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Dendrimers

Dendrimer-Type Peptoid-Decorated Hexaphenylxylenes and Tetraphenylmethanes: Synthesis and Structure in Solution and in the Gas Phase

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Abstract: Branched organic nanostructures are useful scaffolds that find multiple applications in a variety of fields. Here, we present a novel approach to dendrimer-like structures. Our design contains a rigid hydrocarbon-based core (hexaphenylxylylene/tetraethynylphenylmethane) combined with a library of N-substituted oligoglycines (so-called peptoids) providing a flexible shell. The use of click chemistry allows rapid assembly of the nanostructures. The possibility of tuning the size and the solubility of this new type of nanostructure will be advantageous for future applications such as heterogeneous catalysis.

Introduction

Nowadays, dendrimers are a common class of organic nanostructures. Their branched topology offers a broad variety of applications ranging from sensors[1] and catalysis[2] to tissue engineering[3] and drug delivery.[4] Several syntheses have been reported that have led to highly functionalized systems with complete control of the total structure. In particular, through modular synthesis using click chemistry, rapid assembly of the nanostructures is enabled.[5] Herewith, we present a short, straightforward strategy that can be used to synthesize new dendrimer-like structures. Our design is based on a rigid core containing multiple anchoring sites. Recently, we presented hexaphenylxylylene (HPX) as an easily accessible pseudo-octahedral core for covalent organic frameworks.[8] We combined this core with N-substituted oligoglycines (so-called peptoids), which are readily accessible by solid-phase synthesis,[9] to generate highly symmetrical nanostructures having both a rigid core and a soft, flexible shell. This type of well-defined structure could be applied in catalysis and drug-delivery, because the potential of peptoids in these fields is well known.[9,10] A disadvantage is that these flexible compounds are seldom crystalline[6] and therefore there are only a few examples available with a high-resolution X-ray structures.[7] Hence, other techniques such as NMR or mass spectrometric characterization have to be applied.

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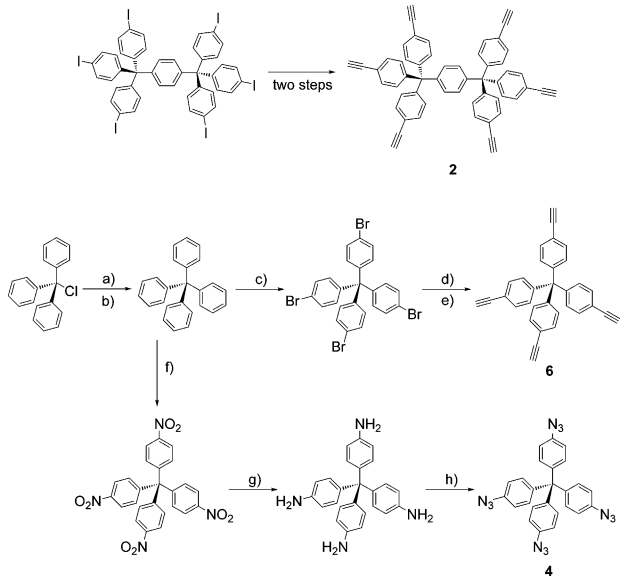
Results and Discussion

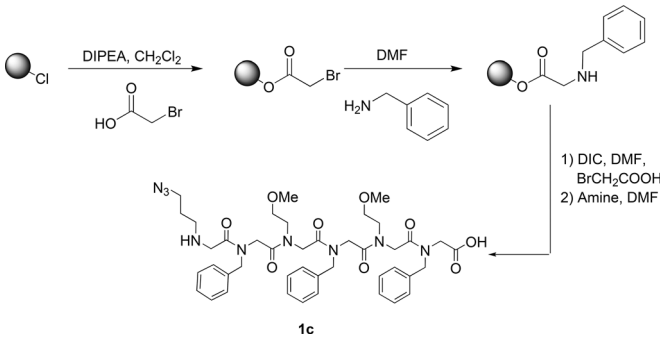
For the assembly of the new dendrimeric structures, two different building blocks were synthesized. First, rigid cores were constructed that were suitably functionalized for the click reaction, then the peptoids were added to provide a flexible, active shell.

HPX structure **2** was synthesized from the corresponding bromide as previously described and shown in Scheme 1.[11] With the HPX core in hand, we had a bulky and rigid scaffold with six functional side chains. The tetraphenylmethane (TPM) cores **4** and **6** are smaller alternatives to the HPX core, with four functional groups, but they nevertheless provide a bulky and rigid framework for the final dendrimer structure. The synthesis of the TPM core started from tetraphenylmethane, and involved nitration, reduction, diazotization, and subsequent addition of sodium azide, to generate the tetraazide core **4** in good yields. Tetraphenylmethane-alkyne core **6** was synthesized from TPM via the tetrabromide.

