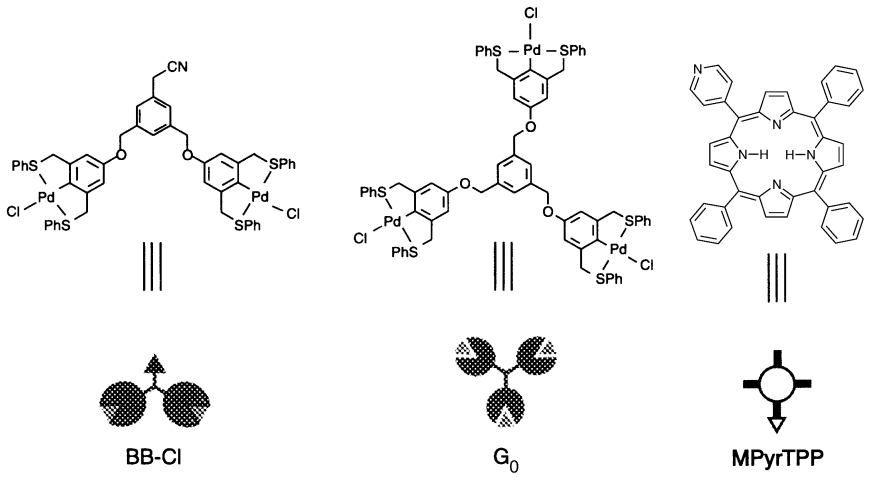
Non-covalent synthesis of multiporphyrin systems

Wilhelm T. S. Huck,[a] Annick Rohrer,[a] A. T. Anilkumar,[a] Roel H. Fokkens,[b] Nico M. M. Nibbering,[b] Frank C. J. M. van Veggel,*[,a] and David N. Reinhoudt*[,a]

[a] *Laboratory of Supramolecular Chemistry and Technology and MESA Research Institute, University of Twente, P.O. Box 217, NL-7500 AE Enschede, The Netherlands*
[b] *Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, NL-1018 WS Amsterdam, The Netherlands*

Non-covalent synthesis was used in the controlled assembly of metallodendrimers containing up to 12 porphyrins on the surface. A porphyrin containing four Pd-Cl complexes was synthesized to assemble dendrimers with a porphyrin in the nucleus. ^{1}H NMR, ES-MS and MALDI-TOF mass spectrometry were used to characterize the nanometer-size assemblies.



Scheme 1

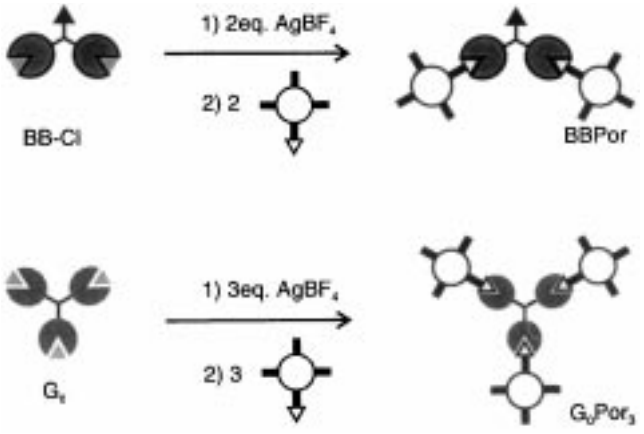
Porphyrin aggregates have been studied extensively as model systems for natural photosynthesis[1] and in molecular electronics.[2] Conventional synthetic strategies to covalently linked porphyrin oligomers usually require a large number of sequential steps and often extensive chromatographic purification of statistical mixtures resulting in low overall yields. Self-assembly has emerged as a viable alternative to covalent synthesis in the construction of large multi-component architectures.[3] Recently, several examples of supramolecular porphyrin assemblies have been published. Both hydrogen[4] and coordination bonds[5] have been used as the source of the non-covalent bonding interactions. As a first step to mimic the light-harvesting system, dendrimers might be used to bring a large number of porphyrins into close proximity. In this paper we report on the assembly of porphyrin-containing dendrimers of nanometer dimensions.

