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Synthesis of novel dendrimers containing pyrimidine units

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Abstract—A novel convergent approach to dendritic macromolecules is described in which 4,6-dichloro-2-(4-methoxyphenyl)-pyrimidine is used as the building block. The nucleophilic aromatic substitution reaction at this AB_2-monomer was used as the key step in the propagation of the dendrons. Different core reagents were used to form the dendrimers, including a 5,15-bis(pyrimidyl)porphyrin core. Fourth-generation dendrons and third-generation dendrimers could be synthesized. The presented dendrimers are promising candidates to be used in applications where a more rigid structure and a larger resistance towards the applied conditions is required.

1. Introduction

The increasing need for highly specialized materials with new and improved properties, useful in different technological applications, creates a demand for new macromolecules with well controlled architectures. A class of products that can supply a possible solution to this demand are the monodisperse dendrimers.[1] These relatively novel macromolecules differ from the classical, linear polymers by their perfectly branched structure. The synthesis can occur through a divergent[2] or a convergent[3] approach to different sizes or 'generations'. Due to the large structural variation that is possible, dendrimers can find application as synthetic models for biological structures, as *exo*- and *endo*-receptors, as new catalysts, as drug carriers, as unimolecular micelles and in new biosensors.[1]

In the synthesis of dendrimers, it is crucial to find reactions with a large effectivity to reduce the probability of defects in the large structure and to simplify purification. Recently, we started to use the nucleophilic aromatic substitution (NAS) of halides with phenolates as a new convergent strategy towards dendrimers.[4–7] To make this substitution successful it is necessary to have an electron poor (e.g. heterocyclic) system in the *ortho*- or *para*-position of the aryl halide, but it is even better to place the halide directly on the heterocyclic structure. In our recent research we successfully synthesized dendrimers consisting of 1,3,4-oxadiazoles[6] and 1,3,5-triazines[7] as heterocyclic building blocks using this approach. The synthesis of the oxadiazole dendrimers was restricted to the second generation because of the poor reactivity of the system towards NAS. The triazine monomer, however, was very reactive towards this substitution and dendrimers until the third generation could easily be synthesized. Unfortunately, the triazine system was so reactive that the deprotecting step (cleavage of a methylarylether with boron tribromide) caused some extent of destructive fragmentation in the dendrimer structure, resulting in a difficult separation of the dendrons of different generations. Moreover the triazine dendrons also possess a high reactivity towards all kinds of nucleophiles, such as water and methanol, therefore demanding extreme caution when handling this system and limiting its applicability.

Because of these earlier difficulties we searched for a system with an intermediate reactivity in order to build up larger structures. From earlier work on porphyrins,[8,9] it is known that the NAS on 4,6-dichloropyrimidines is possible under relatively mild conditions (K_2CO_3 in DMF at 60°C for phenolate substitution). Therefore, a new monomer suggested for the synthesis of dendrimers through the NAS approach is the pyrimidine monomer 4,6-dichloro-2-(4-methoxyphenyl)-pyrimidine **1**.

2. Results

2.1. Monomer synthesis

A heterocyclic system with the appropiate AB_2-symmetry that is well-suited for dendrimer construction is 4,6-dichloro-2-(4-methoxyphenyl)-pyrimidine **1** (Scheme 1). This monomer can be synthesized according to a literature method[10] starting from 4-methoxybenzonitrile by conversion into the benzamidine, which can be condensed with diethyl malonate to the hydroxypyrimidone. Chlorination then gives the desired monomer **1**.

Keywords: dendrimer synthesis; nucleophilic aromatic substitution; pyrimidine; porphyrin.

