this type of coordination complex to real applications which depend on easily distinguished "on" and "off" signals. Studies on the immobilization of these complexes on appropriate conducting surfaces are underway.

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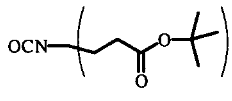
[1] J. M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, **1995**.
[2] N. P. M. Huck, W. F. Jager, B. de Lange, B. L. Feringa, *Science* **1996**, *273*, 1686–1688.
[3] L. Fabbrizzi, A. Poggi, *Chem. Soc. Rev.* **1995**, 197–202.
[4] L. Zelikovich, J. Libman, A. Shanzer, *Nature* **1995**, *374*, 790–792.
[5] J. A. Wytko, C. Boudon, J. Weiss, M. Gross, *Inorg. Chem.* **1996**, *35*, 4469–4477.
[6] R. A. Bissell, E. Cordova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137.
[7] A. Livoreil, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 9399–9400.
[8] S. H. Kawai, S. L. Gilet, R. Ponsinet, J. M. Lehn, *Chem. Eur. J.* **1995**, *1*, 285–293, and references therein.
[9] *Circular Dichroism: Principles and Applications* (Eds.: K. Nakanishi, N. Berova, R. W. Woody), VCH, New York, **1994**.
[10] A. Mi, X. Xiao, L. Wu, Y. Jiang, *Synthetic Commun.* **1991**, *21*, 2207–2212.
[11] N. Wei, N. N. Murthy, Q. Chen, J. Zubieta, K. D. Karlin, *Inorg. Chem.* **1994**, *33*, 1953–1965.
[12] Elemental analyses: **1** ($CuC_{31}H_{26}N_4PF_6$): calcd: C 56.15, H 3.95, N 8.45; found: C 55.91, H 3.75, N 8.35; **2**: ($CuC_{31}H_{26}N_4O_4PF_6Cl$): calcd: C 48.83, H 3.43, N 7.35; found: C 49.10, H 3.61, N 7.34. Complexes **3** and **4** were prepared in situ from **1** and **2**, respectively, and NH_4NCS.
[13] N. Wei, N. N. Murthy, K. D. Karlin, *Inorg. Chem.* **1994**, *33*, 6093–6100.
[14] M. Herve, A. Garnier, L. Tosi, M. Steinbuch, *Eur. J. Biochem.* **1981**, *116*, 177–183.
[15] For example, **1** is reduced in MeCN at $E_{1/2} = -49.9$ mV (reference: $Fc/Fc^+ = 45.6$ mV; Fc = ferrocene). The cyclic voltammogram was measured under N_2 with a standard three-electrode apparatus (glassy-carbon working electrode, Pt-wire auxiliary electrode, and 0.1 M $AgNO_3$ in MeCN as reference electrode) with 0.1 M nBu_4NPF_6 as supporting electrolyte and a scan rate of 50 mV s^{-1}. Addition of SCN^- to the solution resulted in a shift in $E_{1/2}$ of -250 mV and afforded an improvement in the reversibility of the voltammograms. There was no indication of oxidation or reduction of SCN^- under the conditions of the experiment.
[16] Amplitude (A): difference in the $\Delta\varepsilon$ values for the two extrema of split CD curves ($A = |\Delta\varepsilon_{1C.E.}| + |\Delta\varepsilon_{2C.E.}|$).
[17] W. Kauzmann, F. B. Clough, I. Tobias, *Tetrahedron* **1961**, *13*, 57–105.
[18] J. W. Canary, C. S. Allen, J. M. Castagnetto, Y. Wang, *J. Am. Chem. Soc.* **1995**, *117*, 8484–8485.
[19] NH_4NCS was added after every oxidation to correct for loss of NCS^- through oxidation. Oxidation at a controlled potential avoided this problem.
[20] H. Nagao, N. Komeda, M. Mukaida, M. Suzuki, K. Tanaka, *Inorg. Chem.* **1996**, *35*, 6809–6815.

Isocyanate-Based Dendritic Building Blocks: Combinatorial Tier Construction and Macromolecular-Property Modification[**]

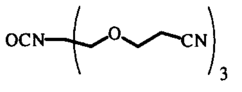
George R. Newkome,[*] Claus D. Weis, Charles N. Moorefield, Gregory R. Baker, Bradley J. Childs, and Jon Epperson

In the current development of dendritic chemistry[1] the application of iterative technology is being examined from many different perspectives. These areas include the use of dendrimers and related materials as unimolecular micelles,[2] ordered network building blocks,[3] chromatography additives,[4] cancer therapeutics,[5] and electrically conducting materials.[6] Central to the construction of these macromolecular assemblies is the design and tuning of properties such as solubility, viscosity, and reactivity for specific applications. Hence it is desirable to design synthetic methods for the ready introduction of functionally diverse terminal groups.

