Figure 4a shows the AFM image of one partially obscured $\{001\}_h$ face of EMT. The hexagonal nature of the face with edge length about 0.6 µm is immediately apparent. Though the overall terrace topology on the crystal surface is not as well defined as for FAU, both a hexagonal nature and a diminishing terrace width towards the edge of the crystal are evident. This hexagonal terrace morphology is a consequence of the symmetry generated along the $[001]_h$ direction by the ABAB stacking of faujasite layers. Although individually the A and B layers have threefold symmetry (see Scheme 1) they are rotated with respect to one another by 60° thereby generating a pseudo sixfold axis. Section analysis again reveals that the terraces are approximately 1.5 nm thick and this thickness is highly uniform. The growth terraces of the EMT structure are less well defined than those of the FAU structure which is a reflection of the larger number of defects in EMT than FAU.[7]

## *Experimental Procedure*

The zeolites were synthesized in the system $10SiO_2:1.0Al_2O_3:2.4Na_2O:140H_2O:1.0$ crown ether. The sources of material were 40 wt% colloidal silica (HS-40 Ludox); 40 wt% sodium aluminate solution; [15]crown-5 and [18]crown-6 (Aldrich). Gels were aged for two days at room temperature followed by crystallization in Teflon bottles for eight days at 95 °C.

AFM images were recorded on a Nanoscope Multimode Microscope from Digital Instruments operating in TappingMode. Samples were secured on an adhesive surface to prevent lateral movement. A first order planefit was conducted on the images in the *x* and *y* directions to level the crystal terraces, and simulated illumination is used to emphasize the crystal steps. Dark areas around crystal edges are due to the surface topography possessing a greater slope than the side of the tip. Thus, these areas contain information on the tip shape only and do not contain topographical information.

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[1] E. Delprato, L. Delmotte, J. L. Guth, L. Huve, *Zeolites* **1990**, *10*, 546–552.

[2] C. Baerlocher, L. B. McCusker, R. Chiapetta, *Microporous Mater.* **1994**, *2*, 269-280.

[3] D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, **1974**, p.56.

[4] J. M. Thomas, M. Audier, J. Klinowski, *J. Chem. Soc. Chem. Commun.* **1981**, 1221–1222; M. M. J. Treacy, J. M. Newsam, R. A. Beyerlein, M. E. Leonowicz, D. E. W. Vaughan, *ibid.* **1986**, 1211–1213; J. M. Newsam, M. M. J. Treacy, D. E. W. Vaughan, K. G. Stohmaier, W. J. Mortier, *ibid.* **1989**, 493–495; J. A. Martens, P. A. Jacobs, S. Cartlidge, *Zeolites* **1989**, *9*, 423–427; S. Ernst, G. T. Kokotailo, J. Weitkamp, *ibid.* **1987**, *7*, 180–182; M. M. J. Treacy, J. M. Newsam, D. E. W. Vaughan, R. A. Beyerlein, S. B. Rice, C. B. deGruyter, *Mater. Res. Soc. Symp. Proc.* **1988**, *111*, 177–190; D. E. W. Vaughan (Exxon), *Eur. Pat. Appl.* 315461, **1988** (*Chem. Abstr. 108*, 115126m); D. E. W. Vaughan, M. G. Barret (Exxon), US-A 4333859, **1982** (*Chem. Abstr. 98*, 75170n); J. Jiric (Mobil Oil), *ibid.* 3972983, **1976** (*Chem. Abstr. 86*, 92954r), *ibid.* 4021331, **1977** (*Chem. Abstr. 86*, 195783p); V. Fülöp, G. Borbély, H. K. Beyer, S. Ernst, J. Weitkamp, *J. Chem. Soc. Faraday Trans. 1* **1989**, *85*, 2127–2139.

[5] M. W. Anderson, K. S. Pachis, F. Prébin, S. W. Carr, O. Terasaki, T. Ohsuna, V. Alfredsson, *J. Chem Soc. Chem Commun.* **1991**, 1660–1664.

[6] O. Terasaki, T. Ohsuna, V. Alfredsson, J.-O. Bovin, D. Watanabe, S. W. Carr, M. W. Anderson, *Chem. Mater.* **1993**, *5*, 452–458.

[7] T. Ohsuna, O. Terasaki, V. Alfredsson, J.-O. Bovin, D. Watanabe, S. W. Carr, M. W. Anderson, *Proc. R. Soc. London A*, in press.