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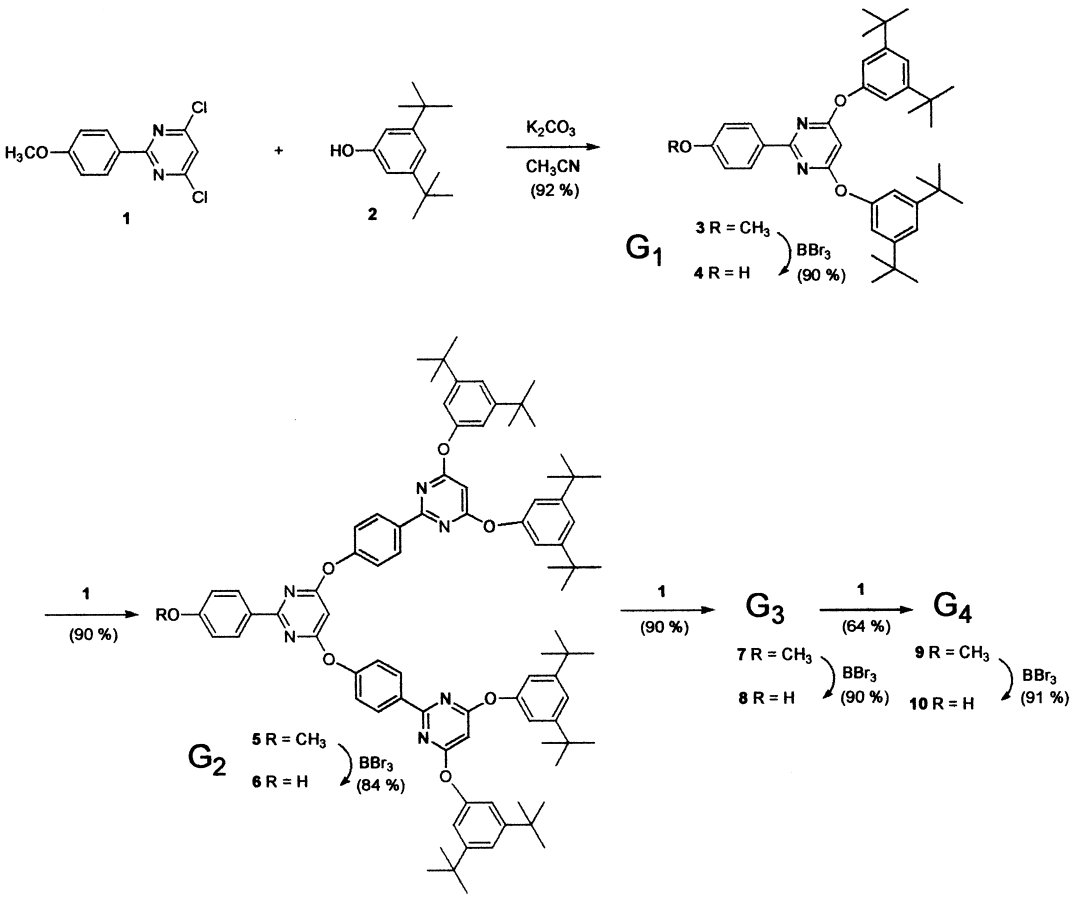


Scheme 1. Dendron synthesis.

2.2. Dendron synthesis—propagation of the dendrons

After the synthesis of the monomer, we constructed the dendrimers using a convergent method. As a consequence of the electron poor haloaryl functions of this heterocyclic building block, NAS was made possible. We intended to use this reaction as the key reaction for the synthesis of our dendrimers.

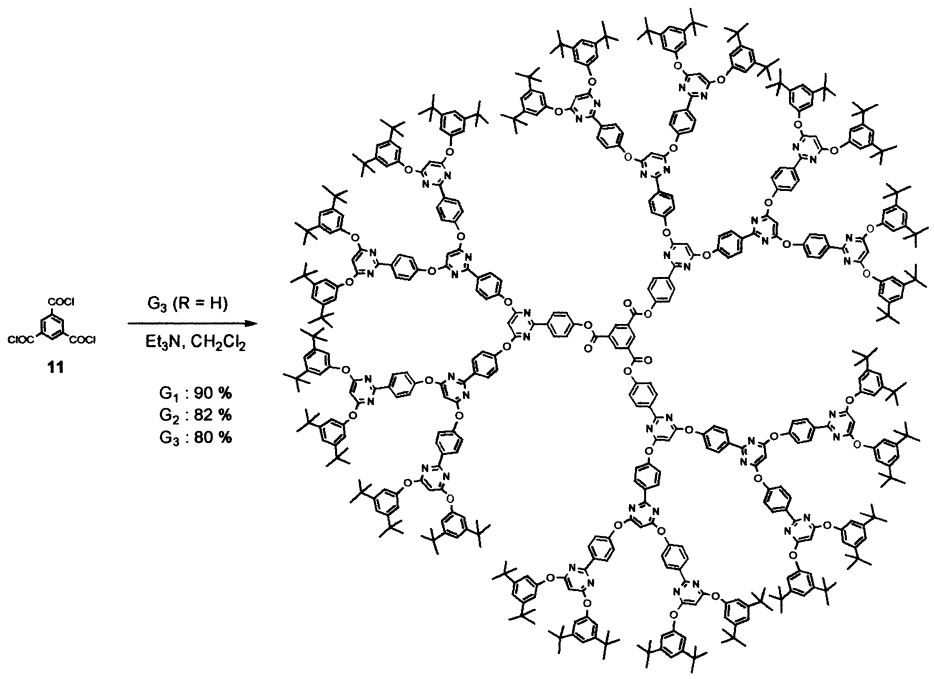
The dendron propagation was started with the substitution of the two chlorine functions by a phenolate with the desired peripheral groups. These peripheral groups have a major influence on the final properties of the dendron or dendrimer. Initially we chose to insert functionalities which would give the dendrimers good solubility in order to be able to perform a complete characterization of the structure by ^{1}H and ^{13}C NMR spectroscopy as well as mass spectrometry. Therefore, the compound we used was 3,5-bis-(*t*-butyl)phenol **2**, which is commercially available at low cost, so we reacted this phenol with monomer **1** to obtain a first generation dendron **3** (Scheme 1), but theoretically all compounds bearing a phenol moiety may be insertable as peripheral groups. The ideal circumstances for the NAS were investigated (different base–solvent systems) and the best results were obtained with anhydrous potassium carbonate base in acetonitrile at reflux.

