_3$), 1.39 (s, 12H, $-O-C-CH_3$), 2.13 (m, 8H, J = 6.0 Hz, $-CH_2-CH_2-CH_2-$) 3.63 (d, 8H, J = 12.0 Hz, $-C-CH_2-O-$), 4.20 (d, 8H, J = 12.0 Hz, $-C-CH_2-O-$), 4.33 (t, 8H, J = 6.0 Hz, $-CH_2-CH_2-O-$), 4.48 (t, 8H, J = 6.4 Hz, $-O-CH_2-CH_2-$), 7.26 (d, 8H, J = 8.4 Hz, *o*-Ar$-H$), 8.12 (d, 8H, J = 8.4 Hz, *m*-Ar$-H$), and 8.98 (s, 8H, β-pyrrole$-H$). ^{13}C NMR ($CDCl_3$): δ 18.77 (CH_3), 22.57 ($-O-C-CH_3$), 24.96 ($-O-C-CH_3$), 29.01 ($-CH_2-CH_2-CH_2-$), 42.05 ($-C-$), 61.96 ($-CH_2-CH_2-O-$), 64.66 ($-O-CH_2-CH_2-$) 66.17 ($-C-CH_2-O$), 98.21 ($-O-C-CH_3$), 112.73 (*o*-Ar*C*), 120.82 (*meso*-porphyrin *C*), 131.98 (β-pyrrole *C*), 135.52 (*m*-Ar*C*), 135.67 (*p*-Ar*C*), 150.60 (α-pyrrole *C*) 158.55 (Ar*C*$-$O), and 174.38 (*C*=O).

HO-G1-prop-TPPZn. HO-G1-prop-TPPZn yielded (82%) a purple solid. ^{1}H NMR (DMSO-d_6): δ 1.16 (s, 12H, $-CH_3$), 2.22 (m, 8H, J = 6.0 Hz, $-CH_2-CH_2-CH_2-$) 3.54 (d, 8H, J = 10.0 Hz, $C-CH_2-O-$), 3.60 (d, 8H, J = 10.0 Hz, $-CH_2-OH$), 4.32 (t, 8H, J = 6.0 Hz, $-CH_2-CH_2-O-$), 4.35 (t, 8H, J = 6.4 Hz, $-O-CH_2-CH_2$), 4.78 (s, 8H, $-OH$), 7.32 (d, 8H, J = 8.4 Hz, *o*-Ar$-H$), 8.07 (d, 8H, J = 8.4 Hz, *m*-Ar$-H$), and 8.82 (s, 8H, β-pyrrole$-H$). ^{13}C NMR (DMSO-d_6): δ 16.94 (CH_3), 28.41 ($-CH_2-CH_2-CH_2-$), 50.34 ($-C-$), 60.76 ($-CH_2-CH_2-O-$), 63.93 ($-O-CH_2-CH_2$), 66.98 ($-C-CH_2-OH$), 112.52 (*o*-Ar*C*), 119.90 (*meso*-porphyrin *C*), 131.47 (β-pyrrole *C*), 135.15 (*m*-Ar*C*), 135.17 (*p*-Ar*C*), 149.55 (α-pyrrole *C*) 157.96 (Ar*C*$-$O), and 174.80 (*C*=O).