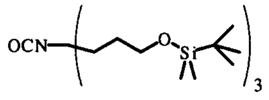
Recently we reported the synthesis of the stable isocyanate triester **1** and its use as a building block in the rapid "dendrimerization" of protic materials and surfaces.[7] In addition, we disclosed the syntheses of the related branched monomers[8] **2**–**5**. Each of these monomers possesses a triad of protected functional groups, an sp^3 C-branching center and a reactive isocyanate moiety. We herein report on the concept of the rapid modification of properties through combinatorial synthesis analogous to that used for the discovery of novel solid-state materials,[9] biologically active substrates,[10] and artificial receptors.[11] While dendrimers have recently been employed[12] and touted[13,14] as vehicles for the generation of standard small-molecule libraries, our combinatorial method relies on mixtures of AB_3-type monomers having varying compositions of different, yet mutually compatible building



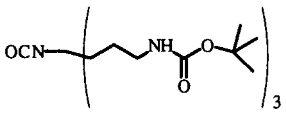
1 [BA]



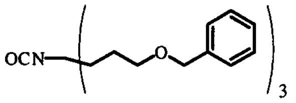
2 [CN]



3 [Si]



4 [N-*t*-BOC]



5 [BE]

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blocks for sequential formation of “tiers” and dendrimer construction.

Reaction of the isocyanate monomers **1**–**5** with a fourth-generation poly(propylene imine) dendrimer (DSM, 32-PPI)[15] bearing 32 NH_2 groups in refluxing *tert*-butyl alcohol or dichloromethane afforded (>90%) the corresponding 96-ester **6**, 96-cyanide **7**, 96-siloxane **8**, 96-*N*-*t*-BOC compound **9**, and 96-benzyl ether **10**. Formation of these compounds is supported by their ^{13}C NMR spectra (Figures 1 and 2, Table 1). Anticipated key absorptions corresponding to the covalently attached 1 →3 branched monomers are observed in each spectrum (δ values): **6**: 172.7 (CO), 80.0 ($C(CH_3)$), 27.9 (CH_3); **7**: 118.4 (CN), 69.8, 65.9 (CH_2OCH_2), 18.8 (CH_2CN); **8**: 63.6 (CH_2O), 26.0 ($C(CH_3)_3$), 18.2 ($C(CH_3)_3$), −5.2 ($Si(CH_3)_2$); **9**: 156.5 (CO), 78.9 ($C(CH_3)_3$), 28.3 ($C(CH_3)_3$); **10**: 138.6, 128.4, 127.6, 127.4 (C-aryl), 72.8 ($CH_2C_6H_5$), 71.0 (CH_2CH_2O). As expected, signals attributed to the imine-based superstructure are broadened and less intense (δ values): **6**: 52.0 ($CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$), 51.0 ($CH_2CH_2CH_2NHCONH$).

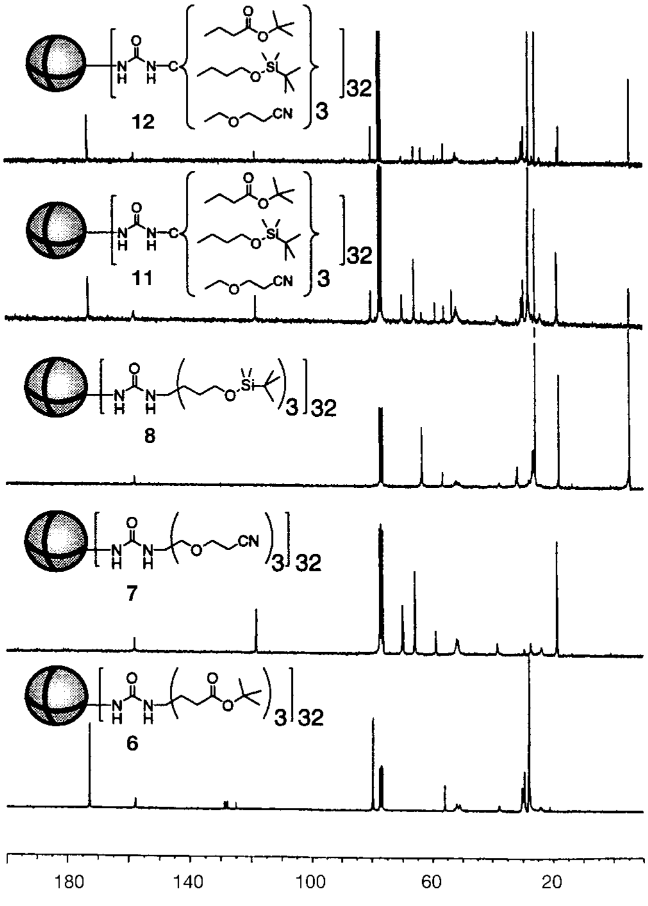


Figure 1. ^{13}C NMR spectra for the peripherally homogeneous ester, cyano, and siloxane dendrimers **6**, **7**, and **8**, respectively, and the peripherally heterogeneous dendrimers **11** (prepared from 0.5, 0.4, and 0.1 equivalents of monomers **1**, **2**, and **3**, respectively) and **12** (0.7, 0.15, and 0.15 equivalents of **1**, **2**, and **3**, respectively). Spheres represent the DSM-32-PPI dendritic core.