The required peptoids were assembled on solid supports by using standard conditions (see the Supporting Information). For this purpose, the peptoids combined methoxyethyl sidechains and hydrophobic residues in different amounts, to tune the solubility of the final products. The solid support used was



Scheme 1. Synthesis of cores **2** (A), **4**, and **6** (B). A) Conditions: Step 1: Ethynyltrimethylsilane, $Cl_2Pd(PPh_3)_2$, PPh_3, CuI, diisopropylamine, 90 °C, 3 d; step 2: K_2CO_3, DCM/MeOH (1:1), r.t., 16 h. 51% yield over two steps. B) Reagents and conditions: a) Aniline, Δ then b) H_2SO_4, isoamyl nitrite, H_3PO_2, 93%; c) Br_2, 90%; d) ethynyltrimethylsilane, NEt_3, $PdCl_2(PPh_3)_2$, CuBr, benzene, 80 °C then; e) TBAF, benzene/MeCN, r.t., 77% (over two steps); f) HNO_3, AcOH, Ac_2O, −10 °C, 72%; g) H_2, Pd/C, MeOH, r.t., quant.; h) HCl, $NaNO_2$, NaN_3, H_2O, −5 °C to r.t., 75%.



Scheme 2. Example of the solid-phase synthesis of peptoid **1c** on 2-chlorotrityl chloride resin.

the 2-chlorotrityl chloride resin, which led to the inclusion of a hydrophilic acid at the end of the peptoid sequence (Scheme 2).

In general, methoxyethyl side chains can generate *cis*- and *trans*-amide bonds in the backbone of the peptoid structure. With an all-*cis* structure, the peptoid sequence tends to adopt a helical-type structure. In addition, we incorporated bulky aniline side-chains to induce *trans*-amide bonds. Therefore, we synthesized a library of nine peptoids **1a**–**i** for the dendrimer synthesis (Figure 1). We anticipated that the peptoids would adopt different secondary structures, which would affect the size and shape of the final compounds. In further experiments, it would then be possible to replace these peptoids with catalytically or biologically active peptoids for specific applications such as catalysis or drug-delivery.

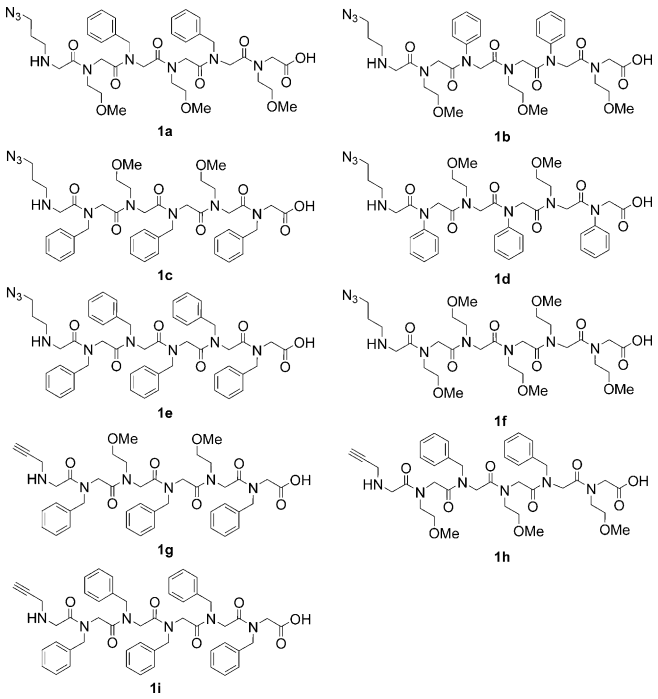
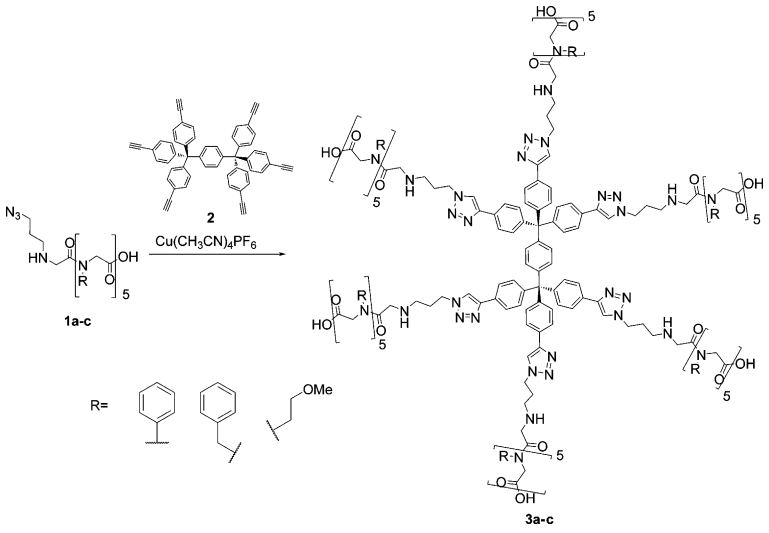