Acetonide-G2-prop-TPPZn. MPLC was performed by eluting with 20/80 EtOAc/Hex and increasing the polarity to 60/40 EtOAc/Hex, yielding (64%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.16 (s, 24H, $-CH_3$), 1.36 (s, 24H, $O-C-CH_3$, and 12H, $-CH_3$), 1.39 (s, 24H, $O-C-CH_3$), 2.31 (m, 8H, J = 6.0 Hz, $-CH_2-CH_2-CH_2-$), 3.62 (d, 16H, J = 12.0 Hz, second generation $-C-CH_2-O-$), 4.16 (d, 16H, J = 12.0 Hz, second generation $-C-CH_2-O-$), 4.33 (t, 8H, J = 6.8 Hz, $-CH_2-CH_2-O-$) 4.39 (s, 16H, first generation $-CH_2-O-$), 4.48 (t, 8H, J = 6.8 Hz, $-O-CH_2-CH_2-$), 7.27 (d, 8H, J = 8.4 Hz, *o*-Ar$-H$), 8.13 (d, 8H, J = 8.4 Hz, *m*-Ar$-H$), and 8.97 (s, 8H, β-pyrrole$-H$). ^{13}C NMR ($CDCl_3$): δ 17.90 (first generation $-CH_3$), 18.63 (second generation $-CH_3$), 22.06 ($-O-C-CH_3$), 25.34 ($O-C-CH_3$), 28.93 ($-CH_2-CH_2-CH_2-$), 42.17 (second generation $-C-$), 46.96 (first generation $-C-$), 62.53 ($-CH_2-CH_2-O-$), 64.54 ($-O-CH_2-CH_2-$), 65.99 (first generation $C-CH_2-O-$), 66.08 (second generation $-CH_2-OH$), 98.20 ($-O-C-CH_3$), 112.64 (*o*-Ar*C*), 120.74 (*meso*-porphyrin *C*), 131.97 (β-pyrrole *C*), 135.48 (*m*-Ar*C*), 135.53 (*p*-Ar*C*), 150.60 (α-pyrrole *C*), 158.42 (Ar*C*$-$O), 172.73 (first generation *C*=O), and 173.66 (second generation *C*=O).

HO-G2-prop-TPPZn. HO-G2-prop-TPPZn yielded (76%) a purple solid. ^{1}H NMR (DMSO-d_6): δ 1.14 (s, 24H, $-CH_3$), 1.34 (s, 12H, $-CH_3$), 2.29 (broad s, 8H, $-CH_2-CH_2-CH_2-$), 3.45$-$3.70 (broad m, 32H, second generation $-CH_2-OH$), 3.82 (t, 8H, J = 6.2 Hz, $-O-CH_2-CH_2-$), 4.33 (broad m, 16H, first generation $-CH_2-O-$), 4.44 (s, 8H, $-CH_2-CH_2-OH$), 4.74 (s (16 H, $-OH$), 7.35 (d, 8H, J = 8.0 Hz, *o*-Ar$-H$), 8.11 (d, 8H, J = 8.0 Hz, *m*-Ar$-H$), and 8.88 (s, 8H, β-pyrrole$-H$). ^{13}C NMR (DMSO-d_6): δ, 16.87 (second generation $-CH_3$), 17.39 (first generation CH_3), 28.94 ($-CH_2-CH_2-CH_2-$), 46.47 (first generation $-C-$), 50.46 (second generation $-C-$), 63.91 ($-CH_2-CH_2-O-$), 65.11 ($-O-CH_2-CH_2-$), 66.68 (first generation $-C-CH_2-O-$), 67.06 (second generation $-CH_2-OH$), 112.48 (*o*-Ar*C*), 119.78 (*meso*-porphyrin *C*), 131.46 (β-pyrrole *C*),

135.18 (*m*-Ar*C*), 135.21 (*p*-Ar*C*), 149.69 (α-pyrrole *C*), 158.05 (Ar*C*−O), 172.69 (first generation *C*═O), and 174.26 (second generation *C*═O).

Acetonide-G3-prop-TPPZn. MPLC was performed by eluting with 30/70 EtOAc/Hex and increasing the polarity to 70/30 EtOAc/Hex, yielding (37%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.15 (s, 48H, −CH_3), 1.15−1.40 (broad m, 12H, first generation −CH_3, 24H, second generation −CH_3, and 96H, −O−C−CH_3,), 2.35 (m, 8H, J = 6.0 Hz, −CH$_2$−CH_2−CH$_2$−), 3.61 (d, 32H, J = 12.0 Hz, third generation −CH$_2$−O−), 4.15 (d, 32H, J = 12.0 Hz, third generation −CH$_2$−O−), 4.25−4.45 (broad m, 32H, second generation −CH$_2$−O−, 16H, first generation −CH$_2$−O−, and 8H, −CH$_2$−CH_2−O−), 4.48 (t, 8H, J = 6.8 Hz, −O−CH_2−CH$_2$−), 7.28 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.11 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.96 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.77 (second generation −*C*H$_3$), 17.45 (first generation −*C*H$_3$), 18.60 (third generation −*C*H$_3$), 22.12 (−O−C−*C*H$_3$), 25.22 (−O−C−*C*H$_3$), 28.93 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.14 (third generation −*C*−), 46.84 (second generation −*C*−), 47.00 (first generation −*C*−), 62.96 (−CH$_2$−*C*H$_2$−O−), 64.60 (−O−*C*H$_2$−CH$_2$−), 64.64 (first generation −*C*H$_2$), 65.98 (second generation −*C*H$_2$−), 66.14 (third generation −*C*H$_2$−), 98.18 (−O−*C*−CH$_3$), 112.74 (*o*-Ar*C*), 120.74 (*meso*-porphyrin *C*), 131.96 (β-pyrrole *C*), 135.58 (*m*-Ar*C*), 135.62 (*p*-Ar*C*), 150.53 (α-pyrrole *C*), 158.44 (Ar*C*−O), 171.95 (second generation *C*═O), 172.25 (first generation *C*═O), and 173.60 (third generation *C*═O).