[8] J. P. Arhancet, M. E. Davis, *Chem. Mater.* **1991**, *3*, 567–569.

[9] S. L. Burkett, M. E. Davis, *Microporous Mater.* **1993**, *1*, 265–282.

[10] A. L. Weisenhorn, J. E. MacDougall, S. A. C. Gould, S. D. Cox, W. S. Wise, J. Massie, P. Maivald, V. B. Elings, G. D. Stucky, P. K. Hansma, *Science* **1990**, *247*, 1330–1333; J. E. MacDougall, S. D. Cox, G. D. Stucky, A. L. Weisenhorn, P. K. Hansma, W. S. Wise, *Zeolites* **1991**, *11*, 429–433; M. Komiyama, T. Yashima, *Jpn J. Appl. Phys. Part 1* **1994**, *33*, 3761–3763.

[11] S. Manne, J. P Cleveland, G. D. Stucky, P. K. Hansma, *J. Cryst. Growth* **1993**, *130*, 333–340; S. D. Durbin, W. E. Carlson, *ibid.* **1992**, *122*, 71–79.

[12] P. E. Hillner, A. J. Gratz, S. Manne, P. K. Hansma, *Geology* **1992**, *20*, 359–362; P. E. Hillner, S. Manne, A. J. Gratz, P. K. Hansma, *Ultramicroscopy* **1992**, *42*, 1387–1393; A. J. Gratz, S. Manne, P. K. Hansma, *Science* **1991**, *251*, 1343–1346.

[13] W. K. Burton, N. Cabrera, F. C. Frank, *Phil. Trans. R. Soc. A* **1951**, *243*, 299–358.

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# Controlled Assembly of Nanosized Metallodendrimers[**]

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There is considerable interest in the synthesis of well-defined structures of nanometer dimensions.[1] These structures can be constructed by formation of covalent bonds, but this requires multistep synthesis.[2] Therefore, various other strategies have been developed that rely on self-assembly through noncovalent interactions, for example hydrogen bonds. Whitesides et al.[3] obtained stable rosettelike structures constructed of melamine and barbituric acid units held together by strong hydrogen bonds. The nanotubular assemblies prepared by Ghadiri et al.[4] are another beautiful example of hydrogen-bonded assemblies. Dative bonds to transition metals can also be employed in self-assembly. Lehn et al. have applied the coordination of oligopyridines to transition metals to form triple helices, ladder polymers, and molecular grids.[5] Previously, we have described the self-assembly of small aggregates and ribbonlike polymers using the uranyl cation.[6] In this paper we describe the synthesis of metallodendrimers by controlled assembly.

Dendrimers are attractive, nanosize compounds with very specific architectures.[7, 8]] Dendrimers can be synthesized by following either a convergent or a divergent route,[9] in which an increasing number of new covalent bonds are formed in each generation. A few dendrimers containing transition metals have been reported.[10] Van Koten et al.[11] have used metalated dendrimers as homogeneous catalysts. Balzani and co-workers reported the synthesis of metallodendrimers containing transition metals in every generation, which relied on sequential reactions on the metal centers and protection/deprotection of ligands.[12] In contrast, Achar and Puddephat built dendrimers by oxidative additions to $Pt^{II}$ complexes.[13]

We have recently described the synthesis of large organopalladium spheres by "genuine" self-assembly.[14] Now we report here that we can control this process and use this method for the synthesis of first-, second-, and third-generation metallodendrimers. Our approach is based on controlled assembly of building blocks that contain all the necessary information. We make use of the coordination chemistry of $Pd^{II}$ and have combined in building block **BB-Cl** two kinetically inert tridentate "pincer-type" ligands and one labile coordinating cyano group (Scheme 1). The nucleus $\mathbf{G_0}$ has in this case $C_3$ symmetry with three Pd centers.

The temporary protection of the metal center by a strongly coordinating $Cl^-$ ion prevents coordination by cyano groups. Further growth of Pd complex $\mathbf{G_0}$ is achieved by replacing the $Cl^-$ ion for a noncoordinating $BF_4^-$ ion, by reaction with $AgBF_4$. Subsequent addition of three equivalents of the protected building block **BB-Cl** yields the next generation dendrimer $\mathbf{G_1}$. By repeating this sequence twice it is possible to build the third-generation metallodendrimer $\mathbf{G_3}$.