The obtained first generation dendron **3** could be activated again for a second substitution by a deprotecting step using boron tribromide. Reiteration of the NAS with the deprotected first generation dendron **4** and the monomer **1** gave the second generation dendron **5**. This sequence could be repeated as far as the fourth generation dendrons (Scheme 1).

2.3. Dendrimer synthesis

2.3.1. 1,3,5-Benzenetricarbonyl trichloride as core reagent. The convergent approach for dendrimer synthesis implies that the synthesized dendrons are attached in the final step to a central core. In our case, any core molecule that can be coupled with a phenol functionality can be applied. An example of such a core is 1,3,5-benzenetricarbonyl trichloride **11**. Using this core, dendrimers until the third generation were synthesized easily and in high yields using mild conditions (triethylamine as base in dichloromethane at room temperature). Scheme 2 gives an example of a third generation dendrimer constructed in this way. Attempts to prepare the fourth generation dendrimer failed, probably because of the increased steric hindrance around the focal group of the G_4-dendron **10**.

2.3.2. Synthesis of novel porphyrin dendrimers. Porphyrins have already been applied as central building blocks (cores) in dendrimer chemistry. Inoue et al. described a beautiful example where eight fourth generation Fréchet-type dendrons[3] were connected to a central porphyrin core.[11] It has been suggested that dendritic porphyrins could



Scheme 2. G_3-dendrimer with 1,3,5-benzenetricarbonyl trichloride **11** as core reagent.

act as model systems for natural electron transfer hemoproteins like cytochrome C or hemoglobin.[12,13]

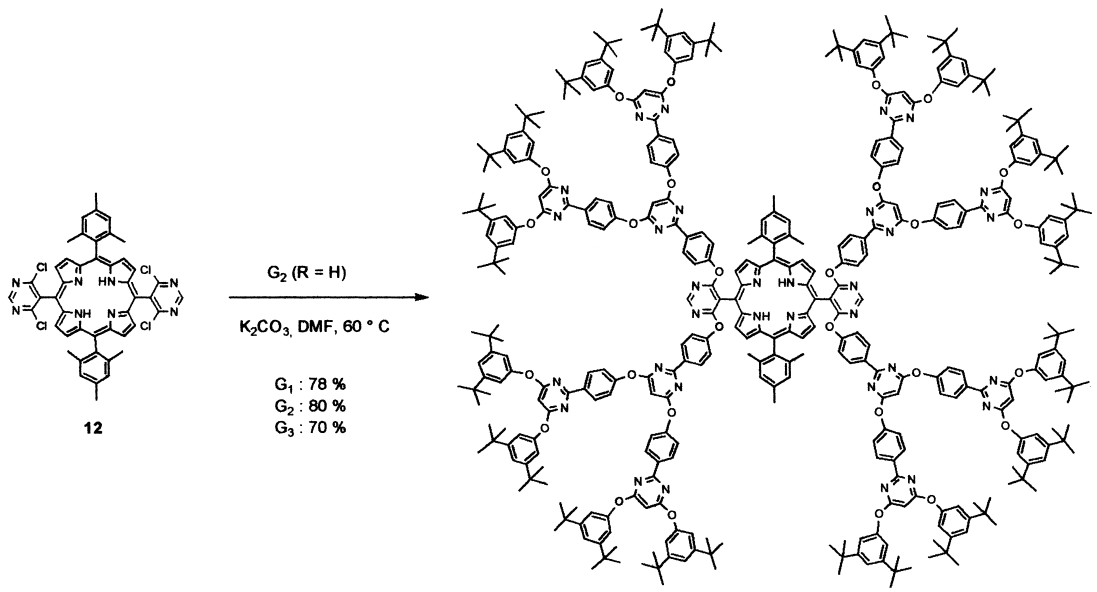
Because of their large size and the possibility of host–guest interactions, porphyrins represent attractive cores for the design of dendritic sensors and catalysts. High valent metalloporphyrins have been employed as catalysts for the oxidation of organic substrates.[14] The introduction of bulky dendritic polymers at the peripheral positions of a metal porphyrin results in steric protection of the metal center and can provide regio- and shape-selective catalysis.[15]