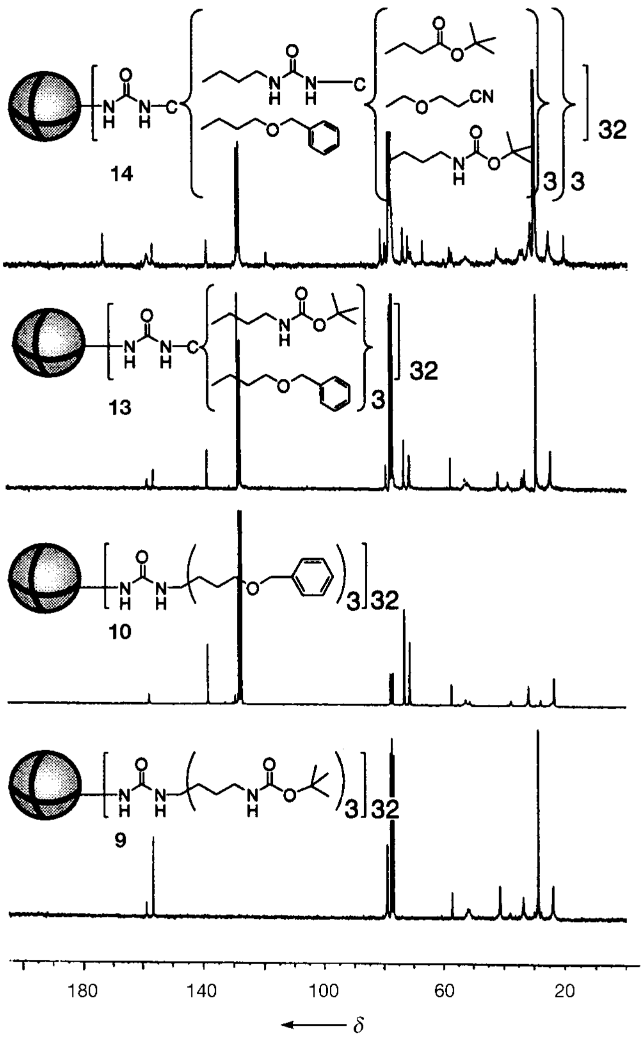


Figure 2. ^{13}C NMR spectra of dendrimers **9** and **10**, which have carbamate and benzyl ether terminal groups, respectively, and the peripherally heterogeneous dendrimers **13** (prepared from 0.5 equivalents each of monomers **4** and **5**) and **14** (prepared from **13**, see text).

Further potential to exploit the connectivity of the isocyanate-based monomers was subsequently examined by treatment of the 32-PPI dendrimer with mixtures of monomers **1**–**3** (total of 32 equivalents). Specifically, mixtures of building blocks **1**, **2**, and **3** in various ratios [(0.5:0.1:0.4) and (0.7:0.15:0.15)] afforded the corresponding combinatorial-based dendrimers **11** and **12** (Figure 1). Evidence for the formation of these *peripherally heterogeneous* dendrimers includes the observation (after chromatographic purification) of all the pertinent ^{13}C NMR signals exhibited in the spectra of the analogous, peripherally homogeneous macromolecules **6**–**8**. More specifically, the spectrum of each peripherally heterogeneous dendrimer exhibits signals at $\delta = 172.8$, 118.3, 80.1, 63.5, 51.5, 18.7, and −5.3 (corresponding to $CO_{[BA]}$, CN, $C(CH_3)_{3[BA]}$, $CH_2O_{[Si]}$, $CH_2CH_{2[DSM]}$, CH_2CN, and $Si(CH_3)_2$, respectively). The observed low intensity and slightly broadened signals at $\delta = 157.8$ and 157.6 ($NHCONH_{[BA, Si, CN]}$) suggest that the surface is relatively rigid as a result of hydrogen bonding between the urea units and crowding of the terminal groups.

Table 1. ^{13}C NMR data for compounds **6**–**14** (subscripts denote absorptions arising from specified units) (62.9 MHz, $\mathrm{CDCl_3}$, 25 °C).