Our route to multiporphyrin assemblies involves the functionalization of metallodendrimers with pyridylporphyrins. We recently described the non-covalent synthesis of various metallodendrimers that were assembled in a repetitive reaction sequence (controlled assembly).[6] The building blocks used for the assembly of the metallodendrimers described in this communication are depicted in Scheme 1. The synthesis of **G_0** and **BB-Cl** has been described before.[7] Controlled assembly of **G_1**[6] starts with the activation of **G_0** with three equivalents of $AgBF_4$ to remove the chloride ligands. Subsequently, three equivalents of **BB-Cl** are added and **G_1** is formed through coordination of the cyano group.

Pyridylporphyrins are often-used building blocks because of their facile and well-known coordination behavior to various metals.[8] Pyridine ligands coordinate strongly to Pd centers and the addition of 5-pyridyl-10,15,20-triphenylporphyrin (MPyrTPP)[9] to activated **BB-Cl** or **G_0** leads to the assembly of **BBPor** and **G_0Por$_3$**, respectively (Scheme 2).

In the ^{1}H NMR spectra of **BBPor** and **G_0Por$_3$** the coordination of the pyridine moiety is evidenced by a downfield shift of 0.2 ppm of the CH_2S proton signal. The signals for the α-pyridine protons are not visible as these are hidden under the porphyrin signals. The assemblies **BBPor** and **G_0Por$_3$** were further characterized by mass spectrometry. The FAB-MS spectrum of **BBPor** shows signals at *m/z* 2260.7 and 2348.4 corresponding to $[\mathbf{BBPor} + H - 2BF_4]^+$, (calcd 2260.5) and to $[\mathbf{BBPor} + 2H - BF_4]^+$, (calcd 2348.3), respectively. The FD-MS spectrum of **G_0Por$_3$** shows signals at *m/z* 1097.6, 1690.3 and 3382.9, which are attributed to $[\mathbf{G_0Por_3} - 3BF_4]^{3+}$, (calcd 1097.6), $[\mathbf{G_0Por_3} - 2BF_4]^{2+}$, (calcd 1689.9), and $[\mathbf{G_0Por_3} + 3H - 2BF_4]^+$ (calcd 3382.8), respectively. The FT-IR spectrum of **BBPor** only shows an absorp-

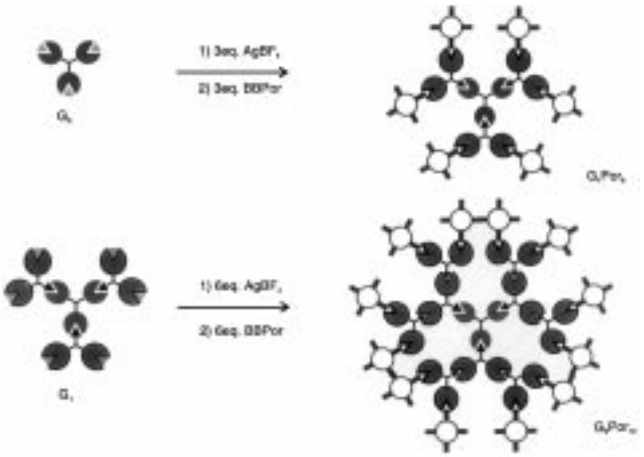
* Fax: +31 53 4894645; E-mail: smct@ct.utwente.nl



Scheme 2

tion at 2252 cm^{-1} indicating that the cyano group is not coordinated and only the pyridine complex has been formed.[10]

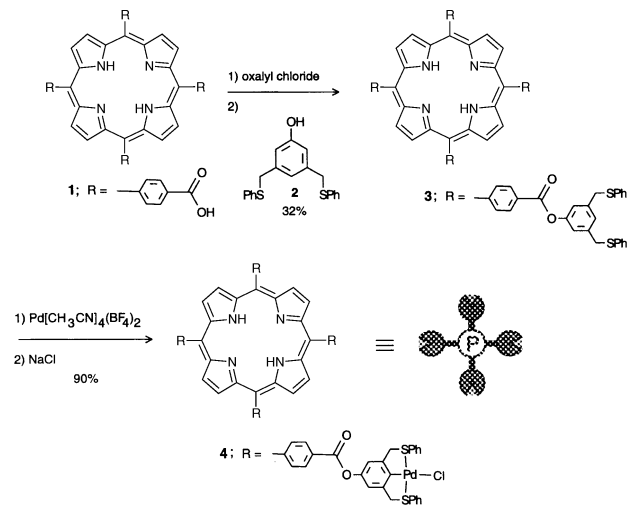
Larger metallodendrimers were constructed by employing both **BB-Cl** and **BBPor** as building blocks. Controlled assembly using activated $\mathbf{G_0}$ and three equivalents of **BBPor** yields $\mathbf{G_1Por_6}$. Dendrimer $\mathbf{G_2Por_{12}}$ was constructed from $\mathbf{G_1}$, which was activated with six equivalents of $AgBF_4$ and extended with six equivalents of **BBPor** (Scheme 3).[11]