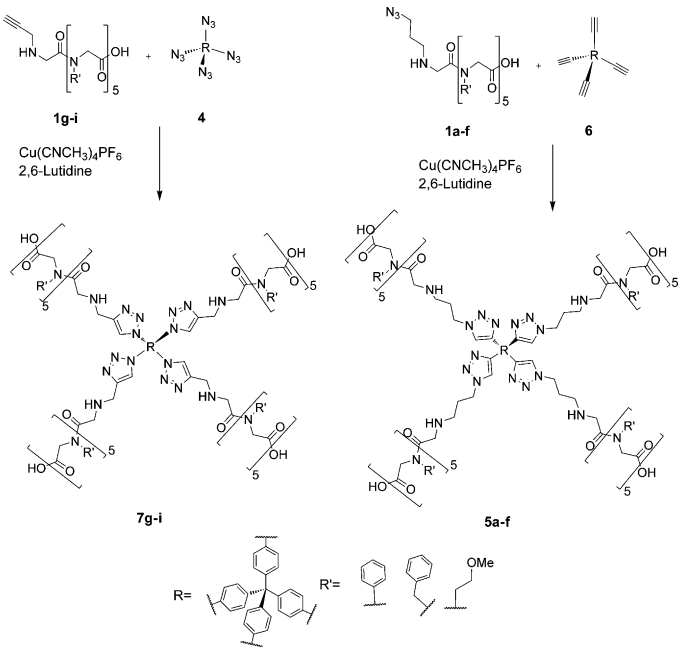
Figure 1. Library of peptoids **1a**–**i**.

The synthetic approach employed to assemble the dendrimers is depicted in Scheme 3 and Scheme 4. Here, the peptoids, containing azido or alkyne groups in their side-chains, were attached to the corresponding alkyne or azido-functionalized core though copper-catalyzed alkyne-azide cycloaddition (CuAAC). The CuAAC reactions were performed by using $Cu(MeCN)_4PF_6$ as a catalyst and *N*,*N*-diisopropylethylamine (DIPEA) as the base.[11] Excess of reagents and most of the copper catalyst could be removed by washing with ethylenediaminetetraacetic acid (EDTA) solution.

The synthesis of dendrimers **3a**–**c** with the peptoids **1a**–**c** and the HPX-core **2** is shown in Scheme 3. Purification of the



Scheme 3. Example of the synthesis of peptoid-HPX hybrids **3a**–**c**.



Scheme 4. Examples of the syntheses of peptoid-TPM hybrids **7g–i** and **5a–f**.

peptoid-HPX hybrids using HPLC and GPC was not possible because of the low solubility of the products **3a–c** in common organic solvents. Therefore, the reaction mixture was washed with dichloromethane, methanol, and EDTA. By switching to the TPM-core (the synthesis for the TPM-core with alkyne and azide groups is shown in Scheme 4) the solubility of the "click-products" **5a–f** and **7g–i** in polar solvents such as acetonitrile could be improved. In this way, the purification could be optimized. Here the purification was achieved by HPLC and monitored by analytical HPLC. For future applications such as heterogeneous catalysis, the possibility of controlling the solubility could be an advantage of this system.