6: $\delta = 172.7$ (CO), 157.9 (NHCONH), 80.0 ($\mathrm{\mathit{C}(CH_3)_3}$), 56.0 (*tert*-C), 52.1 ($\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_2}$, $\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2}$), 51.0 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCONH}$), 37.8 ($\mathrm{\mathit{C}H_2NHCONH}$), 30.2, 29.5 ($\mathrm{\mathit{C}H_2\mathit{C}H_2CO_2}$, $\mathrm{\mathit{C}H_2CH_2NHCONH}$), 27.9 ($\mathrm{C(\mathit{C}H_3)_3}$), 24.2 ($\mathrm{CH_2\mathit{C}H_2\mathit{C}H_2CH_2}$, $\mathrm{CH_2\mathit{C}H_2CH_2}$)

7: $\delta = 158.2$ (NHCONH), 118.4 (CN), 69.8, 65.9 ($\mathrm{CH_2OCH_2}$), 58.9 (*tert*-C), 52.0 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2}$, $\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_2}$), 51.0 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCONH}$), 38.3 ($\mathrm{\mathit{C}H_2NHCONH}$), 29.6 ($\mathrm{CH_2\mathit{C}H_2\mathit{C}H_2CH_2}$), 27.4 ($\mathrm{\mathit{C}H_2CH_2NHCONH}$), 23.8 ($\mathrm{CH_2\mathit{C}H_2CH_2}$), 18.8 ($\mathrm{\mathit{C}H_2CN}$)

8: $\delta = 158.2$ (NHCONH), 63.6 ($\mathrm{CH_2O}$), 56.7 (*tert*-C), 52.2 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2}$, $\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_2}$), 51.0 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCONH}$), 38.0 ($\mathrm{\mathit{C}H_2NHCONH}$), 32.0 ($\mathrm{\mathit{C}H_2CH_2CH_2O}$), 29.0 ($\mathrm{CH_2\mathit{C}H_2\mathit{C}H_2CH_2}$), 26.9 ($\mathrm{\mathit{C}H_2CH_2O}$), 26.0 ($\mathrm{C(\mathit{C}H_3)_3}$), 25.0 ($\mathrm{\mathit{C}H_2CH_2NHCONH}$), 24.2 ($\mathrm{CH_2\mathit{C}H_2CH_2}$), 18.2 ($\mathrm{\mathit{C}(CH_3)_3}$), -5.2 ($\mathrm{Si(CH_3)_2}$)

9: $\delta = 158.7$ (NHCONH), 156.5 (CO), 78.9 ($\mathrm{\mathit{C}(CH_3)_3}$), 57.0 (*tert*-C), 52.4 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2}$, $\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_2}$), 51.4 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCONH}$), 41.2 ($\mathrm{CH_2\mathit{C}H_2NH}$), 37.9 ($\mathrm{\mathit{C}HNHCONH}$), 33.3 ($\mathrm{\mathit{C}H_2CH_2CH_2}$), 29.8 ($\mathrm{\mathit{C}H_2CH_2\text{-}NHCONH}$), 28.7 ($\mathrm{C(\mathit{C}H_3)_3}$), 23.9 ($\mathrm{CH_2\mathit{C}H_2CH_2}$, $\mathrm{CH_2\mathit{C}H_2\mathit{C}H_2CH_2}$)