Scheme 3

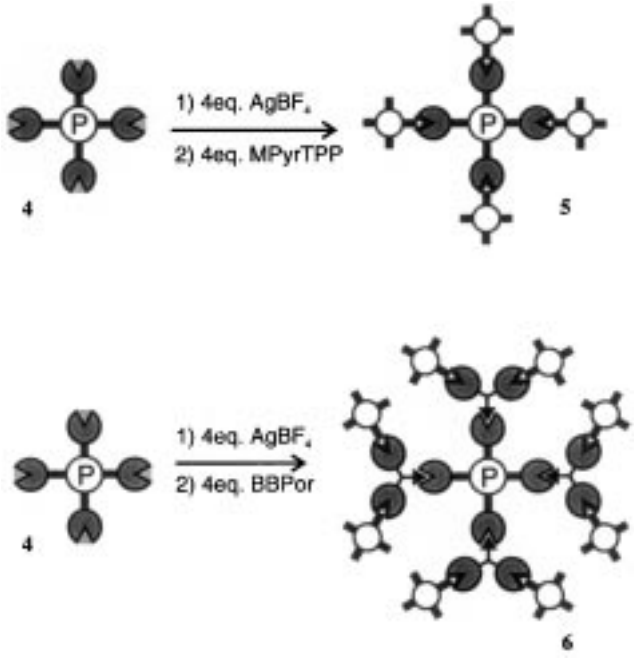
The formation of the multiporphyrin assemblies is evidenced by NMR experiments. NMR spectra were recorded from diluted samples (μM range) to avoid clustering and concomitant broadening of signals. The ^1H NMR spectra of $\mathbf{G_1Por_6}$ and $\mathbf{G_2Por_{12}}$ show two different CH_2S shifts, due to the difference in the coordination environment of the Pd centers. The coordination of pyridine causes a downfield shift of 0.2 ppm relative to the Pd-cyano or Pd-Cl complexes. The intensities of both signals show the expected relative intensities of 1 : 2 for $\mathbf{G_1Por_6}$ and 3 : 4 for $\mathbf{G_2Por_{12}}$.[12] A small difference in chemical shift (Δδ 0.1) upon coordination is also observed for the aromatic protons on the palladated ring ($Ar_{Pd}H$). The signals for the porphyrin ligands are not well-resolved, possibly due to hindered rotation of the porphyrin moieties around the pyridyl–metal bond. FT-IR spectra of $\mathbf{G_1Por_6}$ and $\mathbf{G_2Por_{12}}$ show the characteristic absorption for coordinated CN groups at 2290 cm^{-1}.

So far, porphyrins have been only situated at the surface of the metallodendrimers. However, energy transfer is only possible in a system containing both donor and acceptor sites. This can be realized by assembling dendrimers with a porphyrin in the nucleus (acceptor) and porphyrins on the surface (donors). Therefore, the free base porphyrin **4**, which can be used as a nucleus in the controlled assembly, was synthesized as outlined in Scheme 4. Tetrakisbenzoic acid porphyrin **1** was coupled to pincer ligand **2** *via* esterification using oxalyl chloride. Subsequent cyclopalladation of tetraester **3** with $Pd[CH_3CN]_4(BF_4)_2$ and conversion into the Pd-Cl complex with brine gave **4** in good yields. The MALDI-TOF MS spectrum shows a signal at *m*/z 2636.9 corresponding to $[M + H]^+$ (calcd 2637.0).



Scheme 4

Preliminary experiments showed the possibility to assemble dendrimers with the porphyrin nucleus **4**. Activation of **4** with four equivalents of $AgBF_4$ and addition of four equivalents of MPyrTPP gave the pentameric porphyrin **5**. A nonameric porphyrin array **6** was assembled from **4** and four equivalents of **BBPor** (Scheme 5) also by using controlled assembly.