Acetonide-G1-prop-TPPH$_2$. MPLC was performed by eluting with 30/70 EtOAc/Hex and increasing the polarity to 60/40 EtOAc/Hex, yielding (63%) a purple solid. ^{1}H NMR ($CDCl_3$): δ −2.71 (s broad, 2H, N*H*), 1.28 (s, 12H, −CH_3), 1.46 (s, 12H, −O−C−CH_3), 1.48 (s, 12H, −O−C−CH_3), 2.36 (m, 8H, J = 6.0 Hz, −CH$_2$−CH_2−CH$_2$−) 3.73 (d, 8H, J = 12.0 Hz, −C−CH_2−O−), 4.33 (d, 8H, J = 12.0 Hz, −C−CH$_2$−O−), 4.37 (t, 8H, J = 6.0 Hz, −CH$_2$−CH_2−O−), 4.55 (t, 8H, J = 6.0 Hz, −O−CH_2−CH$_2$−), 7.28 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.13 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.88 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 18.51 (*C*H$_3$), 22.23 (−O−C−*C*H$_3$), 24.84 (−O−C−*C*H$_3$), 28.70 (−CH$_2$−*C*H$_2$−CH$_2$−), 41.83 (−*C*−), 61.67 (−CH$_2$−*C*H$_2$−O−), 64.36 (−O−*C*H$_2$−CH$_2$−), 65.96 (−C−*C*H$_2$−O), 97.95 (−O−*C*−CH$_3$), 112.55 (*o*-Ar*C*), 119.53 (*meso*-porphyrin *C*), 134.60 (β-pyrrole *C*), 135.41 (*m*-Ar*C*), 135.65 (*p*-Ar*C*,), 158.42 (Ar*C*−O), and 174.13 (*C*═O).

HO-G1-prop-TPPH$_2$. HO-G1-prop-TPPH$_2$ yielded (84%) a purple solid. ^{1}H NMR (DMSO-d_6): δ −2.88 (s broad, 2H, N*H*), 1.14 (s, 12H, −CH_3), 2.22 (m, 8H, J = 6.4 Hz, −CH$_2$−CH_2−CH$_2$−), 3.51 (d, 8H, J = 10.0 Hz, C−CH_2−O−), 3.61 (d, 8H, J = 10.0 Hz, −CH_2−OH), 4.32 (t, 8H, J = 6.0 Hz, −CH$_2$−CH_2−O−), 4.35 (t, 8H, J = 6.4 Hz, −O−CH_2−CH$_2$), 4.75 (s, 8H, −O*H*), 7.36 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.10 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.86 (s, 8H, β-pyrrole−*H*). ^{13}C NMR (DMSO-d_6): δ 16.87 (*C*H$_3$), 30.18 (−CH$_2$−*C*H$_2$−CH$_2$−), 50.28 (−*C*−), 61.96 (−CH$_2$−*C*H$_2$−O−), 63.95 (−O−*C*H$_2$−CH$_2$), 66.12 (−C−*C*H$_2$−OH), 112.87 (*o*-Ar*C*), 119.58 (*meso*-porphyrin *C*), 134.78 (β-pyrrole *C*), 135.12 (*m*-Ar*C*), 135.95 (*p*-Ar*C*), 159.75 (Ar*C*−O), and 174.72 (*C*═O).