With these new types of dendrimers in hand, we proceeded to determine the global structure. Considering that it is rarely possible to crystallize such systems, we first evaluated the global structure in solution. A detailed structure determination by NMR spectroscopy was not possible because of severe chemical shift overlap. Thus, we performed NMR diffusion-ordered spectroscopy (DOSY) to assess the size of the click product. Compounds of various sizes can be distinguished by this technique, as has been previously reported for dendrimers.[12] We determined diffusion coefficients of compounds **3c**, **5a**, **5b**, **5e**, and **7h** (Table 1). Their radii can be calculated from the diffusion coefficient D because the latter depends on the molecular shape according to Stokes–Einstein Equation (1):

$$D = \frac{k_B T}{6\pi\eta r} \quad (1)$$

where $k_B = 1.380 \cdot 10^{-23}$ J/K (the Boltzmann constant), T is the absolute temperature, $\eta = 1.991$ cP (the viscosity of dimethyl sulfoxide (DMSO) at 25 °C), and r is the radius of the spherical particle. The respective radii of all compounds are found in Table 1 and all lie within a similar range.

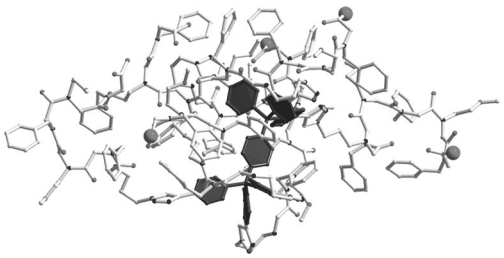
Particles in polar solvents are surrounded by a solvation shell, which may be several layers thick, therefore the size calculation is approximate, and the actual radius determined by the diffusion coefficient is generally larger than that estimated from the molecular structure. Thus, we also determined the diffusion coefficient of one of the corresponding peptoids, **1c**, for comparison. For this compound, a diffusion coefficient of $1.47 \pm 0.05 \cdot 10^{-10}\,m^2\,s^{-1}$ and a radius of 0.74 nm was obtained (see the Supporting Information). Given that the click products have a radius that is approximately three times larger than the peptoid, if all peptoid structures are extended, the diffusion coefficients of the click products thus argue for a monomer and exclude higher oligomer formation.

We then determined the global structure of the products in the gas phase by using mass spectrometric analysis. This result constitutes one of the few examples of structures of peptoids in the gas phase.[14] The high-resolution mass spectra confirmed the composition of compounds **3a–c** and **5a–d** (see the Supporting Information). Interestingly, for the HPX-hybrids, both the tri-anion and the tetra-anion are stable in the gas phase without decarboxylation.[13]

Additionally, the high-resolution mass spectra revealed that compound **3b**, containing the rigid aniline peptoid side-chains, was able to form stable copper complexes, which could be a valuable characteristic for future applications (see Figure 2).

The stable anions in the gas phase allowed the collision cross-section to be determined by ion mobility spectrometry; that is, the size of the molecules could be determined without

Table 1. Experimental and theoretical sizes of peptoid–HPX hybrids and TMP hybrids.



Compound	Diffusion coefficient [$\times 10^{11}$ $m^2\,s^{-1}$]	Radius from NMR [nm] (cross-section [Å^2])	Cross-section [Å^2]	
			Experimental[a]	Theoretical
3a	n.d.	n.d.	764[b], 734[c]	789[b], 775[c]
3b	n.d.	n.d.	759[b], 722[c]	746[b], 705[c]
3c	4.1 ± 0.07	2.7 (2300)	800[b], 726[c]	829[b], 707[c]
5a	5.67 ± 0.04	1.95 (1193)	570[d]	565[d]
5b	n.d.	n.d.	564[d]	543[d]
5c	6.14 ± 0.21	1.80 (1017)	587[d]	559[d]
7h	5.67 ± 0.04	1.95 (1193)	559[d]	557[d]
5e	5.71 ± 0.07	1.94 (1181)	n.d.	n.d.

[a] Error of ± 10 Å^2. [b] Tetraanions. [c] Trianions. [d] Dianions.