Scheme 5

The assemblies containing a porphyrin nucleus were characterized using MALDI-TOF mass spectrometry.[13] The MALDI-TOF mass spectrum of **5** shows a signal at *m/z* 4961.0, which is attributed to $[\mathbf{5} - 4BF_4]^+$, (calcd 4961.2). In the spectrum of **6** the signal at *m/z* 11546 corresponds to $[\mathbf{6} - 12BF_4]^+$, (calcd 11546).

UV/VIS spectroscopy of the assemblies described above all show the expected Soret band at 416 nm and the Q bands at 512, 546, 584 and 646 nm.[14] There are no significant shifts for different generations, indicating that the porphyrins at the dendrimer surface do not interact strongly.

In conclusion, the use of non-covalent synthesis provides a simple route to multiporphyrin assemblies. Metallodendrimers constructed *via* controlled assembly can be used as molecular scaffolds to gather a variable number of porphyrins into one supramolecular architecture. Currently, the photophysical properties of the porphyrin assemblies are being studied.

Experimental

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless indicated otherwise) with Me_4Si as internal standard on a Bruker AC 250 spectrometer. Mass spectra (FAB) were recorded with a Finnigan MAT 90 spectrometer using *m*-NBA as the matrix. CH_2Cl_2 was freshly distilled from K_2CO_3. Nitromethane was washed with 1N HCl and water and distilled from $CaCl_2$. Other chemicals were of reagent grade and were used as received. Column chromatography was performed with silica gel 60H (0.005–0.040 mm) from Merck. $Pd[CH_3CN]_4(BF_4)_2$,[15] MPyrTPP and 3,5-bis(phenylthiamethyl)phenol (**2**)[7] were prepared according to literature procedures.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was carried out using a PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer. A 337 nm UV nitrogen laser producing 3 ns pulses was used in the linear and reflectron mode. The samples were prepared by mixing 10 μl of a 50% nitromethane–chloroform solution of the sample with 20 μl of a 3 mg l^{-1} solution of 2-(4-hydroxyphenylazo)benzoic acid in nitromethane. Of this solution 1 μl was loaded on the gold sample plate.

Field desorption (FD) mass spectrometry was carried out using a JEOL SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS/MP7000 data system. Ten micrometer tungsten wire FD emitters containing carbon microneedles with an average length of 30 μm were used. The sample was dissolved in nitromethane and then loaded onto the emitter with the dipping technique. An emitter current of 0–15 mA was used to desorb the sample.

General procedure for the assembly of G_0Por_3, BBPor, G_1Por_6 and G_2Por_{12}

G_0Por_3. Nucleus G_0 (0.075 g, 0.048 mmol) was dissolved in CH_3NO_2–CH_2Cl_2 (1 : 1, 25 mL) and 3 equiv. $AgBF_4$ (0.028 g, 0.114 mmol), dissolved in 0.028 mL water, were added; the reaction mixture was stirred for 15 min. MPyrTPP (0.090 g, 0.146 mmol) was then added in one portion. After stirring for 5 min all the solvent was removed under reduced pressure and the residue dissolved in CH_3NO_2. The product was evaporated to dryness and the process of dissolving and evaporating was repeated twice to ensure complete coordination. Finally, G_0Por_3 was dissolved in CH_3NO_2 and filtered through hyflo/cotton to remove precipitated AgCl, yielding pure G_0Por_3 (0.16 g, 0.048 mmol) quantitatively as a purple solid. mp >280 °C (dec). ^1H NMR (CD_3NO_2, 80 °C) δ 9.04–8.97 (m, 18H, $H_{pyrrolic}$), 8.58–8.50 (m, 12H, $H_{pyrrolic} + Pyr_\alpha H$), 8.29–8.23 (m, 18H, $Ar_{por}H$), 8.10 (br s, 6H, $Pyr_\beta H$), 8.14–8.08 (m, 12H, SPh), 7.90–7.80 (m, 27H, $Ar_{por}H$), 7.62–7.59 (m, 18H, SPh), 7.54 (s, 3H, ArH), 7.08 (s, 6H, $Ar_{Pd}H$), 5.20 (s, 6H, CH_2O), 5.0 (br s, 12H, CH_2S); UV/VIS (λ, CH_3NO_2) 414, 514, 548, 588, 646 nm; FD-MS *m/z* 1097.6 ($[\mathbf{G_0Por_3} - 3BF_4]^{3+}$, calcd 1097.6), 1690.3 ($[\mathbf{G_0Por_3} - 2BF_4]^{2+}$, calcd 1689.9), 3382.9 ($[\mathbf{G_0Por_3} + 3H - 2BF_4]^+$, calcd 3382.8).