Acetonide-G2-prop-TPPH$_2$. MPLC was performed by eluting with 40/60 EtOAc/Hex and increasing the polarity to 70/30 EtOAc/Hex, yielding (57%) a purple solid. ^{1}H NMR ($CDCl_3$): δ −2.51 (s broad, 2H, N*H*), 1.19 (s, 24H, CH_3), 1.42 (s, 24H, O−C−CH_3, and 12H, CH_3), 1.44 (s, 24H, O−C−CH_3), 2.31 (m, 8H, J = 6.0 Hz, −CH$_2$−CH_2−CH$_2$−), 3.67 (d, 16H, J = 12.0 Hz, second generation −C−CH_2−O−), 4.26 (m, 16H, second generation −C−CH_2−O, and 8H, −CH$_2$−CH_2−O−), 4.47 (s, 16H, first generation −*C*H$_2$−O−), 4.51 (t, 8H, J = 6.0 Hz, −O−CH_2−CH$_2$−), 7.27 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.16 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.94 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.78 (first generation *C*H$_3$), 18.41 (second generation −*C*H$_3$), 21.88 (−O−C−*C*H$_3$), 25.32 (O−C−*C*H$_3$), 28.70 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.04 (second generation −*C*−), 46.84 (first generation −*C*−), 62.32 (−CH$_2$−*C*H$_2$−O−), 64.38 (−O−*C*H$_2$−CH$_2$−), 65.29 (first generation C−*C*H$_2$−O−), 65.95 (second generation −*C*H$_2$−OH), 98.03 (−O−*C*−CH$_3$), 112.68 (*o*-Ar*C*), 119.71 (*meso*-porphyrin *C*), 134.64 (β-pyrrole *C*), 135.47 (*m*-Ar*C*), 135.55 (*p*-Ar*C*), 158.48 (Ar*C*−O), 172.56 (first generation *C*═O), and 173.49 (second generation *C*═O).

HO-G2-prop-TPPH$_2$. HO-G2-prop-TPPH$_2$ yielded (78%) a purple solid. ^{1}H NMR (DMSO-d_6): δ −2.88 (s broad, 2H, N*H*), 1.19 (s, 24H, CH_3), 1.28 (s, 12H, −CH_3), 2.27 (broad s, 8H, −CH$_2$−CH_2−CH$_2$−), 3.45−3.70 (broad m, 32H, second generation −CH_2−OH), 3.59 (t, 8H, J = 6.0 Hz, −O−CH_2−CH$_2$−), 4.35 (broad m, 16H, first generation −CH$_2$−O−), 4.42 (s, 8H, −CH$_2$−CH_2−OH), 4.70 (s, 16H, −O*H*), 7.39 (d, 8H, J = 8.0 Hz, *o*-Ar−*H*), 8.12 (d, 8H, J = 8.0 Hz, *m*-Ar−*H*), and 8.88 (s, 8H, β-pyrrole-*H*). ^{13}C NMR (DMSO-d_6): δ, 16.71 (second generation −*C*H$_3$), 16.93 (second generation −*C*H$_3$), 17.22 (first generation *C*H$_3$), 28.80 (−CH$_2$−*C*H$_2$−CH$_2$−), 46.32 (first generation −*C*−), 50.29 (second generation −*C*−), 63.70 (−CH$_2$−*C*H$_2$−O−), 64.97 (−O−*C*H$_2$−CH$_2$−), 66.53 (first generation −C−*C*H$_2$−O−), 66.92 (second generation −*C*H$_2$−OH), 112.87 (*o*-Ar*C*), 119.60 (*meso*-porphyrin *C*), 133.92 (β-pyrrole *C*), 135.28 (*m*-Ar*C*), 135.32 (*p*-Ar*C*), 158.32, (Ar*C*−O), 172.51 (first generation *C*═O), and 174.09 (second generation *C*═O).

