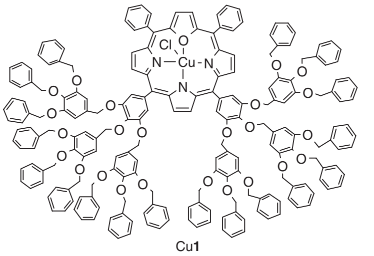
Synthesis and Formation of Supramolecular Spherical Aggregates from Poly(benzyl ether) Dendrimers Having 21-Oxoporphyrin Core

D. Kumaresan and M. Ravikanth*
Department of Chemistry, Indian Institute of Technology, Powai, Mumbai-400 076, India

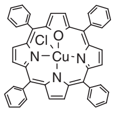
(Received September 4, 2003; CL-030813)

Synthesis of second generation poly(benzyl ether) dendrimers having N_3O porphyrin at its core and the first observation of large micro-meter sized spherical aggregates as confirmed by optical microscopy and AFM analysis are reported.

The formation of supramolecular architectures having well-defined shapes and dimensions by the self-assembly of molecules is a topic of current interest.[1] Dendrimers are attractive building blocks to form such materials due to their well-defined in both molecular weight and architecture. In particular aggregates of dendrimers may serve as micelle mimics, models for biomembranes, drug delivery, chemical sensors, and photosensitive materials.[2] Recently several workers have shown the self aggregation of dendrimers into supramolecular assemblies. Percec et al.[3] have shown that dendrons self-assembled in a thermotropic fashion, Newkome et al.[4] observed the self-assembly of bola-form of arborols in aqueous phases and Aida et al.[5] showed the gel formation with peptide-core ploy(benzyl ether) dendrons in organic solvents to name few recent studies on supramolecular aggregates of dendrons. Interestingly the studies on supramolecular aggregation of dendrimers having chromophores such as porphyrin as core are very few.[6] In this paper, we report the synthesis of second generation poly(benzyl ether) dendron having N_3O porphyrin **1** at its core and the material studies of copper(II) derivative of **1** (Cu**1**) which showed for the first time the formation of self-assembled giant spherical suprastructures upto 7.5 µm size. This kind of large spherical suprastructures were not observed with the copper(II) derivative of N_3O porphyrin without dendron units (Cu**2**).

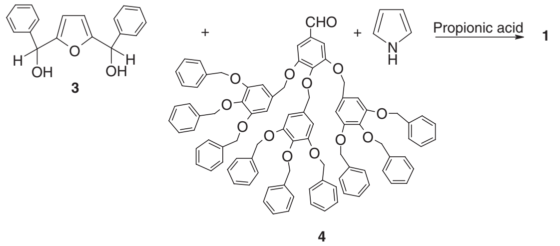


Cu1



Cu2

The methodology for the preparation of porphyrin **1** is outlined in the scheme 1. The bis-alcohol **3** was prepared by treating the dianion of furan with benzaldehyde as reported in the literature.[7] The second generation dendritic wedge having aldehyde functionality **4** (G_2–CHO) was synthesized in 82% yield over sequence of steps of reactions starting from 3,4,5-trihydroxybenzoic acid (gallic acid). The dendritic aldehyde was characterized with ^1H NMR, ^{13}C NMR, infra-red, melting point, mass and elemental analysis.



Scheme 1. Synthetic scheme for the preparation of **1**.

One equivalent of bis-alcohol **3** was condensed with two equivalents of dendritic aldehyde **4** and three equivalents of pyrrole in propionic acid at refluxing temperature for 2 h. The tlc analysis of crude reaction mixture showed the formation of two porphyrins: the desired 21-oxoporphyrin (N_3O) with dendritic wedges in cis fashion **1** and normal porphyrin (N_4) with four dendritic wedges at *meso* positions. The two porphyrins were separated by silica gel column chromatography. The desired porphyrin **1** was collected as second band using CH_2Cl_2/CH_3OH (97:3) and afforded in 4.6% yield.[8] Porphyrin **2** with no dendritic wedges at *meso*-positions was synthesized by following reported procedure.[9] The absorption spectra of **1** and Cu**1** showed typical Q-bands and soret bands with no shift in peak maxima compared to **2** and Cu**2**, respectively indicating that there is no interaction between the dendritic wedge and porphyrin core. In addition to porphyrin bands, a weak absorption around 285 nm due to dendritic wedge was also observed for **1** and Cu**1**. This was not present in **2** and Cu**2**. The fluorescence and excitation spectra of **1** were recorded in toluene. On excitation at 285 nm where the dendritic wedges absorb strongly, showed a weak emission from the dendritic wedge and strong emission from porphyrin unit indicating the energy transfer from dendritic wedges to porphyrin unit. This was further confirmed by excitation spectrum recorded at 730 nm, which was matching exactly with its absorption spectrum. Similar observations were made by others with N_4 porphyrin based dendrimers.[10]

We studied the material properties of **1** and Cu**1**. Most interestingly porphyrin **1** and Cu**1** form supramolecular self-aggregates in chloroform and THF. Porphyrins **1** and Cu**1** in chloroform with concentrations higher than 10^{-5} M was allowed at 20 °C overnight to form translucent solutions. This solution was then spread over onto the glass substrate and analysed by UV–vis spectroscopy. The soret band of the Cu**1** exhibited 11 nm red-shift compared to the soret band of the same observed in solution. This may be attributed to the aggregation of Cu**1** which can be explained by intramolecular exciton coupling arises upon aggregation.[11]

The optical microscopy of 100 µM solutions of Cu**1** in chloroform showed the formation of large and small spherical aggregates upto 7.5 µm size. On the contrary, the optical microscopy of Cu**2** showed the random aggregates. In solution, the

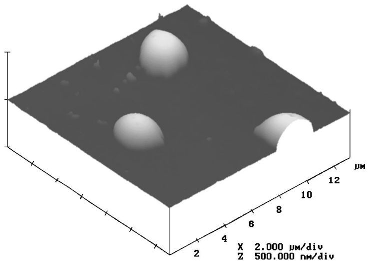


Figure 1. AFM image of Cu**1** on glass substrate.