BBPor. Purple solid. mp 276–278 °C. ^1H NMR δ 8.96–8.90 (m, 12H, $H_{pyrrolic}$), 8.53–8.49 (m, 8H, $H_{pyrrolic} + Pyr_\alpha H$), 8.29–8.21 (m, 12H, $Ar_{por}H$), 8.10 (d, 4H, $J = 5.9$ Hz, $Pyr_\beta H$), 8.10–8.00 (m, 8H, SPh), 7.89–7.78 (m, 18H, $Ar_{por}H$), 7.65–7.58 (m, 13H, SPh + ArH), 7.50 (s, 2H, ArH), 7.00 (s, 4H, $Ar_{Pd}H$), 5.20 (s, 4H, CH_2O), 5.0 (br s, 8H, CH_2S), 3.92 (s, 2H, CH_2CN); FAB-MS *m/z* 2260.7 ($[\mathbf{BBPor} + H - 2BF_4]^+$, calcd 2260.5); 2348.4 ($[\mathbf{BBPor} + 2H - BF_4]^+$, calcd 2348.3); IR (KBr) 2252 cm^{-1} (C≡N).

G_1Por_6. Purple solid. mp 232–235 °C (dec). ^1H NMR (CD_3NO_2, 80 °C) δ 9.05 (br s, 36H, $H_{pyrrolic}$), 8.58 (br s, 24H, $H_{pyrrolic} + Pyr_\alpha H$), 8.30 (br, 36H, $Ar_{por}H$), 8.08 (br s, 12H, $Pyr_\beta H$), 8.00 (br s, 36H, SPh), 7.90 (br s, 54H, $Ar_{por}H$), 7.50 (br s, 66H, SPh + ArH), 7.05 (br s, 12H, $Ar_{Pd}H$), 6.95 (br s, 6H, $Ar_{Pd}H$), 5.21 (br s, 18H, CH_2O), 5.02 (br s, 24H, CH_2S), 4.83 (br s, 12H, CH_2S), 3.94 (br s, 6H, CH_2CN); UV/VIS (λ, CH_3NO_2) 416, 514, 548, 588, 646 nm; IR (KBr) 2291 cm^{-1} (C≡N).

G_2Por_{12}. Purple solid. mp 221–224 °C (dec). ^1H NMR (CD_3NO_2, 80 °C) δ 9.00 (br s, 72H, $H_{pyrrolic}$), 8.62 (br s, 48H, $H_{pyrrolic} + Pyr_\alpha H$), 8.32 (br, 72H, $Ar_{por}H$), 8.00 (br s, 108H, $Pyr_\beta H$ + SPh), 7.90 (br s, 108H, $Ar_{por}H$), 7.60 (br s, 156H, SPh + ArH), 7.05 (br s, 24H, $Ar_{Pd}H$), 6.91 (br s, 18H, $Ar_{Pd}H$), 5.20 (br s, 42H, CH_2O), 5.06 (br s, 48H, CH_2S), 4.89 (br s, 36H, CH_2S), 3.90 (br s, 18H, CH_2CN); UV/VIS (λ, CH_3NO_2) 416, 514, 548, 588, 646 nm; IR (KBr) 2288 cm^{-1} (C≡N).

Tetraesterporphyrin 3

Tetrakis(carboxyphenyl)porphyrin **1** (50 mg, 0.063 mmol) and oxalyl chloride (1 mL, 13 mmol) were refluxed for 2 h under an Ar atmosphere. The excess of reagent was removed under reduced pressure and the acid chloride dried *in vacuo*. A solution of **2** (240 mg, 0.70 mmol) and Et_3N (0.4 mL, 2.8 mmol) in CH_2Cl_2 (50 mL) was added and the mixture was refluxed for 20 h under Ar atmosphere. After cooling to room temperature, the reaction was quenched with H_2O (25 mL), washed with brine (25 mL) and dried over $MgSO_4$. After concentration, the product was crystallized from CH_2Cl_2–MeOH and further purified by column chromatography (silica gel, CH_2Cl_2), which yielded **3** as a purple solid (42 mg, 32%). mp 180–182 °C. ^1H NMR δ 8.80 (s, 8H, $H_{pyrrolic}$), 8.55 (d, 8H, $J = 6.2$ Hz, $Ar_{por}H$), 8.30 (d, 8H, $J = 6.2$ Hz, $Ar_{por}H$), 7.30–7.15 (m, 52 H, SPh + ArH), 4.10 (s, 16H, CH_2S); FAB-MS *m/z* 2072.7 (M^+, calcd 2072.6). Anal. calcd for $C_{128}H_{94}N_4O_8S_8$, C 74.25; H 4.58; N 2.71%. Found C 74.20; H 4.61; N 2.90%.