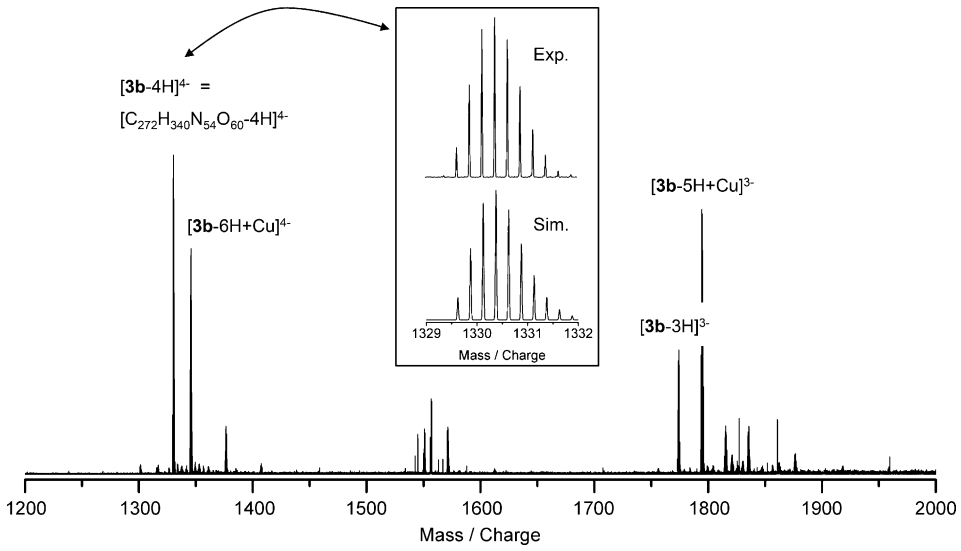


Figure 2. ESI mass spectrum of **3b**.

needing to consider the solvation shell (see Table 1). The experimental collision cross-sections were obtained by recording several arrival time distributions at different drift voltages (see the Supporting Information). The arrival time distributions were significantly broader than the experimental resolution, indicating that several isomers (different deprotonation positions) or slowly interconverting conformers were present. To estimate the structure and to corroborate the size determination, we performed MD simulations (Amber force field). The experimental and calculated cross-sections agree within 5% for a typical MD run (see Table 1), indicating that the MD simulations reproduce the gas-phase structures (see Figure 3).

The cross section variations within each run are quite large, indicating a rather flexible structure (see Figure 3). Furthermore, the experimental cross sections of the quadruply charged ions are larger than the cross sections of the corresponding triply charged ions due to the larger Coulomb repulsion of four negative charges, which results in more open structures.

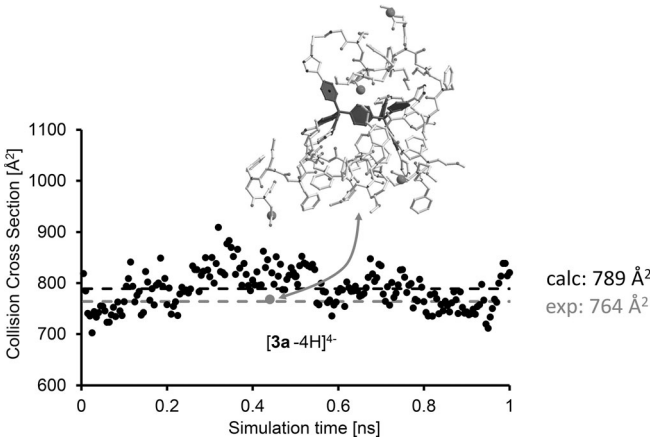


Figure 3. MD simulation of [**3a**−4H]$^{4-}$. See text for details.

Conclusion

We have presented a new type of rigid–soft nanostructure with aromatic cores (HPX and TPM) coupled to a peptoid outer rim. The solubility of the click products can be tuned by using different cores. The radii and cross sections in DMSO as determined by NMR diffusion measurements are considerably larger than those calculated by using gas-phase methods. This discrepancy can be explained by a solvent layer around the molecules in solution. Moreover, in polar solvents such as DMSO, the peptoid branches may be more extended than in vacuum due to the entropically favorable interactions with solvent molecules. In the gas phase, in contrast, the lower dielectric constant leads to a compression of the structure.[15] Taken together, the possibility of tuning the size and the solubility of these new types of nanostructures could be very important for future applications.

Experimental Section

Synthesis

Step A: 1,4-Bis[tris(4-ethynylphenyl)methyl]benzene (1.00 equiv), the desired peptoid (6.50 equiv), and $Cu(MeCN)_4PF_6$ (0.200 equiv) were dissolved under an argon atmosphere in a mixture of methanol and dichloromethane (1:1 v/v, 10 mL). After addition of 2,6-lutidine (12.0 equiv), the mixture was stirred for 3 d. The solvent was removed under reduced pressure and the residual solid was dissolved again in methanol/dichloromethane (1:1 v/v). The peptoid (0.500 equiv), a catalytic amount of $Cu(MeCN)_4PF_6$, and 2,6-lutidine (0.500 equiv) were then added under inert conditions. The mixture was stirred for 3 d and the precipitated product was washed with water, acetonitrile, and dichloromethane.