Porphyrins and metalloporphyrins are useful photophysical probes for evaluating the properties of the dendritic structure due to their sensitivity to the type and the position of the substitution as well as the presence of neighboring chromophores.[16] Several studies investigating dendrimers having a porphyrin or metalloporphyrin core functionality have been reported.[11,17–22] Recently, De Schryver et al. have undertaken a study to correlate the molecular structure of such compounds with their hydrodynamic and photophysical properties in solution.[23]

A porphyrin molecule that can be used as a dendrimer core is 5,15-bis(pyrimidyl)porphyrin **12**.[8] The synthesis of this A_2B_2-porphyrin was performed by a McDonald-condensation of mesityldipyrromethane[24] with 4,6-dichloropyrimidin-5-carbaldehyde,[25] which can be formed from 4,6-dihydroxypyrimidine under Vilsmeier conditions (DMF, $POCl_3$).

As mentioned earlier, NAS reactions on this porphyrin were already applied with a large variety of alcoholates and phenolates.[9] For the phenolates this substitution could be performed under soft conditions (K_2CO_3, DMF, 60°C) and in high yields (60% and more) so we tried to do an analogous reaction with our dendrons. In this way porphyrin dendrimers until the third generation were synthesized in relatively good yields (70–80%). An example of such a dendrimer is given in Scheme 3. This second-generation dendrimer could be formed from the G_2-dendron **6** and **12** as core reagent.

All compounds synthesized were fully characterized using NMR spectroscopy (^1H and ^{13}C) and mass spectrometry (CI, Electrospray and MALDI-TOF). The ^1H NMR spectra of the different generation dendrons clearly show the signals corresponding with the different monomer layers and the integration indicates which generation is involved. However, the signals in the ^1H NMR spectrum of the G_3-porphyrin dendrimer were broadened and therefore the extent of substitution on the porphyrin core could not be established unambiguously by integration. This broadening may be caused by restricted movement of the dendron arms. The uncertainty about the degree of substitution was confirmed by the MALDI-TOF mass spectrum of this G_3-porphyrin dendrimer. Although the spectrum gives a proof of the existence of the fully substituted porphyrin dendrimer, there is also a significant peak corresponding to the dendrimer lacking one dendron. It is not clear if this peak is originating from the triple substituted porphyrin dendrimer or it is generated by fragmentation during acquisition of the spectrum. The reported ^{13}C NMR data of the (higher generation) dendrimers do not include all carbon atoms because the abundance of some (core) signals was too low. Since the detection limit of our electrospray ionization (ESI) mass spectrometer was m/e=4000, the higher generation dendrons and dendrimers were identified by their double and triple charged ions or by MALDI-TOF spectra. The UV-absorption spectra of the different generation porphyrin dendrimers show the intense absorption peak of the dendrons (around 285 nm) and the different porphyrin bands (Soret-band and Q-bands).



Scheme 3. The second generation porphyrin dendrimer.

3. Discussion

The dendrimers presented are promising candidates for use in several applications. First of all, dendrimers with a range of functional groups (and chromophores) at the periphery are easily accessible just by altering the phenol moiety used to form the first generation dendron (Scheme 1). Any compound bearing a phenol functionality can (theoretically) easily be introduced. Since the dendrimers are built in a convergent way, the core functionality can also be adapted according to the application needs.

The dendrimers in this project are relatively rigid which could create larger cavities and thus allow the inclusion of larger guests. Moreover, the large number of heteroatoms could also enable strong complexation. Many of the dendrimers synthesized so far (ex. the Fréchet dendrimers[3]) are quite unstable in conditions of heat, acids, bases, oxidation and reduction. The stable functionalities in our dendrimers could provide a higher resistance towards a more reactive environment.

In recent publications it has been shown that polymers consisting of heterocyclic building blocks can be used in organic light-emitting diodes (LEDs) because of their electroluminescent properties.[26] Since the heterocyclic dendrimers in this project are very similar to these polymers, they could also be used for this purpose. The major advantage of dendrimers[27] (over linear polymers) in these organic LEDs is that the electronic and physical properties could be optimized independently. The prepared macromolecules are therefore candidates to be incorporated in the construction of organic LEDs.

4. Conclusion

The NAS reaction has been used to build up dendrimers based on pyrimidine as a heterocyclic building block. A convergent approach to dendrimers is described with 4,6-dichloro-2-(4-methoxyphenyl)-pyrimidine **1** as AB_2-monomer and different cores, including a bis(pyrimidyl)-porphyrin core **12**, have been employed to prepare the pyrimidine dendrimers. At this moment we can routinely prepare third generation dendrimers and fourth generation dendrons. The presented dendrimer system provides a new, promising, rigid dendrimer backbone for various applications. It therefore presents an alternative to commonly used dendrimers, containing aliphatic amides or amines,[2] or benzyl ether[3] linkages.