Acetonide-G3-prop-TPPH$_2$. MPLC was performed by eluting with 50/50 EtOAc/Hex and increasing the polarity to 80/20 EtOAc/Hex, yielding (74%) a purple solid. ^{1}H NMR ($CDCl_3$): δ −2.74 (s broad, 2H, N*H*), 1.15 (s, 48H, −CH_3), 1.15−1.40 (broad m, 12H, first generation −CH_3, 24H, second generation −CH_3, and 96H, −O−C−CH_3,), 2.36 (m, 8H, J = 6.0 Hz, −CH$_2$−CH_2−CH$_2$−), 3.64 (d, 32H, J = 12.0 Hz, third generation −CH$_2$−O−), 4.16 (d, 32H, J = 12.0 Hz, third generation −CH$_2$−O−), 4.25−4.45 (broad m, 32H, second generation −CH$_2$−O−, 16H, first generation −CH$_2$−O−, and 8H, −CH$_2$−CH_2−O−), 4.54 (t, 8H, J = 6.8 Hz, −O−CH_2−CH$_2$−), 7.29 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.13 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.87 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 18.13 (second generation −*C*H$_3$), 18.21 (first generation −*C*H$_3$), 18.90 (third generation −*C*H$_3$), 22.38 (−O−C−*C*H$_3$), 25.63 (−O−C−*C*H$_3$), 29.25 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.51 (third generation −*C*−), 47.12 (second generation −*C*−), 47.30 (first generation −*C*−), 63.24 (−CH$_2$−*C*H$_2$−O−), 64.95 (−O−*C*H$_2$−CH$_2$−), 65.35 (first generation −*C*H$_2$), 66.31 (second generation −*C*H$_2$−), 66.36 (third generation −*C*H$_2$−), 98.47 (−O−*C*−CH$_3$), 112.98 (*o*-Ar*C*), 119.56 (*meso*-porphyrin *C*), 133.97 (β-pyrrole *C*), 135.02 (*m*-Ar*C*), 135.17 (*p*-Ar*C*), 158.98, (Ar*C*−O), 171.87 (second generation *C*═O), 172.23 (first generation *C*═O), and 174.05 (third generation *C*═O).

HO-G3-prop-TPPH$_2$. HO-G3-prop-TPPH$_2$ yielded (74%) a purple solid. ^{1}H NMR (DMSO-d_6): δ −2.77 (s broad, 2H, N*H*), 1.04 (s, 48H, −CH_3) 1.23 (s, 24H, CH_3), 1.30 (s, 12H, −CH_3), 2.28 (broad m, 8H, −CH$_2$−CH_2−CH$_2$−), 3.40−3.60 (broad m, 64H, third generation −CH_2−OH), 3.59 (t, 8H, J = 6.0 Hz, −O−CH_2−CH$_2$−), 4.05−4.50 (broad m, 16H, first generation −CH$_2$−O−, 32H, second generation −CH$_2$−O−, and 8H, −CH$_2$−CH_2−OH), 4.66 (s (32H, −O*H*), 7.39 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.12 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.88 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ((DMSO-d_6): δ 18.12 (second generation −*C*H$_3$), 18.16 (first generation −*C*H$_3$), 18.70 (third generation −*C*H$_3$), 28.83 (−CH$_2$−*C*H$_2$−CH$_2$−), 46.35 (second generation −*C*−), 46.56 (first generation −*C*−), 50.25 (third generation −*C*−), 63.64 (−CH$_2$−*C*H$_2$−O−), 64.07 (−O−*C*H$_2$−CH$_2$−), 65.34 (first generation −*C*H$_2$), 66.56 (second generation −*C*H$_2$−), 66.96 (third generation −*C*H$_2$−), 113.08 (*o*-Ar*C*), 120.07 (*meso*-porphyrin *C*), 133.91 (β-pyrrole *C*), 134.15 (*m*-Ar*C*), 135.22 (*p*-Ar*C*), 158.90, (Ar*C*−O), 172.29 (second generation *C*═O), 172.54 (first generation *C*═O), and 173.89 (third generation *C*═O).