The synthesis of **BB-Cl** and $\mathbf{G_0}$ is outlined in Scheme 2. The S-C-S pincer ligand was prepared in seven steps from dihydroxy-

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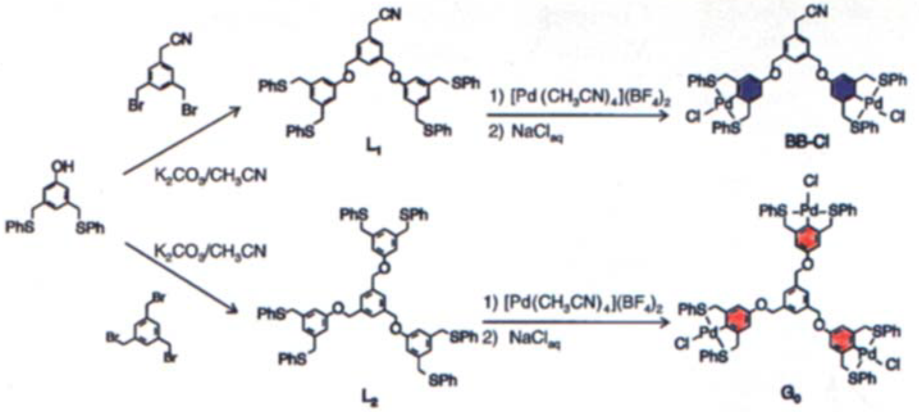
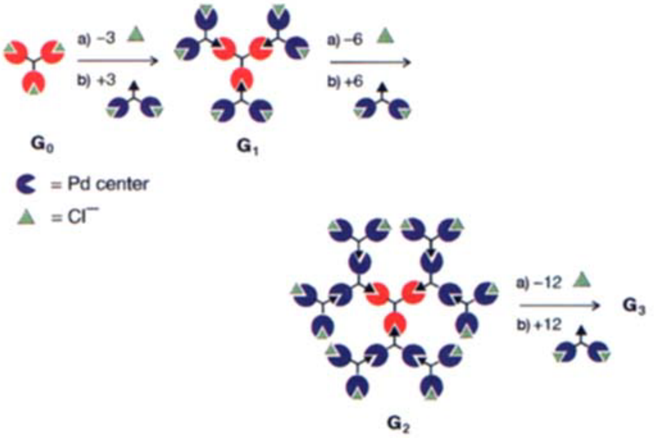


Scheme 1. Graphical representation of the controlled assembly process.



Scheme 2. Synthesis of dendrimer building blocks.

isophthalic acid.[14] The pincer ligands were coupled to a tribromomesitylene spacer to afford the nucleus $\mathbf{L_2}$, or to dibromomonocyanomesitylene to yield the dendrimer building block $\mathbf{L_1}$. Simple cyclopalladation of $\mathbf{L_1}$ and $\mathbf{L_2}$ with $[Pd(CH_3CN)_4(BF_4)_2]$[15] gave in quantitative yield the bis- and trispalladium complexes, which were directly converted into the chloride complexes **BB-Cl** and $\mathbf{G_0}$, respectively, by stirring with aqueous NaCl. The palladation is quantitative and occurs exclusively at the position activated by both S donor atoms, as can be deduced from $^1$H NMR spectroscopy. A broad singlet at $\delta = 4.4$ for the $CH_2S$ protons reflects the slow conformational interconversion of the five-membered Pd cycle, and the absence of a singlet at $\delta = 6.85$ indicates complete cyclopalladation. After purification by column chromatography (silica gel, eluting with $CH_2Cl_2$/MeOH 97/3) **BB-Cl** and $\mathbf{G_0}$ were obtained in yields of 70 and 40%, respectively.

Nucleus $\mathbf{G_0}$ was activated by stirring with three equivalents of $AgBF_4$ in $CH_2Cl_2$/nitromethane (1/1), and three equivalents of **BB-Cl** were added to form the assembly $\mathbf{G_1}$. Repeating the same procedure yielded in a very simple way metallodendrimers $\mathbf{G_2}$ and $\mathbf{G_3}$. These complexes were purified by filtration over hyflo and column chromatography (silica gel reversed phase, eluting with nitromethane) to remove the precipitated silver chloride. The yellow-colored metallodendrimers were obtained as a single fraction in quantitative yield after chromatography. The synthesis of an $n$th generation metallodendrimer is a one-pot procedure, because intermediate generations need not be isolated. The assembly process is controlled by the repetitive addition of $AgBF_4$ and **BB-Cl**. Dendrimers $\mathbf{G_1}$–$\mathbf{G_3}$ were fully characterized by $^1$H and $^{13}$C NMR and FT-IR spectroscopy,[16] electrospray mass spectrometry (ES-MS), and elemental analysis (Table 1).