5. Experimental

5.1. Materials and methods

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz or Bruker AMX 400 MHz) and chemical shifts (δ) are reported in parts per million referenced to internal residual solvent protons (^{1}H) or the carbon signal of deuterated solvents (^{13}C). Mass spectrometry data were obtained with an HP MS apparatus 5989A (chemical ionization (CI), CH_4) or a Micromass Quattro II apparatus (ESI, solvent mixture: CH_2Cl_2/MeOH+NH_4OAc). MALDI-TOF mass spectra were recorded on a KRATOS ANALYTICAL (Manchester, UK) KOMPACT MALDI-2K-PROBE instrument in positive high (20 kV) mode, which uses a 3 ns pulse from a nitrogen laser (λ=337 nm) at a target area of 100 μm in diameter and pulse extracts the ions down a linear flight tube (2 m), employing α-cyano-4-hydroxy-cinnamic acid as a matrix. UV–Vis spectra were taken on a Perkin–Elmer Lambda 20 spectrometer. IR spectra were obtained on a Perkin–Elmer 1600 instrument as KBr pellets. Melting points (not corrected) were determined using a Reichert Thermovar apparatus.

DMF was dried on molecular sieves 4 Å. Other solvents were used without further purification.

5.2. General procedure for the synthesis of the protected dendrons (R=CH_3)

The G_x-dendron (3,5-bis-(*t*-butyl)phenol **2**, **4**, **6** or **8**) (2.2 equiv.) in CH_3CN solution was stirred at room temperature for 0.5 h with an excess of anhydrous K_2CO_3 (5.5 equiv.). After another 0.5 h of reflux, the monomer **1** (1 equiv.) was added and the mixture was refluxed for 4 days. After evaporation of the solvent, water was added and the mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. The products were purified by column chromatography (silica, eluent CH_2Cl_2) and obtained as white solids.

5.3. General procedure for the synthesis of the deprotected dendrons (R=H)

To a solution of the protected G_x-dendron **3**, **5**, **7** or **9** (1 equiv.) in CH_2Cl_2 an excess of BBr_3 (1 M in CH_2Cl_2, 5 equiv./generation) was added at −78°C under dry conditions and then the mixture was placed in the freezer (−18°C). After 4 days of reaction at −18°C, ice water was added. After separation of the organic layer, the aqueous phase was extracted with CH_2Cl_2. The organic layers were collected, dried over $MgSO_4$ and evaporated in vacuum. The products were purified by column chromatography (silica, eluent CH_2Cl_2) and obtained as white solids.

5.3.1. G_1 (R=CH_3) 3. R_f (CH_2Cl_2) 0.75. Mp 194–197°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.28 (d, 2H, *J*=8.8 Hz), 7.28 (t, 2H, *J*=1.6 Hz), 7.04 (d, 4H, *J*=1.6 Hz), 6.87 (d, 2H, *J*=8.8 Hz), 5.88 (s, 1H), 3.84 (s, 3H), 1.31 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=172.2, 164.2, 162.1, 152.6, 152.2, 130.2, 129.4, 119.3, 115.7, 113.5, 87.6, 55.3, 35.0, 31.4; MS (CI) *m*/*z*=595 [MH^+, 100], 579 [$M-CH_3$, 12]; IR (KBr) ν_{max}=3431.9, 3073.6, 2961.5, 2870.0, 1654.3, 1567.5, 1423.9, 1367.4, 1297.5, 1263.5, 1198.9, 1149.1, 1033.6, 973.4, 871.7, 818.1, 784.0, 705.0, 589.9; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=227 (4.427), 292 (4.462). Anal. calcd for $C_{39}H_{50}N_2O_3$: C, 78.75%; H, 8.47%; N, 4.71%. Found: C, 78.65%; H, 8.58%; N, 4.59%.

5.3.2. G_1 (R=H) 4. R_f (CH_2Cl_2) 0.15. Mp 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.23 (d, 2H, *J*=8.8 Hz), 7.28 (t, 2H, *J*=1.6 Hz), 7.03 (d, 4H, *J*=1.6 Hz), 6.80 (d, 2H, *J*=8.8 Hz), 5.88 (s, 1H), 5.18 (s(br), 1H), 1.31 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.2, 164.1, 158.3, 152.6, 152.2, 130.6, 129.7, 119.3, 115.7, 115.1, 87.6, 35.0, 31.4; MS (CI) *m*/*z*=581 [MH^+, 100], 565 [$M-CH_3$, 13]; IR (KBr) ν_{max}=3413.7, 2961.5, 2869.9, 2364.4, 1555.6, 1372.3, 1292.8, 1248.5, 1198.3, 1146.1, 1036.7, 972.1, 871.6, 822.4, 705.2; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=224 (4.492), 287 (4.371). Anal. calcd for $C_{38}H_{48}N_2O_3$: C, 78.58%; H, 8.33%; N, 4.82%. Found: C, 77.93%; H, 8.32%; N, 4.65%.