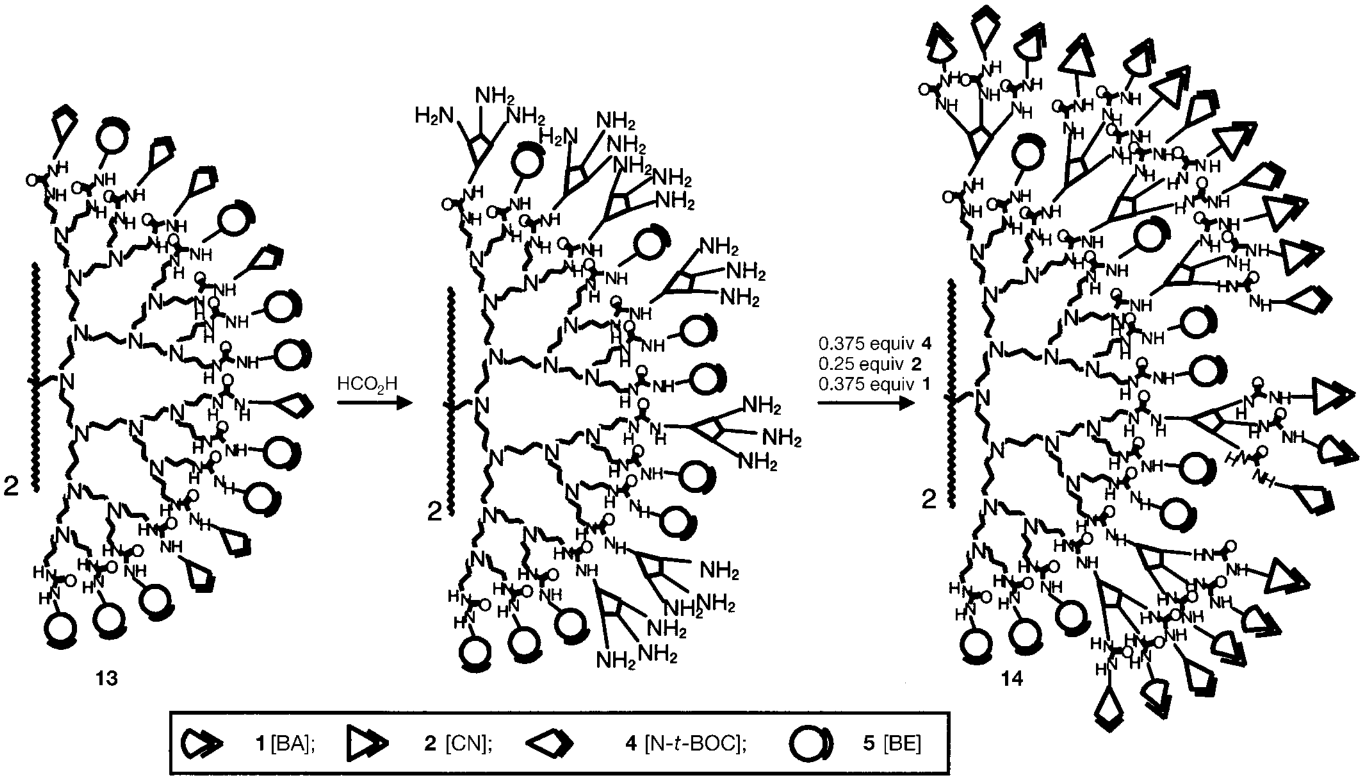
10: $\delta = 158.2$ (NHCONH), 138.6 ($\mathrm{C_1}$-Aryl), 128.4 ($\mathrm{C_2}$-Aryl), 127.6 ($\mathrm{C_3}$-Aryl), 127.4 ($\mathrm{C_4}$-Aryl), 72.8 ($\mathrm{\mathit{C}H_2C_6H_5}$), 71.0 ($\mathrm{CH_2\mathit{C}H_2O}$), 56.9 (*tert*-C), 52.3 ($\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_2}$, $\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2}$), 50.9 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCONH}$), 37.7 ($\mathrm{\mathit{C}H_2NHCONH}$), 32.1 ($\mathrm{\mathit{C}H_2CH_2CH_{2O}}$), 28.2 ($\mathrm{\mathit{C}H_2CH_2NHCONH}$), 23.8 ($\mathrm{CH_2\mathit{C}H_2CH_2O}$)

11/12: $\delta = 172.8$ ($\mathrm{CO_{[BA]}}$), 157.8, 157.6 ($\mathrm{NHCONH_{[BA,\,Si,\,CN]}}$), 118.3 (CN), 80.1 ($\mathrm{\mathit{C}(CH_3)_{3[BA]}}$), 69.9, 65.8 ($\mathrm{\mathit{C}H_2O\mathit{C}H_{2[CN]}}$), 63.5 ($\mathrm{CH_2O_{[Si]}}$), 58.9 (*tert*-$\mathrm{C_{[CN]}}$), 56.0 (*tert*-$\mathrm{C_{[BA]}}$), 51.5 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_{2[DSM]}}$, $\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_{2[DSM]}}$, $\mathrm{\mathit{C}H_2CH_2CH_2NHCONH_{[DSM]}}$), 38.8 ($\mathrm{\mathit{C}H_2NHCONH_{[DSM]}}$), 32.0 ($\mathrm{\mathit{C}H_2CH_2O_{[Si]}}$), 30.3, 29.6, 28.0 ($\mathrm{\mathit{C}H_2\mathit{C}H_2CO_2}$, $\mathrm{C(\mathit{C}H_3)_{3[BA]}}$), 25.9 ($\mathrm{C(\mathit{C}H_3)_{3[Si]}}$), 24.2 ($\mathrm{CH_2\mathit{C}H_2CH_{2[DSM]}}$), 18.7 ($\mathrm{\mathit{C}H_2CN_{[CN]}}$), 18.2 ($\mathrm{\mathit{C}(CH_3)_{3[Si]}}$), -5.3 ($\mathrm{Si(CH_3)_2}$)