The $^1$H NMR spectra of $\mathbf{G_1}$–$\mathbf{G_3}$ are remarkably simple because of the high symmetry of the nucleus and the similarity of the building blocks. The formation of the desired compounds can be deduced from the ratios of the intensities of the signals of the $CH_2CN$ and $CH_2O$ protons, which is 1:3 for $\mathbf{G_1}$, 3:7 for $\mathbf{G_2}$, and 1:2 for $\mathbf{G_3}$. The signals in the $^1$H NMR spectrum of $\mathbf{G_3}$ show some broadening, indicating the restricted motion of the inner generations. The $^{13}$C NMR spectra show no shifts on going from $\mathbf{G_0}$ to $\mathbf{G_3}$.[17]

Molecular masses were determined by ES-MS. The transformed ES mass spectra (Fig. 1)[18] show signals at $m/z$ 1516.2

Table 1. Selected physical data for $\mathbf{G_0}$–$\mathbf{G_3}$.

$\mathbf{G_0}$: M.p. 164–166 °C; $^1$H NMR ($CDCl_3$): $\delta = 7.81$ (m, 12H; $Ar_SH$), 7.39 (s, 3H; ArH), 7.35 (m, 18H; $Ar_SH$), 6.63 (s, 6H; $Ar_{Pd}H$), 4.93 (s, 6H; $CH_2O$), 4.53 (br. s, 12H; $CH_2S$); $^{13}$C NMR ($CDCl_3$): $\delta = 156.5$, 150.2, 137.7, 132.3, 131.4, 129.8, 129.7, 109.2, 69.8, 51.7; ES-MS: $m/z$: 1516.2 $[M-Cl]^+$. Analysis: calcd for $C_{69}H_{57}O_3S_6Pd_3Cl_3\cdot H_2O$: C 52.78, H 3.79; found: C 52.51, H 3.70.

$\mathbf{G_1}$: M.p. 154–157 °C; $^1$H NMR ($CD_3NO_2$): $\delta = 7.63$ (m, 36H; $Ar_SH$), 7.45 (s, 3H; ArH), 7.40 (s, 9H; ArH), 7.29 (m, 54H; $Ar_SH$), 6.62 (s, 18H; $Ar_{Pd}H$), 4.93 (s, 18H; $CH_2O$), 4.49 (br. s, 36H; $CH_2S$), 3.78 (s, 6H; $CH_2CN$); $^{13}$C NMR ($CD_3NO_2$, 80 °C): $\delta = 153.1$, 147.0, 145.8, 134.9, 128.3, 127.9, 126.4, 125.8, 106.1, 46.2, 19.8; ES-MS: $m/z$: 4759.5 $[M-2Cl-2BF_4]^+$. Analysis calcd for $C_{219}H_{177}B_3N_3O_9F_{12}S_{18}Cl_6Pd_9\cdot CH_3NO_2$: C 51.47, H 3.58, N 1.11, Cl 4.20; found: C 51.99, H 3.74, N 1.33, Cl 4.09.

$\mathbf{G_2}$: M.p. 148–152 °C; $^1$H NMR ($CD_3NO_2$): $\delta = 7.75$ (m, 84H; $Ar_SH$), 7.4 (m, 156H; ArH), 6.75 (s, 42H; $Ar_{Pd}H$), 5.00 (s, 42H; $CH_2O$), 4.54 (br. s, 84H; $CH_2S$), 3.89 (s, 18H; $CH_2CN$); $^{13}$C NMR ($CD_3NO_2$, 80 °C): $\delta = 153.1$, 147.0, 145.8, 134.9, 128.2, 127.9, 126.5, 125.8, 122.8, 106.1, 66.2, 46.2, 19.8; ES-MS: $m/z$: 11907.0 $[M]^+$. Analysis calcd for $C_{519}H_{426}B_9N_9O_{21}F_{36}S_{42}Cl_{12}Pd_{21}\cdot 2CH_3NO_2$: C 51.99, H 3.62, N 1.29, Cl 3.53; found: C 51.74, H 3.75, N 1.86, Cl 3.16.