5.3.3. G_2 (R=CH_3) 5. R_f (CH_2Cl_2) 0.70; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.40 (d, 4H, *J*=8.8 Hz), 8.06 (d, 2H, *J*=8.8 Hz), 7.29 (t, 4H, *J*=1.6 Hz), 7.23 (d, 4H, *J*=8.8 Hz), 7.06 (d, 8H, *J*=1.6 Hz), 6.83 (d, 2H, *J*=8.8 Hz), 6.14 (s, 1H), 5.98 (s, 2H), 3.81 (s, 3H), 1.32 (s, 72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.3, 163.9, 163.6, 162.2, 155.2, 152.6, 152.1, 133.8, 130.1, 130.0, 129.0, 121.2, 119.4, 115.6, 113.7, 89.5 88.4, 55.3, 35.0, 31.4; MS (ESI) *m*/*z*=1344.0 [(M^+)+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=227 (4.692), 282 (4.959).

5.3.4. G_2 (R=H) 6. R_f (CH_2Cl_2) 0.10; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.39 (d, 4H, *J*=8.8 Hz), 8.00 (d, 2H, *J*=8.8 Hz), 7.30 (t, 4H, *J*=1.6 Hz), 7.22 (d, 4H, *J*=8.8 Hz), 7.06 (d, 8H, *J*=1.6 Hz), 6.74 (d, 2H, *J*=8.8 Hz), 6.15 (s, 1H), 5.98 (s, 2H), 5.53 (s(br), 1H), 1.32 (s, 72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.4, 171.3, 164.0, 163.7, 158.6, 155.3, 152.7, 152.2, 133.9, 130.5, 130.0, 129.2, 121.2, 119.4, 115.6, 115.3, 89.5, 88.5, 35.0, 31.4; MS (ESI) *m*/*z*=1329.6 [(M^+)+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=226 (4.888), 282 (4.947).

5.3.5. G_3 (R=CH_3) 7. R_f (CH_2Cl_2) 0.75; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.41 (d, 8H, *J*=8.8 Hz), 8.21 (d, 4H, *J*=8.8 Hz), 8.04 (d, 2H, *J*=8.8 Hz), 7.28 (t, 8H, *J*=1.6 Hz), 7.24 (d, 8H, *J*=8.8 Hz), 7.17 (d, 4H, *J*=8.8 Hz), 7.05 (d, 16H, *J*=1.6 Hz), 6.81 (d, 2H, *J*=8.8 Hz), 6.20 (s, 2H), 6.10 (s, 1H), 5.96 (s, 4H), 3.80 (s, 3H), 1.30 (s, 144H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.5, 171.2, 164.1, 163.6, 163.5, 162.2, 155.3, 155.1, 152.6, 152.1, 134.1, 133.4, 130.2, 130.1, 129.9, 128.9, 121.4, 121.2, 119.4, 115.6, 113.6, 90.1, 89.2, 88.5, 55.2, 35.0, 31.7; MS (ESI) *m*/*z*=2840.6 [(M^+)+H], 1421.2 [(M^{2+})+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=230 (4.980), 284 (5.260).

5.3.6. G_3 (R=H) 8. R_f (CH_2Cl_2) 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.42 (d, 8H, *J*=8.8 Hz), 8.20 (d, 4H, *J*=8.8 Hz), 8.00 (d, 2H, *J*=8.8 Hz), 7.28 (t, 8H, *J*=1.6 Hz), 7.25 (d, 8H, *J*=8.8 Hz), 7.18 (d, 4H, *J*=8.8 Hz), 7.03 (d, 16H, *J*=1.6 Hz), 6.76 (d, 2H, *J*=8.8 Hz), 6.21 (s, 2H), 6.11 (s, 1H), 5.96 (s, 4H), 5.44 (s(br), 1H), 1.30 (s, 144H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.5, 171.2, 164.0, 163.6, 163.6, 158.5, 155.3, 155.2, 152.6, 152.2, 134.1, 133.5, 130.5, 130.1, 129.9, 129.1, 121.4, 121.2, 119.4, 115.6, 115.2, 90.1, 89.2, 88.5, 35.0, 31.4; MS (ESI) *m*/*z*=2827.7 [(M^+)+H], 1415.0 [(M^{2+})+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=225 (5.213), 283 (5.185).

