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Evaluation of an Intramolecular Approach for the Synthesis of the Elusive $C_{58}N_2$ Heterofullerene Family

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A new approach towards the synthesis of the elusive heterofullerene $C_{58}N_2$ is presented. The synthetic strategy is based on the intramolecular 1,3-dipolar cycloaddition of a spacer-linked azide to a monoazaheterofullerene ($C_{59}N$) core. Since this cycloaddition can theoretically result in 16 different isomeric products, the design of the spacer moiety was based on extensive molecular modelling. Two fundamental synthetic routes towards suitably functionalized $C_{59}N$ derivatives were designed and carried out. Subsequent one-pot experiments, each making use of the same conditions as had previously been employed for the introduction of the first nitrogen atom into the fullerene framework, were performed. Immediate analysis by FAB mass spectrometry indicated that up to 20 % of the submitted material indeed gave $C_{58}N_2$ species as fragmentation products. This result not only represents the first strategic synthesis of a $C_{58}N_2$ derivative, but also holds great promise for further efforts directed towards the preparative isolation of a member of the diaza[60]fullerene family.
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Introduction

In 1995, five years after the development of a large-scale process[1] for the synthesis of buckminsterfullerene (C_{60}),[2] several groups reported the mass spectrometric observation of the aza[60]fulleronium ion ($C_{59}N^+$) as a fragmentation product from cage-opened C_{60} derivatives.[3–5] Inspired by those findings, the development of a synthetic route to bi(aza[60]fullerenyl) ($C_{59}N)_2$ (**2**) (Figure 1) was first accomplished by Wudl's[3] group and shortly after that, by an alternative route, by our group.[4b]

1 2

Figure 1. Aza[60]fullerenyl radical **1** and the stable bi(aza[60]fullerenyl) **2**.

Here we would like to present a synthetic approach directed towards the elusive diazaheterofullerene family ($C_{58}N_2$). In close analogy to the discoveries described above, it is oriented towards the observation of $C_{58}N_2$ as a fragmentation product under mass spectrometry conditions.

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Generally, heterofullerenes[6] are defined as compounds in which one or more carbon atoms of the fullerene cage are substituted by non-carbon atoms.

In the above case, the heteroatom is nitrogen, which means that the parent aza[60]fullerene $C_{59}N$ (**1**) is an open-shell molecule, thus forming the stable dumbbell-shaped dimer ($C_{59}N)_2$ (**2**) (Figure 1). Monoazafullerenes so far represent the only class of heterofullerenes that is accessible on a preparative scale, and their unique properties[7] and modes of chemical functionalization[8] have been widely investigated. In this context, it seems surprising that no diaza[60]fullerene has been prepared until now. There is only one study[9] that provides mass spectrometric evidence for the existence of $C_{60-n}N_n$ molecules with even-numbered ratios of carbon/nitrogen atoms. Several conventional synthetic approaches have been proposed and attempted in the past 10 years,[8b,10] but all have proven unsuccessful. Nevertheless, there are two reasons why a diaza[60]fullerene is still a highly appealing synthetic target. Firstly, according to theoretical calculations,[11] most members of the diaza[60]-fullerene family (16 theoretically possible constitutional isomers for $C_{58}N_2$) would be closed-shell molecules and thus, unlike monoaza[60]fullerene ($C_{59}N$), should exist as monomers. Secondly, and more importantly, according to other computational studies,[12] $C_{58}N_2$ would possess fascinating physical properties: in particular, the range of the HOMO–LUMO gap[13] could lead to interesting applications.

Since the synthetic approach towards $C_{58}N_2$ presented in this paper is fundamentally based on Wudl's synthesis of ($C_{59}N)_2$, that reaction sequence is briefly discussed here (Scheme 1).[14] A 1,3-dipolar cycloaddition between C_{60} (**3**) and MEM-azide (**4**) leads to a triazoline **5**,[15] which at high

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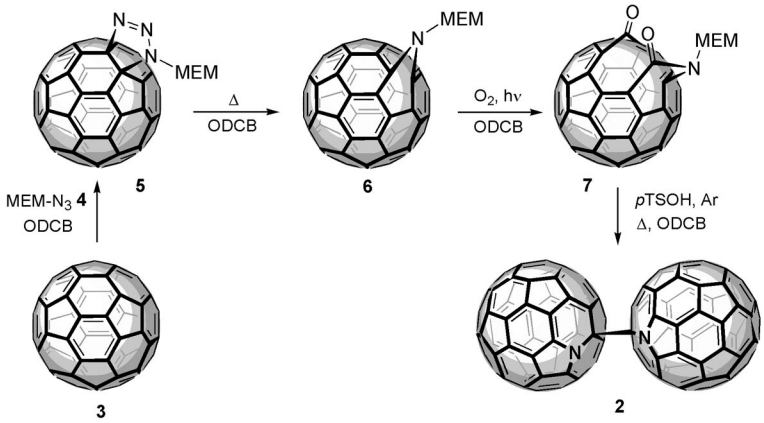