13: $\delta = 158.5$ ($\mathrm{NHCONH_{[N\text{-}\mathit{t}\text{-}BOC,\,BE]}}$), 156.4 ($\mathrm{CO_{[N\text{-}\mathit{t}\text{-}BOC]}}$), 138.7 ($\mathrm{C_1\text{-}Aryl_{[BE]}}$), 128.6 ($\mathrm{C_2\text{-}Aryl_{[BE]}}$), 127.8 ($\mathrm{C_{3,4}\text{-}Aryl_{[BE]}}$), 78.9 ($\mathrm{\mathit{C}(CH_3)_{3[N\text{-}\mathit{t}\text{-}BOC]}}$), 72.9 ($\mathrm{\mathit{C}H_2C_6H_{5[BE]}}$), 71.0 ($\mathrm{CH_2\mathit{C}HO_{[BE]}}$), 57.0 (*tert*-$\mathrm{C_{[N\text{-}\mathit{t}\text{-}BOC,\,BE]}}$), 52.4 ($\mathrm{\mathit{C}H_2CH_2\text{-}CH_2\mathit{C}H_{2[DSM]}}$, $\mathrm{\mathit{C}H_2CH_2\mathit{C}H_{2[DSM]}}$), 51.4 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCONH_{[DSM]}}$), 41.2 ($\mathrm{CH_2\mathit{C}H_2NH_{[N\text{-}\mathit{t}\text{-}BOC]}}$), 37.9 ($\mathrm{\mathit{C}H_2NHCONH_{[DSM]}}$), 33.2 ($\mathrm{\mathit{C}H_2CH_2CH_{2[N\text{-}\mathit{t}\text{-}BOC]}}$), 32.3 ($\mathrm{\mathit{C}H_2CH_2CH_2O_{[BE]}}$), 28.8 ($\mathrm{C(\mathit{C}H_3)_{3[N\text{-}\mathit{t}\text{-}BOC]}}$), 23.9 ($\mathrm{CH_2\mathit{C}H_2CH_{2[N\text{-}\mathit{t}\text{-}BOC,\,BE]}}$, $\mathrm{CH_2\mathit{C}H_2\mathit{C}H_2CH_{2[DSM]}}$)

14: $\delta = 173.1$ ($\mathrm{CO_{[BA]}}$), 158.2 ($\mathrm{NHCONH_{[BA,\,CN,\,N\text{-}\mathit{t}\text{-}BOC,\,BE]}}$), 156.5 ($\mathrm{CO_{[N\text{-}\mathit{t}\text{-}BOC]}}$), 138.7 ($\mathrm{C_1\text{-}Aryl_{[BE]}}$), 128.5 ($\mathrm{C_2\text{-}Aryl_{[BE]}}$), 127.7 ($\mathrm{C_{3,4}\text{-}Aryl_{[BE]}}$), 118.7 ($\mathrm{CN_{[CN]}}$), 80.5 ($\mathrm{\mathit{C}(CH_3)_{3[BA]}}$), 78.9 ($\mathrm{\mathit{C}(CH_3)_{3[N\text{-}\mathit{t}\text{-}BOC]}}$), 72.9 ($\mathrm{\mathit{C}H_2C_6H_{5[BE]}}$), 71.1 ($\mathrm{CH_2\mathit{C}H_2\text{-}O_{[BE]}}$), 70.1, 66.0 ($\mathrm{\mathit{C}H_2O\mathit{C}H_{2[CN]}}$), 57.1, 56.2 (*tert*-$\mathrm{C_{[BA,\,CN,\,N\text{-}\mathit{t}\text{-}BOC,\,BE]}}$), 51.4 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_{2[DSM]}}$, $\mathrm{\mathit{C}H_2CH_2CH_2\mathit{C}H_{2[DSM]}}$, $\mathrm{\mathit{C}H_2CH_2CH_2NHCONH_{[DSM]}}$), 41.1 ($\mathrm{CH_2CH_2CN_{[CN]}}$), 38.3 ($\mathrm{CH_2NHCONH_{[DSM]}}$), 33.2 ($\mathrm{\mathit{C}H_2CH_2CH_{2[N\text{-}\mathit{t}\text{-}BOC]}}$, $\mathrm{\mathit{C}H_2CH_2CH_2O_{[BE]}}$), 32.2, 29.9 ($\mathrm{\mathit{C}H_2\mathit{C}H_2CO_{2[BA]}}$), 28.7, 28.3 ($\mathrm{C(\mathit{C}H_3)_{3[BA,\,N\text{-}\mathit{t}\text{-}BOC]}}$), 23.8 ($\mathrm{CH_2\mathit{C}H_2CH_{2[N\text{-}\mathit{t}\text{-}BOC,\,BE]}}$, $\mathrm{CH_2\mathit{C}H_2\mathit{C}H_2CH_{2[DSM]}}$), 18.9 ($\mathrm{\mathit{C}H_2CN_{[CN]}}$)