Acetonide-G4-prop-TPPH$_2$. MPLC was performed by eluting with 60/40 EtOAc/Hex and increasing the polarity to 80/20 EtOAc/Hex, yielding (74%) a purple solid. ^{1}H NMR ($CDCl_3$): δ −2.82 (s broad, 2H, N*H*), 1.12 (s, 96H, −CH_3), 1.20−1.45 (broad m, 12H, first generation −CH_3, 24H, second generation −CH_3, 48H, third generation −CH_3, and 192H, −O−C−CH_3), 2.35 (m, 8H, J = 6.0 Hz, −CH$_2$−CH_2−CH$_2$−), 3.61 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.15 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.25−4.45 (broad m, 64H, third generation −CH$_2$−O−, 32H, second generation −CH$_2$−O−, 16H, first generation −CH$_2$−O−, and 8H, −CH$_2$−CH_2−O−), 4.51 (t, 8H, J = 6.0 Hz, −O−CH_2−CH$_2$−

), 7.28 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.10 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.84 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.42 (first generation −*C*H$_3$), 17.62 (second generation −*C*H$_3$), 17.74 (third generation −*C*H$_3$), 18.54 (fourth generation −*C*H$_3$), 22.08 (−O−C−*C*H$_3$), 25.25 (−O−C−*C*H$_3$), 28.94 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.08 (fourth generation −*C*−), 46.77 (third generation −*C*−), 46.81 (second generation −*C*−), 46.95 (first generation −*C*−), 62−98 (−CH$_2$−*C*H$_2$−O−), 64.32 (−O−*C*H$_2$−CH$_2$−) 64.89 (first generation −*C*H$_2$), 65.05 (second generation −*C*H$_2$−), 66.95 (third generation −*C*H$_2$−), 65.99 (fourth generation −*C*H$_2$−), 98.11 (−O−*C*−CH$_3$), 112.77 (*o*-Ar*C*), 119.72 (*meso*-porphyrin *C*), 134.87 (β-pyrrole *C*), 134.67 (*m*-Ar*C*), 135.79 (*p*-Ar*C*), 158.90 (Ar*C*−O), 1721.52 (second generation *C*═O), 171.89 (third generation *C*═O), 172.01 (first generation *C*═O), and 173.59 (fourth generation *C*═O).

HO-G4-prop-TPPH$_2$. HO-G4-prop-TPPH$_2$ yielded (71%) a purple solid. ^{1}H NMR (DMSO-d_6): δ −2.74 (s broad, 2H, N*H*), 1.02 (s, 96H, −C*H*$_3$), 1.17 (s, 48H, −C*H*$_3$), 1.23 (s, 24H, C*H*$_3$), 1.24 (s, 12H, −C*H*$_3$), 2.16 (broad m, 8H, −CH$_2$−C*H*$_2$−CH$_2$−), 3.40−3.60 (broad m, 128H, fourth generation −C*H*$_2$−OH), 3.59 (broad s, 8H, −O−C*H*$_2$−CH$_2$−), 4.05−4.50 (broad m, 16H, first generation −CH$_2$−O−, 32H, second generation −CH$_2$−O−, 64H, third generation −CH$_2$−O−, and 8H, −CH$_2$−C*H*$_2$−OH), 4.62 (s (64 H, −O*H*), 7.39 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.12 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.88 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ((DMSO-d_6): δ 17.70 (second generation −*C*H$_3$), 17.72 (third generation −*C*H$_3$), 17.82 (first generation −*C*H$_3$), 19.17 (fourth generation −*C*H$_3$), 29.45 (−CH$_2$−*C*H$_2$−CH$_2$−), 46.91 (second generation −*C*−), 46.93 (third generation −*C*−), 46.99 (first generation −*C*−), 50.83 (fourth generation −*C*−), 64.21 (−CH$_2$−*C*H$_2$−O−), 64.71 (−O−*C*H$_2$−CH$_2$−) 65.01 (first generation −*C*H$_2$), 67.09 (second generation −*C*H$_2$−), 67.19 (third generation −*C*H$_2$−), 68.48 (fourth generation −*C*H$_2$−), 113.06 (*o*-Ar*C*), 120.12 (*meso*-porphyrin *C*), 134.15 (β-pyrrole *C*), 134.79 (*m*-Ar*C*), 135.12 (*p*-Ar*C*), 158.95, (Ar*C*−O), 172.41 (second generation *C*═O), 172.47 (third generation *C*═O), 172.58 (first generation *C*═O), and 174.28 (fourth generation *C*═O).