Tetrakis(Pd-Cl)porphyrin 4

Ligand **3** (20 mg, 9.66 mol) was dissolved in a 1 : 1 mixture of CH_3CN and CH_2Cl_2 (25 mL) and $Pd[CH_3CN]_4(BF_4)_2$ (17.2 mg, 0.039 mmol) was added in one portion. After stirring for 30 min brine (25 mL) was added and the reaction mixture was stirred overnight. The layers were separated and the organic layer concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, CH_2Cl_2–MeOH 99 : 1) which gave **4** as a purple solid (22.9 mg, 90%). mp 200–201 °C. ^1H NMR δ 8.80 (s, 8H, $H_{pyrrolic}$), 8.55 (d, 8H, $J = 6.2$ Hz, $Ar_{por}H$), 8.30 (d, 8H, $J = 6.2$ Hz, $Ar_{por}H$), 7.99–7.84 (m, 16H, SPh), 7.54–7.41 (m, 24H, SPh), 7.05 (s, 8H, $Ar_{Pd}H$), 4.7 (br s, 16H, CH_2S); MALDI-TOF MS *m/z* 2636.9 ($[M + H]^+$, calcd 2637.0).

References

1 R. W. Wagner, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1996, **118**, 11 166 and references cited therein.

2 *Nanostructures Based on Molecular Materials*, ed. W. Göpel and Ch. Ziegler, VCH, Weinheim, 1992; R. W. Wagner and J. S. Lindsey, *J. Am. Chem. Soc.*, 1994, **116**, 9759; R. W. Wagner, J. S. Lindsey, J. Seth, V. Palaniappan and D. F. Bocian, *J. Am. Chem. Soc.*, 1996, **118**, 3996.
3 D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155.
4 C. M. Drain, K. C. Russell and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1996, 337; J. L. Sessler, B. Wang and A. J. Harriman, *J. Am. Chem. Soc.*, 1995, **117**, 704.
5 X. Chi, A. J. Guerin, R. A. Haycock, C. A. Hunter and L. D. Sarson, *J. Chem. Soc., Chem. Commun.*, 1995, 2567; A. P. H. J. Shenning, F. B. G. Benneker, H. P. M. Geurts, X. Y. Liu and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1996, **118**, 8549; J.-C. Chambron, V. Heitz and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1993, **115**, 12 378; A. M. Brun, S. J. Atherton, A. Harriman, V. Heitz and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1992, **114**, 4632.
6 W. T. S. Huck, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1213; W. T. S. Huck, A. J. R. L. Hulst, P. Timmerman, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1006.
7 W. T. S. Huck, F. C. J. M. van Veggel, B. L. Kropman, D. H. A. Blank, E. G. Keim, M. M. A. Smithers and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 8293.
8 C. A. Hunter and R. H. Hyde, *Angew. Chem., Ind. Ed. Engl.*, 1996, **35**, 1936 and references cited therein.
9 E. B. Fleischer and A. M. Shachter, *Inorg. Chem.*, 1991, **30**, 3763.
10 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, **23**, 1.
11 Direct addition of MPyrTPP to an activated $\mathbf{G}_n$ ($n \geqslant 1$) dendrimer causes scrambling because the strongly coordinating pyrridine ligands displace building blocks that are initially coordinated *via* cyano ligands.
12 The assemblies $\mathbf{G_1Por_6}$ and $\mathbf{G_2Por_{12}}$ gave no intensity at high m/z ratios in the mass spectrometer, probably due to extensive fragmentation.
13 Due to the large number of Pd atoms, signals in the MALDI-TOF spectrum are broadened to 5–10 Da.
14 *The Porphyrins*, ed. D. Dolphin, Academic, New York, 1978/1979, vol. 1–7.
15 A. Sen and L. Ta-Wang, *J. Am. Chem. Soc.*, 1981, **103**, 4627.

Received 6*th February 1997*; *Paper* 7/08323H