Scheme 1 illustrates the concept of combinatorial growth as it relates to the construction of dendrimers such as **14** having surfaces with multifarious functional groups. Thus, treatment of the DSM-32-PPI dendrimer with a mixture of monomers **4** and **5** (16 equivalents each) in refluxing dichloromethane afforded the heterogeneous macromolecule **13**. Following isolation and purification, the structure of the new *hetero*-dendrimer **13** was confirmed by its ^{13}C NMR spectrum (Figure 2, Table 1), which contains the relevant signals exhibited in the spectra of both the corresponding homogeneous macromolecules **9** and **10**. Principal signals are observed at $\delta = 138.7$, 128.6, 127.8 ($\mathrm{C\text{-}aryl_{[BE]}}$), 78.9 ($\mathrm{\mathit{C}(CH_3)_{3[N\text{-}\mathit{t}\text{-}BOC]}}$), 72.9 ($\mathrm{\mathit{C}H_2C_6H_{5[BE]}}$), 71.1 ($\mathrm{CH_2\mathit{C}HO_{[BE]}}$), 41.2 ($\mathrm{CH_2\mathit{C}H_2NH_{[N\text{-}\mathit{t}\text{-}BOC]}}$), 28.8 ($\mathrm{C(\mathit{C}H_3)_{3[N\text{-}\mathit{t}\text{-}BOC]}}$). Removal of the BOC groups by treatment with formic acid and subsequent reaction of the free amines with a mixture of isocyanate monomers **1**, **2**, and **4** (0.375, 0.25, 0.375 equivalents, respectively) yielded the peripherally hetereogeneous dendrimer **14**. Its structure was verified by its ^{13}C NMR spectrum (Figure 2), which displays the expected peaks at $\delta = 173.1$ ($\mathrm{\mathit{C}O_{[BA]}}$), 156.5



Scheme 1. Combinatorial synthesis of dendrimer **14**, which is characterized by diversity in the surface functional groups.

($CO_{[N\text{-}t\text{-}BOC]}$), 138.7, 128.5, 127.7 ($C\text{-aryl}_{[BE]}$), 118.7 (CN), 80.5 ($C(CH_3)_{3[BA]}$), 78.9 ($C(CH_3)_{3[N\text{-}t\text{-}BOC]}$), 72.9 ($CH_2C_6H_{5[BE]}$), 28.7, 28.3 ($C(CH_3)_{3[N\text{-}t\text{-}BOC,\ BA]}$), 18.9 ($CH_2CN_{[CN]}$). Similar signals are observed in the spectra of the homogeneous macromolecules **6**, **7**, **9**, and **10**. Higher generation materials can easily be constructed by further selective deprotection of functional groups and subsequent treatment with any mixture of compatible isocyanate-based monomers.

A great advantage of this protocol is the potential to adjust dendritic properties by modifying the surface groups. The polyamine dendrimer afforded by liberation of the NH_2 moieties on dendrimer **13** (50:50 mixture of *N*-*t*-BOC and BE terminal groups) displays amphiphilic behavior. For example, it is highly soluble in MeOH as well as partially soluble in both H_2O and $CHCl_3$; this compound is thus reminiscent of a "universal micelle". Key ^{13}C NMR signals arising from the NH_2- and $PhCH_2O$-terminated arms collapse and broaden in the deuterated solvents $CDCl_3$ and D_2O, respectively. This can be rationalized by considering that surface groups with termini that favor solvation are extended and freely rotating, while groups with unfavorable solvent interactions are contracted and folded back into the molecular superstructure where less freedom of movement is afforded. Fréchet et al.[16] observed analogous behavior when dendritic wedges were attached to polyethylene glycol star polymers. This behavior can be modified by altering the ratio of the functional groups on the dendrimer surface. For example, a dendrimer with a 75:25 mixture of amino and benzyl ether moieties is completely miscible in H_2O and insoluble in $CHCl_3$.

Combinatorial construction of dendrimers is well suited to the rapid design and construction of nanoscale superstructures having a variety of forms and functions. The large-scale screening of vastly differing material properties should thus be possible. These dendritic materials are likely to have cavities and clefts within the framework, resulting in various degrees of local as well as overall asymmetry. As such, these materials can be viewed as being intermediate between dendrimers and classical polymers: a "polycelle". We are currently investigating their potential use as catalysts and phase-transfer agents.