Acetonide-G5-prop-TPPH$_2$. MPLC was performed by eluting with 60/40 EtOAc/Hex and increasing the polarity to 80/20 EtOAc/Hex, yielding (73%) a purple solid. ^{1}H NMR ($CDCl_3$): δ −2.85 (s broad, 2H, N*H*), 1.04 (s, 192H, −C*H*$_3$), 1.15−1.40 (broad m, 12H, first generation −C*H*$_3$, 24H, second generation −C*H*$_3$, 48H, fourth generation −C*H*$_3$, 96H, third generation −C*H*$_3$, and 384H, −O−C−C*H*$_3$), 2.24 (broad m, 8H, −CH$_2$−C*H*$_2$−CH$_2$−), 3.54 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.03 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.20−4.45 (broad m, 128H fourth generation −CH$_2$−O−, 64H, third generation −CH$_2$−O−, 32H, second generation −CH$_2$−O−, 16H, first generation −CH$_2$−O−, and 8H, −CH$_2$−C*H*$_2$−O−), 4.52 (broad s, 8H, −O−C*H*$_2$−CH$_2$−), 7.19 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.10 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.92 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.51 (first generation −*C*H$_3$), 17.74 (second generation −*C*H$_3$), 18.51 (third generation −*C*H$_3$), 18.63 (fourth generation −*C*H$_3$), 18.65 (fifth generation −*C*H$_3$), 22.02 (−O−C−*C*H$_3$), 25.28 (−O−C−*C*H$_3$), 29.83 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.03 (fifth generation −*C*−), 46.71 (fourth generation −*C*−), 46.84 (third generation −*C*−), 46.90 (second generation −*C*−), 47.35 (first generation −*C*−), 63.78 (−CH$_2$−*C*H$_2$−O−), 64.42 (−O−*C*H$_2$−CH$_2$−), 64.54 (first generation −*C*H$_2$), 65.64 (second generation −*C*H$_2$−), 65.84 (third generation −*C*H$_2$−), 65.91 (fourth generation −*C*H$_2$−), 65.96 (fifth generation −*C*H$_2$−), 98.08 (−O−*C*−CH$_3$), 112.85 (*o*-Ar*C*), 120.02 (*meso*-porphyrin *C*), 131.60 (β-pyrrole *C*), 135.08 (*m*-Ar*C*), 135.23 (*p*-Ar*C*), 150.60 (α-pyrrole *C*), 159.72 (Ar*C*−O), 171.44 (second generation *C*═O), 171.46 (third generation *C*═O), 171.86 (first generation *C*═O), 172.22 (fourth generation *C*═O), and 173.48 (fifth generation *C*═O).

Synthesis of Acetonide-G*n*-prop-TPPZn (n = 4, 5): General Procedure Zinc Insertion, Exemplified by Acetonide-G4-prop-TPPZn. Acetonide-G4-TPPH$_2$ (300 mg, 0.033 mmol) was dissolved in 5 mL of pyridine and 5 mL of THF. Zinc acetate (70 mg, 0.33 mmol, 10 equiv) was added and the reaction was stirred at 70 °C for 6 h and followed by UV−Vis spectroscopy. The solvents were evaporated; the crude product was dissolved in THF, extracted with brine three times, dried with $MgSO_4$, and filtered, and the solvents were removed to yield (87%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 96H, −C*H*$_3$), 1.15−1.40 (broad m, 12H, first generation −C*H*$_3$, 24H, second generation −C*H*$_3$, 48H, third generation −C*H*$_3$, and 192H, −O−C−C*H*$_3$), 2.35 (m, 8H, J = 6.0 Hz, −CH$_2$−C*H*$_2$−CH$_2$−) 3.61 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.19 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.25−4.45 (broad m, 64H, third generation −CH$_2$−O−, 32H, second generation −CH$_2$−O−, 16H, first generation −CH$_2$−O−, and 8H, −CH$_2$−C*H*$_2$−O−), 4.50 (t, 8H, J = 6.0 Hz, −O−C*H*$_2$−CH$_2$−), 7.28 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.10 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.93 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.67 (second generation −*C*H$_3$), 17.72 (first generation −*C*H$_3$), 17.80 (third generation −*C*H$_3$), 18.59 (fourth generation −*C*H$_3$), 23.23 (−O−C−*C*H$_3$), 25.50 (−O−C−*C*H$_3$), 29.33 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.14 (fourth generation −*C*−), 46.86 (third generation −*C*−), 46.95 (second generation −*C*−), 47.10 (first generation −*C*−), 63.51 (−CH$_2$−*C*H$_2$−O−), 64.24 (−O−*C*H$_2$−CH$_2$−), 64.90 (first generation −*C*H$_2$), 65.93 (second generation −*C*H$_2$−), 66.02 (third generation −*C*H$_2$−), 66.07 (fourth generation −*C*H$_2$−), 98.20 (−O−*C*−CH$_3$), 112.67 (*o*-Ar*C*), 120.74 (*meso*-porphyrin *C*), 131.59 (β-pyrrole *C*), 135.11 (*m*-Ar*C*), 135.16 (*p*-Ar*C*), 150.45 (α-pyrrole *C*), 159.93 (Ar*C*−O), 172.00 (second generation *C*═O), 172.04 (third generation *C*═O), 172.14 (first generation *C*═O), and 173.54 (fourth generation *C*═O).