5.3.7. G_4 (R=CH_3) 9. R_f (CH_2Cl_2) 0.80; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.40 (d, 16H, *J*=8.8 Hz), 8.23 (d, 8H, *J*=8.8 Hz), 8.23 (d, 4H, *J*=8.8 Hz), 7.99 (d, 2H, *J*=8.8 Hz), 7.28 (t, 16H, *J*=1.6 Hz), 7.23 (d, 16H, *J*=8.8 Hz), 7.19 (d, 8H, *J*=8.8 Hz), 7.19 (d, 4H, *J*=8.8 Hz), 7.04 (d, 32H, *J*=1.6 Hz), 6.75 (d, 2H, *J*=8.8 Hz), 6.18 (s, 4H), 6.16 (s, 1H), 6.10 (s, 2H), 5.97 (s, 8H), 3.72 (s, 3H), 1.30 (s, 288H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.6, 171.1, 164.0, 163.9, 163.5, 162.1, 155.4, 155.2, 155.1, 152.6, 152.2, 134.1, 133.8, 133.3, 132.5, 130.9, 130.1, 130.0, 129.0, 128.8, 121.4, 121.3, 121.2, 119.4, 115.7, 113.7, 90.1, 89.6, 88.6, 55.2, 35.0, 31.4; MS (ESI) *m*/*z*=2918.0 [(M^{2+})+H], 1945.9 [(M^{3+})+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=226 (5.412), 283 (5.503).

5.3.8. G_4 (R=H) 10. R_f (CH_2Cl_2) 0.80; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.44 (d, 16H, *J*=8.8 Hz), 8.23 (d, 8H, *J*=8.8 Hz), 8.22 (d, 4H, *J*=8.8 Hz), 7.99 (d, 2H, *J*=8.8 Hz), 7.30 (t, 16H, *J*=1.6 Hz), 7.27 (d, 16H, *J*=8.8 Hz), 7.20 (d, 12H, *J*=8.8 Hz), 7.07 (d, 32H, *J*=1.6 Hz), 6.83 (d, 2H, *J*=8.8 Hz), 6.26 (s, 4H), 6.19 (s, 1H), 6.19 (s, 2H), 6.01 (s, 8H), 1.32 (s, 288H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3,

171.5, 170.8, 164.0, 163.8, 163.6, 163.4, 155.5, 155.3, 155.2, 152.6, 152.2, 134.1, 134.0, 133.7, 133.0, 130.0, 129.9, 128.8, 121.4, 121.3, 119.4, 115.6, 115.3, 90.2, 89.8, 88.5, 35.0, 31.4; MS (ESI) m/z=2912.0 [(M^{2+})+H], 1941.7 [(M^{3+})+H]; MALDI m/z=5861.6; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=228 (5.264), 282 (5.542).

5.4. General procedure for the synthesis of dendrimers with 1,3,5-benzenetricarbonyl trichloride core 11

To a solution of the G_x-dendron **4**, **6** or **8** (3.3 equiv.) in CH_2Cl_2, Et_3N (3.6 equiv.) was added and the mixture was stirred for 0.5 h at room temperature. 1,3,5-Benzenetricarbonyl trichloride (1 equiv.) was added to this solution and the mixture was stirred for another 6 h and then evaporated in vacuum. After purification through column chromatography (silica, eluent CH_2Cl_2) the title compounds were obtained.

5.4.1. G_1-dendrimer. R_f (CH_2Cl_2) 0.75; ^{1}H NMR (400 MHz, $CDCl_3$) δ=9.22 (s, 3H), 8.41 (d, 6H, J=8.8 Hz), 7.30 (t, 6H, J=1.6 Hz), 7.29 (d, 6H, J=8.8 Hz), 7.06 (d, 12H, J=1.6 Hz), 6.00 (s, 3H), 1.33 (s, 108H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 163.3, 163.0, 152.8, 152.6, 152.2, 136.1, 135.0, 131.2, 130.0, 121.2, 119.4, 115.7, 88.6, 35.0, 31.4; MS (ESI) m/z=1896.7 [(M^+)+H], 948.9 [(M^{2+})+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=226 (4.950), 271 (4.900).

5.4.2. G_2-dendrimer. R_f (CH_2Cl_2) 0.70; ^{1}H NMR (400 MHz, $CDCl_3$) δ=9.22 (s, 3H), 8.42 (d, 12H, J=8.8 Hz), 8.23 (d, 6H, J=8.8 Hz), 7.29 (t, 12H, J=1.6 Hz), 7.24 (d, 12H, J=8.8 Hz), 7.22 (d, 6H, J=8.8 Hz), 7.06 (d, 24H, J=1.6 Hz), 6.15 (s, 3H), 5.98 (s, 6H), 1.32 (s, 216H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.5, 163.6, 163.4, 162.9, 155.1, 152.9, 152.6, 152.2, 136.1, 134.5, 134.1, 131.1, 130.1, 130.0, 121.5, 121.2, 119.4, 115.6, 90.3, 88.6, 35.0, 31.4; MS (ESI) m/z=2071.1 [(M^{2+})+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=226 (5.318), 278 (5.365).