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Keywords: combinatorial synthesis • dendrimers • isocyanates

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[1] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH Weinheim, **1996**; C. N. Moorefield, G. R. Newkome, *Adv. Dendritic Macromol.* **1994**, *1*, 1; J. Issberner, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413; J. M. J. Fréchet, C. J. Hawker, K. L. Wooley, *J. Macromol. Sci. Part A* **1994**, *31*, 1627; J. M. J. Fréchet, *Science* **1994**, *263*, 1710; D. A. Tomalia, A. M. Naylor, W. A. Goddard, III, *Angew. Chem.* **1990**, *102*, 119; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138; B. I. Voit, *Acta Polymer* **1995**, *46*, 87; N. Ardoin, D. Astruc, *Bull. Soc. Chim. Fr.* **1996**, *132*, 875.

[2] S. Stevelmans, J. C. M. van Hest, J. F. G. A. Jansen, D. A. F. J. van Boxtel, E. M. M. de Brabander-van den Berg, E. W. Meijer, *J. Am. Chem. Soc.* **1996**, *118*, 7398; G. R. Newkome, Z.-q. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.* **1985**, *50*, 2003.

[3] G. R. Newkome, R. Güther, C. N. Moorefield, F. Cardullo, L. Echegoyen, E. Pérez-Cordero, H. Luftmann, *Angew. Chem.* **1995**, *107*, 2159; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2023.

[4] S. A. Kuzdzal, C. A. Monnig, G. R. Newkome, C. N. Moorefield, *J. Chem. Soc. Chem. Commun.* **1994**, 2139; *J. Am. Chem. Soc.* **1997**, *119*, 2255.

[5] G. R. Newkome, C. N. Moorefield, J. M. Keith, G. R. Baker, G. H. Escamilla, *Angew. Chem.* **1994**, *106*, 701; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 666; R. F. Barth, A. H. Soloway, *Mol. Chem. Neuropathol.* **1994**, *21*, 139; R. F. Barth, D. M. Adams, A. H. Soloway, F. Alam, M. V. Darby, *Bioconjugate Chem.* **1994**, *5*, 58.

[6] R. J. Duan, L. L. Miller, D. A. Tomalia, *J. Am. Chem. Soc.* **1995**, *117*, 10783.

[7] G. R. Newkome, C. D. Weis, C. N. Moorefield, F. R. Fronczek, *Tetrahedron Lett.* **1997**, *38*, 7053; G. R. Newkome, C. D. Weis, U.S. Patent 5703271 (December 30, 1997).

[8] G. R. Newkome, C. D. Weis, B. J. Childs, *Designed Monomers Polym.* **1997**, in press

[9] X.-D. Xiang, X. Sun, G. Briceño, Y. Lou, K.-A. Wang, H. Chang, W. G. Wallace-Freedman, S.-W. Chen, P. G. Schultz, *Science* **1995**, *268*, 1783.

[10] T. Carell, E. A. Wintner, A. J. Sutherland, J. Rebek, Jr., Y. M. Dunayevskiy, P. Vouros, *Chem. Biol.* **1995**, *2*, 171; L. Bourel, X. Willard, I. Pop, R. Bandelle, D. Horvath, B. Déprey, P. Melnyk, A. Tartar, *L'Actual. Chem.* **1995**(12), 33; M. Cardno, M. Bradley, *Tetrahedron Lett.* **1996**, *37*, 135.

[11] M. Goodman, V. Jubian, B. Linton, A. D. Hamilton, *J. Am. Chem. Soc.* **1995**, *117*, 11610.

[12] R. M. Kim, M. Manna, S. M. Hutchins, P. R. Griffin, N. A. Yates, A. M. Bernick, K. T. Chapman, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 10012.

[13] V. Swali, N. J. Wells, G. J. Langley, M. Bradley, *J. Org. Chem.* **1997**, *62*, 4902.

[14] D. Seebach, R. E. Marti, T. Hintermann, *Helv. Chim. Acta* **1996**, *79*, 1710.

[15] Commercially available poly(propylene imine) dendrimers were generously provided by DSM. The preparation and characterization was reported: E. M. M. de Brabander-van den Berg, E. W. Meijer, *Angew. Chem.* **1993**, *105*, 1370; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1308; C. Wörner, R. Mülhaupt, *Angew. Chem.* **1993**, *105*, 1367; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1306.

[16] I. Gitsov, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1996**, *118*, 3785; *Macromolecules* **1993**, *26*, 6536.

Self-Assembly of Novel Polyrotaxanes: Main-Chain Pseudopolyrotaxanes with Poly(ester crown ether) Backbones**

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Physically linked molecules, rotaxanes and catenanes,[1] comprise a major research field of supramolecular chemistry[2] which has fascinated scientists in recent decades. Polyrotaxanes, in which a cyclic and a linear species (one of which is part of a macromolecule) are mechanically interlocked with each other, have also been extensively studied since their properties are different than those of conventional covalent polymers.[1, 3–10] The novel properties of these compounds often result from their unusual architectures. Therefore, designing

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