

SYNLETT Spotlight 45

DABdendr as a Building Block

Compiled by Joaquín C. García-Martínez



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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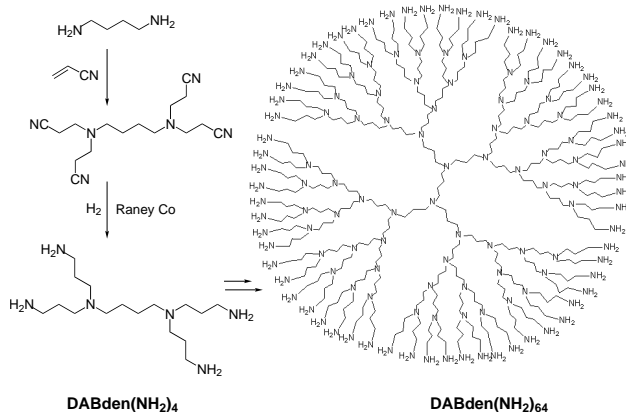
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Introduction

Since dendrimers were first reported, by Tomalia et al.,¹ researchers in the field of dendrimer science have focused primarily on the synthesis and chemical modification of these systems. At present, a wide variety of dendrimers with different properties are known^{2,3} and many of these materials contain poly(propyleneimine) dendrimers (DABdendr) as building blocks. It is well established that the physical properties of dendrimers are determined by the nature of the peripheral groups³ and, in this context, DABdendr systems have been used to prepare compounds for different applications: for example, monolayers on gold,⁴ liquid crystals⁵ or additives to a liquid crystal matrix,⁶ dioxygen binding by copper complexes,⁷ cationic dendrimers for gene delivery,⁸ organometallic photonucleases,⁹ carbohydrate-coated dendrimers,¹⁰ cyclodextrin binding by cobaltocenium-functionalized dendrimers,¹¹ amorphous calcium carbonate stabilizers,¹² photoswitchable supramolecular systems,¹³ guest molecules in encapsulation.¹⁴

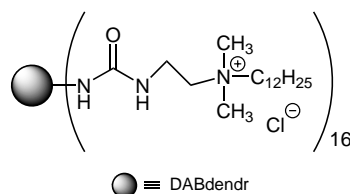
Preparation

The first approach to the synthesis of DABdendr was reported by Vögtle.¹⁵ However, procedures for the large-scale preparation of these materials in their different generations was first described by Wörner and Mühlaupt¹⁶ and, independently, de Brabander-van den Berg and Meijer (in back-to-back manuscripts) in 1993.¹⁷ The synthetic route is shown in the scheme below. Today, DABdendr materials are commercially available up to the fifth generation.

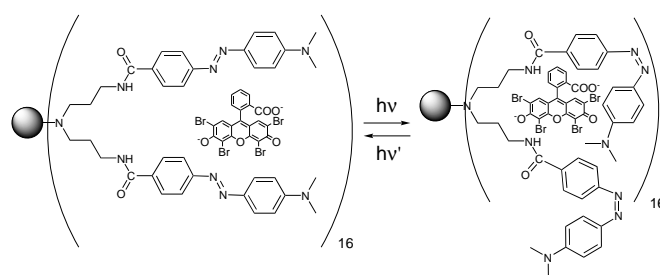


Abstracts

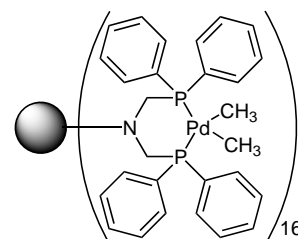
Dimethyldodecylammonium chloride-functionalized third generation DABdendr systems have proven to have strong anti-bacterial properties. These compounds are over two orders of magnitude more potent against *Escherichia coli* than their low molecular weight counterpart (*n*-dodecyltrimethylammonium chloride).¹⁸



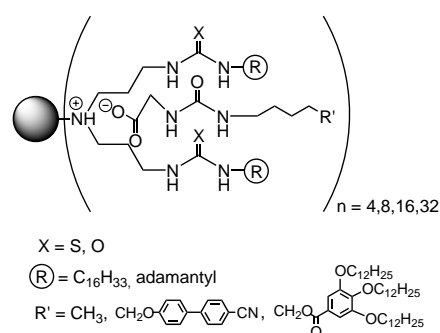
Since the first report of a *dendritic box*,¹⁹ the open and close control of dendrimers has been the focus of many research groups. Balzani and Vögtle²⁰ have described a fourth generation DABdendr bearing up to 32 photoisomerizable azobenzene groups in the periphery. These materials have been used as potential hosts for Eosin Y. The all-*E* azobenzene dendrimers can be reversibly switched to their *Z* form by light excitation. Eosin is hosted more efficiently by the dendrimers in the *Z* form than the *E* form.