$\mathbf{G_3}$: M.p. 139–142 °C; $^1$H NMR ($CD_3NO_2$): $\delta = 7.7$ (m, 180H; $Ar_SH$), 7.5 (m, 336H; ArH), 6.8 (s, 90H; $Ar_{Pd}H$), 5.0 (s, 90H; $CH_2O$), 4.5 (br. s, 180H; $CH_2S$), 3.9 (s, 42H; $CH_2CN$); $^{13}$C NMR ($CD_3NO_2$, 80 °C): $\delta = 153.1$, 147.0, 145.8, 134.9, 128.2, 127.9, 126.5, 125.8, 122.8, 106.1, 66.2, 46.2, 19.8; ES-MS: $m/z$: 24032 $[M-19BF_4]+$. Analysis calcd for $C_{1119}H_{918}B_{21}N_{21}O_{45}F_{84}S_{90}Cl_{24}Pd_{45}\cdot 10CH_3NO_2$: C 51.16, H 3.60, N 1.74, Cl 3.22; found: C 51.16, H 3.61, N 2.22, Cl 3.21.

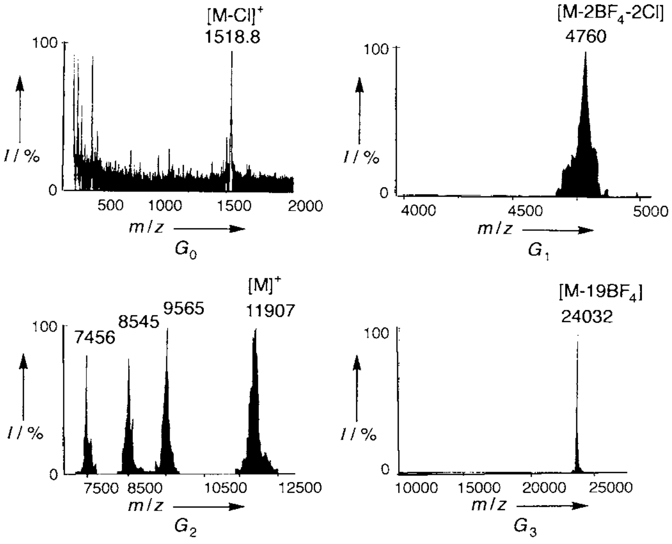


Fig. 1. ES mass spectra for $\mathbf{G_1}$–$\mathbf{G_3}$.

($[G_0 - Cl]^+$), 4783.5, ($[G_1 - Cl - 2\,BF_4]^+$), 11907.0 ($[G_2]^+$) and 24030.2 ($[G_3 - 19\,BF_4]^+$). The loss of anions takes place inside the mass spectrometer, generating the multiply charged ions needed for detection and calculation of the molecular weight.[19]

Molecular mechanics calculations[20] were performed on $G_0$–$G_3$. The square-planar coordination environment of the Pd centers is well preserved. It is clear that after the second generation the structure of the dendrimer becomes quite entangled (Fig. 2).

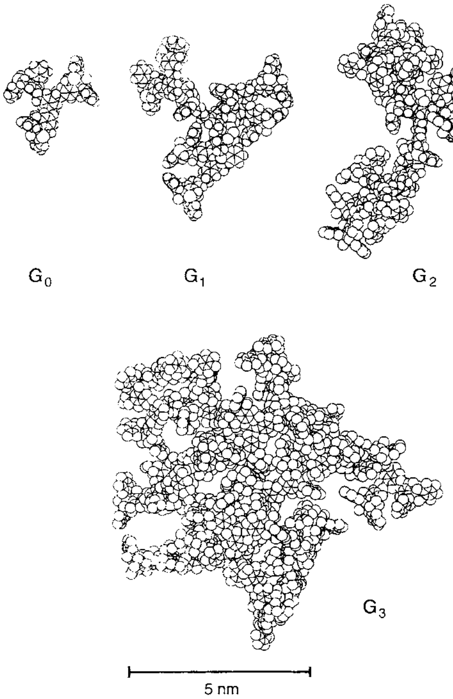


Fig. 2. Optimized structures of $G_0$–$G_3$.

We have shown that organometallic structures of nanometer dimensions can now be constructed in a very simple and controlled way. This method of controlled assembly provides a new and versatile tool for dendrimer synthesis. The method allows large variation in the metal in each generation, the coordinating ligands, and the structure of the nucleus.