5.4.3. G_3-dendrimer. R_f (CH_2Cl_2) 0.75; ^{1}H NMR (400 MHz, $CDCl_3$) δ=9.20 (s, 3H), 8.39 (d, 24H, J=8.8 Hz), 8.28 (d, 6H, J=8.8 Hz), 8.22 (d, 12H, J=8.8 Hz), 7.25 (t, 24H, J=1.6 Hz), 7.22 (d, 30H, J=8.8 Hz), 7.17 (d, 12H, J=8.8 Hz), 7.03 (d, 48H, J=1.6 Hz), 6.18 (s, 6H), 6.06 (s, 3H), 5.96 (s, 12H), 1.28 (s, 432H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.6, 171.5, 163.5, 163.4, 155.2, 155.1, 152.6, 152.2, 134.1, 133.8, 130.8, 130.2, 130.1, 121.3, 121.2, 119.3, 115.6, 90.1, 88.6, 35.0, 31.4; MALDI m/z=8636.4; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=226 (5.626), 280 (5.659).

5.5. General procedure for the synthesis of dendrimers with porphyrin core 12

To a solution of porphyrin **12** (1 equiv.) and G_x-dendron **4**, **6** or **8** (4.4 equiv.) in dry DMF, anhydrous K_2CO_3 (5 equiv.) was added. The mixture was stirred for 40 h at 60°C under argon atmosphere. The solution was allowed to reach room temperature and CH_2Cl_2 was added. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed and the residue purified by column chromatography (silica, eluent CH_2Cl_2).

5.5.1. G_1-dendrimer. R_f (CH_2Cl_2) 0.80; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.97 (d, 4H, J=4.7 Hz), 8.81 (s, 2H), 8.77 (d, 4H, J=4.7 Hz), 8.18 (d, 8H, J=8.8 Hz), 7.31 (s, 4H), 7.24 (t, 8H, J=1.6 Hz), 6.97 (d, 8H, J=8.8 Hz), 6.96 (d, 16H, J=1.6 Hz), 5.86 (s, 4H), 2.67 (s, 6H), 1.85 (s, 12H), 1.26 (s, 144H), −2.45 (s(br), 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.1, 169.8, 163.4, 157.8, 155.1, 152.5, 152.1, 139.5, 138.0, 137.8, 133.9, 129.8, 127.8, 121.1, 119.3, 118.7, 115.7, 108.7, 106.0, 88.4, 35.0, 31.4, 21.9, 21.5; IR (KBr) ν_{max}=3440.7, 2960.6, 2869.1, 1554.4, 1506.3, 1420.1, 1373.1, 1294.3, 1200.8, 1147.9, 1039.7, 970.2, 867.8, 705.4; MS (ESI) m/z=3015.9 [(M^+)+H], 1508.2 [(M^{2+})+H]; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=227 (5.115), 278 (5.124), 420 (5.582), 515 (4.380), 549 (3.923), 591 (3.834), 648 (3.569).

5.5.2. G_2-dendrimer. R_f (CH_2Cl_2) 0.75; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.93 (d, 4H, J=4.7 Hz), 8.74 (d, 4H, J=4.7 Hz), 8.74 (s, 2H), 8.33 (d, 16H, J=8.8 Hz), 8.03 (d, 8H, J=8.8 Hz), 7.27 (t, 16H, J=1.6 Hz), 7.21 (s, 4H), 7.14 (d, 16H, J=8.8 Hz), 7.04 (d, 32H, J=1.6 Hz), 6.94 (d, 8H, J=8.8 Hz), 6.06 (s, 4H), 5.98 (s, 8H), 2.54 (s, 6H), 1.80 (s, 12H), 1.29 (s, 288H), −2.47 (s(br), 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.3, 171.4, 169.9, 163.5, 155.1, 152.6, 152.2, 139.4, 134.0, 130.0, 129.8, 121.5, 121.1, 119.3, 115.6, 88.6, 35.0, 31.4, 21.8, 21.4; MS (ESI) m/z=3004.9 [(M^{2+})+H], 2004.0 [(M^{3+})+H]; MALDI m/z=6011.4; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=226 (5.410), 282 (5.479), 420 (5.638), 515 (4.334), 550 (3.860), 592 (3.784), 646 (3.546).

5.5.3. G_3-dendrimer. R_f (CH_2Cl_2) 0.80; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.96 (br), 8.73 (br), 8.43 (d), 8.21 (d), 8.01 (d), 7.27 (m), 7.08 (m), 6.77 (d), 6.22 (s), 6.11 (s), 5.97 (s), 2.57 (br), 1.81 (br), 1.31 (s), −2.45 (br); MALDI m/z=11998.4, 9209.6; UV–Vis (CH_2Cl_2) λ_{max} (log ε)=228 (5.597), 283 (5.787), 420 (5.537), 515 (4.217), 549 (3.803), 592 (3.738), 648 (3.550).

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