Test experiments involving the Heck reaction have demonstrated that dendritic diphosphane palladium complexes have a significantly higher catalytic activity (typically, turnover numbers of 50 versus 16 for the parent compound). This phenomenon is attributable to the higher thermal stability of the dendritic complexes. After precipitation from the reaction mixture, the isolated Pd-containing dendrimer was reused in the same reaction and displayed comparable catalytic activity.²¹



DABdendr systems have been modified by the incorporation of palmityl and adamantyl endgroups through either a thiourea or urea linkage. The resulting materials have been used as multivalent hosts in organic solvents for a number of guest molecules containing a terminal urea-glycine unit, with multiple secondary interactions (hydrogen and ionic bondings) being responsible for the guest-host compatibility.²²



References

- (1) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryeder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117.
- (2) (a) Fischer, M.; Vögtle, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 885. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, **2001**.
- (3) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.
- (4) (a) Noble, C. O. I. V.; McCarley, R. L. *J. Am. Chem. Soc.* **2000**, *122*, 6518. (b) Noble, C. O. I. V.; McCarley, R. L. *Org. Lett.* **1999**, *1*, 1021.
- (5) Yonetake, K.; Masuko, T.; Morishita, T.; Suzuki, K.; Ueda, M. *Macromolecules* **1999**, *32*, 6578.
- (6) Baars, M. W. P. L.; van Boxtel, M. C. W.; Bastiaansen, C. W. M.; Broer, D. J.; Söntjens, S. H. M.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 715.
- (7) Klein-Gebbink, R. J. M.; Bosman, A. W.; Feiters, M. C.; Meijer, E. W.; Nolte, R. J. M. *Chem.–Eur. J.* **1999**, *5*, 65.
- (8) Ren, T.; Zhang, G.; Liu, D. *Tetrahedron Lett.* **2001**, *42*, 1007.
- (9) Hurley, A. L.; Moler, D. L. *Org. Lett.* **2000**, *2*, 2745.
- (10) Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Nepogodiev, S. A.; Meijer, E. W.; Peerlings, H. W. I.; Stoddart, J. F. *Chem.–Eur. J.* **1997**, *3*, 974.
- (11) González, B.; Casado, C. M.; Alonso, B.; Cuadrado, I.; Morán, M.; Wang, Y.; Kaifer, A. E. *Chem. Commun.* **1998**, 2569.
- (12) Donners, J. J. J. M.; Heywood, B. R.; Meijer, E. W.; Nolte, R. J. M.; Roman, C.; Schenning, A. P. H. J.; Sommerdijk, N. A. J. M. *Chem. Commun.* **2000**, 1937.
- (13) (a) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S.; Berg, R. H. *Chem.–Eur. J.* **1998**, *4*, 699. (b) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V. *J. Am. Chem. Soc.* **1998**, *120*, 12187. (c) Stephan, H.; Spies, H.; Johannsen, B.; Kauffmann, C.; Vögtle, F. *Org. Lett.* **2000**, *2*, 2343. (d) Tsuda, K.; Gensch, T.; Hofkens, J.; Latterini, L.; Weener, J. W.; Meijer, E. W.; De Schryver, F. C. *J. Am. Chem. Soc.* **2000**, *122*, 3445. (e) Dol, G. C.; Tsuda, K.; Weener, J. W.; Bartels, M. J.; Asavei, T.; Gensch, T.; Hofkens, J.; Latterini, L.; Schenning, A. P. H. J.; Meijer, E. W.; De Schryver, F. C. *Angew. Chem. Int. Ed.* **2001**, *40*, 1710.
- (14) (a) Schenning, A. P. H. J.; Elissen-Román, C.; Weener, J. W.; Baars, M. W. P. L.; van der Gaast, S. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 8199. (b) Pistolis, G.; Malliaris, A.; Tsiourvas, D.; Paleos, C. M. *Chem.–Eur. J.* **1999**, *5*, 1440. (c) Pan, Y.; Ford, W. T. *Macromolecules* **2000**, *33*, 3731.
- (15) Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155.
- (16) Wörner, C.; Mülhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1306.
- (17) de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308.
- (18) Chen, C. Z.; Tan, N. C. B.; Cooper, S. L. *Chem. Commun.* **1999**, 1585.

- (19) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.
- (20) Archut, A.; Azellini, G. C.; Balzani, V.; De Cola, L.; Vögtle, F. *J. Am. Chem. Soc.* **1998**, *120*, 12187.
- (21) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1526.
- (22) (a) Baars, M. W. P. L.; Karlsson, A. J.; Sorokin, V.; de Waal, B. F. W.; Meijer, E. W. *Angew. Chem. Int. Ed.* **2000**, *39*, 4262. (b) Boas, U.; Karlsson, A. J.; de Waal, B. F. M.; Meijer, E. W. *J. Org. Chem.* **2001**, *66*, 2136.