Acetonide-G5-prop-TPPZn. Acetonide-G5-prop-TPPZn yielded (78%) a purple solid. ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 192H, −C*H*$_3$), 1.15−1.40 (broad m, 12H, first generation −C*H*$_3$, 24H, second generation −C*H*$_3$, 48H, fourth generation −C*H*$_3$, 96H, third generation −C*H*$_3$, and 384H, −O−C−C*H*$_3$), 2.33 (m, 8H, J = 6.0 Hz, −CH$_2$−C*H*$_2$−CH$_2$−), 3.61 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.22 (d, 64H, J = 12.0 Hz, fourth generation −CH$_2$−O−), 4.25−4.45 (broad m, 128H, fourth generation −CH$_2$−O−, 64H, third generation −CH$_2$−O−, 32H, second generation −CH$_2$−O−, 16H, first generation −CH$_2$−O−, and 8H, −CH$_2$−C*H*$_2$−O−), 4.52 (t, 8H, J = 6.0 Hz, −O−C*H*$_2$−CH$_2$−), 7.26 (d, 8H, J = 8.4 Hz, *o*-Ar−*H*), 8.14 (d, 8H, J = 8.4 Hz, *m*-Ar−*H*), and 8.97 (s, 8H, β-pyrrole−*H*). ^{13}C NMR ($CDCl_3$): δ 17.68 (first generation −*C*H$_3$), 17.72 (second generation −*C*H$_3$), 17.74 (third generation −*C*H$_3$), 17.81 (fourth generation −*C*H$_3$), 18.62 (fifth generation −*C*H$_3$), 23.21 (−O−C−*C*H$_3$), 25.62 (−O−C−*C*H$_3$), 29.74 (−CH$_2$−*C*H$_2$−CH$_2$−), 42.22 (fifth generation −*C*−), 46.14 (fourth generation −*C*−), 46.76 (third generation −*C*−), 46.89 (second generation −*C*−), 47.08 (first generation −*C*−), 63.75 (−CH$_2$−*C*H$_2$−O−), 64.23 (−O−*C*H$_2$−CH$_2$−), 64.92 (first generation −*C*H$_2$), 65.93 (second generation −*C*H$_2$−), 66.00 (third generation −*C*H$_2$−), 66.02 (fourth generation −*C*H$_2$−), 66.18 (fifth generation −*C*H$_2$−), 98.76 (−O−*C*−CH$_3$), 112.64 (*o*-Ar*C*), 120.74 (*meso*-porphyrin *C*), 131.49 (β-pyrrole *C*), 135.14 (*m*-Ar*C*), 135.21 (*p*-Ar*C*), 150.45 (α-pyrrole *C*), 159.98 (Ar*C*−O), 172.00 (second generation *C*═O), 172.04 (third generation *C*═O), 172.14 (first generation *C*═O), 172.16 (fourth generation *C*═O), and 173.65 (fifth generation *C*═O).

Acknowledgment. This work is supported by "Photonics in defense applications"—a program run jointly by the Swedish Defence Research Agency (FOI) and Defence Material Administration (FMV). Peter Löwenhielm is thanked for the SEC analyses and Andreas Woldegiorgis at KTH Chemistry, Analytical chemistry, for the MALDI-TOF analyses.

CM035354E