Step B: Tetra(4-ethynylphenyl)methane (1.00 equiv), the desired peptoid (5.50 equiv) and $Cu(MeCN)_4PF_6$ (0.500 equiv) were dissolved under an argon atmosphere in anhydrous methanol/dichloromethane (1:1 v/v, 10 mL). After addition of 2,6-lutidine (24.0 equiv), the mixture was stirred for 1 d and the progress of the reaction was monitored. The crude material was purified by HPLC.

NMR Evaluation

Peptoids **5a**–**d** were dissolved in deuterated DMSO at a concentration of 16 mg mL^{-1}. DOSY spectra were acquired with the ledbpgp2s pulse sequence from the Bruker library at 25 °C. This pulse sequence contains a stimulated echo with bipolar gradient pulses and longitudinal eddy current compensation.[16] We measured 64 different gradient values varying from 2 to 95% of the maximum gradient strength. Diffusion time was 100 ms, with a gradient length of 3 ms (peptoid **3c**) or 170 ms with a gradient of

2.2 ms (peptoids **5a**–**d** and **1c** employed a maximum gradient strength of 5.35 G/cm). The spectra were multiplied by an exponential window function with line broadening of 3 Hz and baseline corrected. The data was interpreted by using the dynamics module of the BRUKER Topspin 3.0 software. A single exponential curve fit was derived for each peak in the spectrum, from which the diffusion coefficient of the peptoid and the monomer were derived [Eq. (2)]:

$$I(x) = I_0 e^{-\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) D} \quad (2)$$

where g is the gradient strength that is varied from one experiment to the next, γ the gyromagnetic ratio, δ the duration of the gradient and Δ the diffusion time. The diffusion coefficient D is to be determined.

Gas-phase ion mobility

The gas-phase collision cross-sections were obtained in a home-built ion-mobility mass spectrometer consisting of an electrospray ionization source, a drift-cell filled with 2.5 mbar of helium, and a quadrupole mass filter (Extrel). Details of the experimental setup are given elsewhere.[17] Briefly, the arrival time distribution of the respective ion (mass/charge ratio selected by the mass filter) was recorded for various drift voltages (U) at a given helium pressure (p). The maximum of the arrival time distribution (t) of an ion depends linearly on the p/U ratio in the cell, the slope was proportional to the ion mobility K_0 which, in turn, can be converted into the collision cross-section by Equation (3):[18]

$$\Omega = \frac{3q}{16N_0}\sqrt{\frac{2\pi}{\mu k_B T}}\frac{1}{K_0} \quad (3)$$

where q and μ are the charge and reduced mass of the ion, respectively, and N_0 and T are the helium number density and temperature, respectively. We determined the collision cross-section for the triply and quadruply charged anions **3a**–**c** and doubly charged anions **5a**–**c** and **7h**.

Computational methods

The experimental collision cross-sections were compared with molecular dynamics (MD) simulations calculated with the AMBER force field[19] as implemented in the Hyperchem 8.0 package.[20] To speed up the conformational search, the simulations were run at 600 K for 3 ps with 1 ps heating and cooling intervals at 300 K. We used a dielectric constant of 5 to account for the polarizability of the ion and sampled the structures every 5 ps; the total simulation was run for 1 ns, that is, 200 candidate structures were obtained. For each of these candidates we calculated the collision cross-section with the projection approximation[21] as implemented in the MOBCAL package.[22] The time-averaged cross-section was compared with the experimental value. Typically both values agreed to within 5%, confirming rather compact gas-phase structures.

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Keywords: click chemistry · dendrimers · structure elucidation · NMR spectroscopy · peptoids

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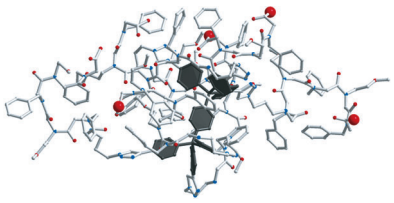
FULL PAPER

A new scaffold: The use of a rigid hydrocarbon-based core (hexaphenylxylylene/tetraethynylphenylmethane) combined with a library of N-substituted oligoglycines (so-called peptoids) has provided new dendrimer-type structures (see figure). The global shapes in the gas phase and in solution were elucidated by mass-spectrometry and NMR spectroscopy, respectively.



Dendrimers

*K. Peschko, A. Schade, S. B. L. Vollrath, U. Schwarz, B. Luy, C. Muhle-Goll, P. Weis, S. Bräse**

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Dendrimer-Type Peptoid-Decorated Hexaphenylxylenes and Tetraphenylmethanes: Synthesis and Structure in Solution and in the Gas Phase