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[1] Review: G. Ozin, *Adv. Mater.* **1992**, *15*, 612–648.

[2] For the synthesis of a receptor molecule with a nanosize cavity see: P. Timmerman, W. Verboom, F. C. J. M. van Veggel, W. P. van Hoorn, D. N. Reinhoudt, *Angew. Chem.* **1994**, *106*, 1313–1316; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1292–1295.

[3] J. P. Mathias, E. E. Simanek, G. M. Whitesides, *J. Am. Chem. Soc.* **1994**, *116*, 4326–4340.

[4] N. Khazanovich, J. R. Granja, D. E. McRee, R. A. Milligan, M. R. Ghadiri, *J. Am. Chem. Soc.* **1994**, *116*, 6011–6012.

[5] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**, pp. 139–197, and references therein.

[6] D. M. Rudkevich, W. Verboom, Z. Brzøzka, M. J. Palys, W. P. R. V. Stauthamer, G. J. van Hummel, S. M. Franken, S. Harkema, J. F. J. Engbersen, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1994**, *116*, 4341–4351.

[7] D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem.* **1990**, *102*, 119–156; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138–175.

[8] J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, *266*, 1226–1229.

[9] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7642.

[10] Y. H. Liao, J. R. Moss, *J. Chem. Soc. Chem. Commun.* **1993**, 1774–1777; G. R. Newkome, F. Cardullo, E. C. Constable, C. N. Moorefield, A. M. W. Cargill Thompson, *ibid.* **1993**, 925–927; M. F. Ottaviani, S. Bossmann, N. J. Turro, D. A. Tomalia, *J. Am. Chem. Soc.* **1994**, *116*, 661–671; A. Miedaner, C. J. Curits, R. M. Barkley, D. L. Dubois, *Inorg. Chem.* **1994**, *33*, 5483–5498; G. R. Newkome, R. Guther, C. N. Moorefield, F. Cardullo, L. Echegoyen, E. Peréz-Cordero, H. Luftmann, *Angew. Chem.* **1995**, *107*, 2159–2162; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2023–2026.

[11] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659–662.

[12] S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto, V. Balzani, *Chem. Eur. J.* **1995**, *1*, 211–221.

[13] S. Achar, R. J. Puddephat, *Angew. Chem.* **1994**, *106*, 895–897; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 847–849.

[14] W. T. S. Huck, F. C. J. M. van Veggel, B. L. Kropman, D. H. A. Blank, E. G. Keim, M. M. A. Smithers, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 8293–8294.

[15] S. J. Loeb, G. K. H. Shimizu, *J. Chem. Soc. Chem. Commun.* **1993**, 1395–1397.

[16] Coordination of the cyano group is deduced from the characteristic shift from 2252 cm$^{-1}$ (free C≡N) to 2290 cm$^{-1}$ upon coordination. B. N. Storhoff, H. C. Lewis, *Coord. Chem. Rev.* **1977**, *23*, 1–23.

[17] M. H. P. van Genderen, M. W. P. L. Baars, J. C. M. van Hest, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 573–574.

[18] The signals at lower $m/z$ values in the spectrum of $G_2$ correspond to species after the respective loss of one, two, and three dendrimer building blocks and corresponding anions.

[19] Examples of loss of counterions are known from literature: E. Leize, A. van Dorsselaer, R. Krämer, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1993**, 990–993; G. Hopfgarter, C. Piguet, J. D. Henion, A. F. Williams, *Helv. Chim. Acta* **1993**, *76*, 1759–1766.

[20] Universal Force Field in the Cerius$^2$ program package: A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard, III, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.

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# Molecular Boxes Based on Calix[4]arene Double Rosettes**

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The construction of noncovalently bonded, well-defined aggregates has received increasing attention over the last few years. The study of molecular self-assembly is expected to provide information on how interactions between molecular functionalities lead to entities with new shapes and functions. The shapes of recently described ensembles range from boxes[1, 2] and channels[3] to more complex three-dimensional networks and other discrete aggregates.[4–6] Reported molecular boxes based on noncovalent interactions all have rather small cavities, since they result from the dimerization of two molecules with concave structures.[2] Recently we prepared receptors with large hydrophobic cavities by the covalent combination of calix[4]arenes and resorcin[4]arenes.[7] The successful synthesis

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