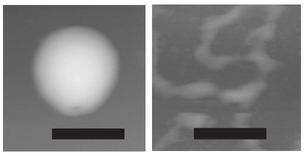


Figure 2. Contact mode AFM images of Cu**1** (left; bar represents 1.25 μm; height scale is 500 nm) and Cu**2** (right; bar represents 1 μm; height scale is 100 nm).

average size of these spherical aggregates of Cu**1** was estimated as 1.30 μm on the basis of time of transition theory. The formation of large spherical suprastructures of Cu**1** was further confirmed by AFM analysis in contact mode (Figure 1). The average size of these assemblies measured from the AFM images is 1.88 μm. The comparison of AFM images of Cu**1** and Cu**2** (Figure 2) indicates that the Cu**1** forms nearly spherical, robust and isolated assemblies on the glass surface. The aggregate structure was more spherical in case of Cu**1** for smaller assemblies and it was slightly deviated for the larger assemblies. The average diameter and average height for larger and smaller assemblies are 2.66/0.36 μm and 0.52/0.135 μm, respectively. However as shown in the Figure 2, Cu**2** forms random aggregates. Thus, the study suggests that the weak van der Waals forces involved between the dendritic wedges and porphyrin–porphyrin interactions could be driving the formation of giant self-assembled spherical aggregates.

In conclusion, we synthesized second generation poly(benzyl ether) based dendrimers having N_3O porphyrin core. The optical microscopy and AFM study indicated that the dendritic wedges assist in the formation of large spherical suprastructures with well-defined dimensions.

We thank BRNS for funding and Mr. S. P. Pai, Mr. U. D. Vaishnav for AFM measurements.

References and Notes

1 a) M. Fischer and F. Vogtle, *Angew. Chem., Int. Ed. Engl.*, **38**, 884 (1999). b) A. W. Bosman, H. M. Janssen, and E. W. Meijer, *Chem. Rev.*, **99**, 1665 (1999). c) J. M. J. Frechet, *Science*, **263**, 1710 (1994).

2 K. Tsuda, G. C. Dol, T. Gensch, J. Hofkens, L. Latterini, J. W. Weener, E. W. Meijer, and F. C. De Schryver, *J. Am. Chem. Soc.*, **122**, 3445 (2000) and references cited therein.

3 V. S. K. Balagurusamy, G. Ungar, V. Percec, and G. Johansson, *J. Am. Chem. Soc.*, **119**, 1539 (1999).

4 G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera, G. H. Escamillia, and M. J. Saunders, *Angew. Chem., Int. Ed. Engl.*, **38**, 884 (1992).

5 W.-D. Jiang, D.-L. Jiang, and T. Aida, *J. Am. Chem. Soc.*, **122**, 3232 (2000).

6 a) N. Tomioka, D. Takasu, T. Takahashi, and T. Aida, *Angew. Chem., Int. Ed. Engl.*, **37**, 1531 (1998). b) H. R. Stapert, N. Nishiyama, D.-L. Jiang, T. Aida, and K. Kataoka, *Langmuir*, **16**, 8182 (2000).

7 Z. Gross, I. Saltsman, R. P. Pandian, and C. M. Barzilay, *Tetrahedron Lett.*, **38**, 2383 (1997).

8 Spectral data for selected compounds **1**: ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 4.90 (s, 48H, CH_2), 6.79 (s, 12H, Ar), 7.03–7.52 (m, 90H, Ar), 7.62–7.79 (m, 10H, Ar), 8.12 (m, 4H, Ar), 8.53 (m, 4H, β-pyrrole), 8.86 (s, 2H, β-pyrrole), 9.19 (s, 2H, β-furan). ESI–MS $C_{212}H_{173}N_3O_{25}$ calcd. av. mass 3162.66, obsd. m/z: 3162.58. UV–vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 288 (105471), 425 (224126), 509 (23005), 543 (7580), 612 (4416), 675 (3955). Cu**1**: Deep greenish purple compound (yield: 81%). UV–vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 292 (32908), 380 (40637), 443 (94800), 549 (12619), 595 (9963), 646 (5132). ESI–MS calcd: 3260.65 obsd m/z: 3259.64 [M$^+$].

9 B. Sridevi, S. J. Narayannan, A. Srinivasan, T. K. Chandrasekar, and J. Subramanian, *J. Chem. Soc., Dalton Trans.*, **1998**, 1979.

10 a) K. W. Pollak, E. M. Sanford, and J. M. J. Frechet, *J. Mater. Chem.*, **8**, 2967 (1998). b) M. S. Matos, J. Hofkens, W. Verheijen, F. C. De Schryver, S. Hecht, K. W. Pillak, J. M. J. Frechet, B. Forier, and W. Dehaen, *Macromolecules*, **33**, 2967 (2000). c) D.-L. Jiang and T. Aida, *J. Am. Chem. Soc.*, **120**, 10895 (1998).

11 H. A. M. Bieman, A. E. Rowan, A. Verhoeven, L. Latterini, J. Foekema, A. P. H. J. Schenning, E. W. Meijer, F. C. De Schryver, and R. J. M. Nolte, *J. Am. Chem. Soc.*, **120**, 11054 (1998).

Published on the web (Advance View) November 10, 2003; DOI 10.1246/cl.2003.1120