Scheme 1. Synthesis of $(C_{59}N)_2$, showing the two isolated intermediates: 1,6-aza[N-MEM]homo[60]fullerene **6** and C_{60}N-MEM-oxo-lactam **7**.

temperature is converted with nitrogen extrusion into a mixture of three different adducts. Under carefully chosen conditions, the relatively stable [5,6] adduct **6** is the main product and can be isolated. This intermediate is then subjected to a self-sensitized photooxygenation, leading to the exclusive formation of C_{60}N-MEM-oxo-lactam **7**. The final step is the conversion of oxo-lactam **7** into the bi(azafullerenyl) dimer $(C_{59}N)_2$ (**2**). It is important to note that when **7** is subjected to FAB mass spectrometry, significant peaks for the azafulleronium cation ($C_{59}N^+$) can already be observed.[3]

To accomplish this process on a preparative scale, the oxo-lactam **7** is treated at elevated temperature with *para*-toluenesulfonic acid (*p*-TsOH), which initiates a three-step, one-pot process.[3] The first step is the acid-catalysed cleavage of the MEM group, which gives rise to a reactive *N*-methyl carbonium intermediate. The second step is an intramolecular ring formation followed by loss of formaldehyde and carbon monoxide to give an azafulleronium ion. The last step is the in situ reduction of the $C_{59}N^+$ cation to the $C_{59}N$ radical, which undergoes rapid dimerization to the bi(azafullerenyl) dimer $(C_{59}N)_2$ (**2**). The elaborate strategic design of $C_{59}N$ derivatives that are able to perform an intramolecular process analogous to the intermolecular one shown in Scheme 1 is presented below.

Results and Discussion

Design of Promising Precursor Molecules

An analysis of the synthesis of $(C_{59}N)_2$ (Scheme 1) suggests four plausible ways to synthesize a diazafullerene ($C_{58}N_2$):

(1) Reaction between an excess of MEM-azide and C_{60}: This is probably the most obvious approach, and indeed, a bis(equivalent) of adduct **6** has successfully been isolated.[16] This diazafulleroid **8** (Figure 2) could only be converted into $C_{59}N$, however; formation of $C_{58}N_2$ was never observed.[4] A plausible explanation for the failure of this approach is that in the diazafulleroid **8** the two MEM-substituted nitrogen atoms are only separated by one carbon atom and that a synchronous introduction of those two atoms into the fullerene framework would lead to intermediates that are sterically not possible.

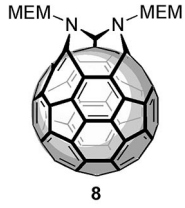

Figure 2. Structure of 1,6;1,9-bis[aza(N-MEM)]homo[60]fullerene **8**.

(2) Reaction between C_{60} and bis(azides): This approach was previously attempted in our group, both in an inter- and an intramolecular fashion. While the intermolecular approach again only gave $C_{59}N$ species, the intramolecular approach [bis(azide) covalently attached to C_{60}] failed for synthetic reasons.[17]

(3) Reaction between $(C_{59}N)_2$ or a $C_{59}N$ derivative and MEM-azide under the conditions described in Scheme 1: This is another obvious approach previously attempted in our group. No stable intermediate or product could ever be isolated, and no $C_{58}N_2$ species could be detected by mass spectrometry. Certainly a problem with this approach is that addition of an azide to a $C_{59}N$ derivative can result in 16 different constitutional isomers.

(4) Intramolecular addition of a spacer-bound azide group to a double bond of the heterofullerene core: Figure 3 shows a schematic representation of a corresponding precursor molecule.

The general advantage of this approach, in relation to strategies (1) and (2), is that one nitrogen atom is already incorporated into the fullerene framework, so that this process is carried out in a stepwise manner instead of simultaneously, as in the cases of (1) and (2). The main advantage over strategy (3) is that, through appropriate design of both linker and spacer geometry it seems feasible to achieve control over the isomeric outcome of the decisive dipolar 1,3-

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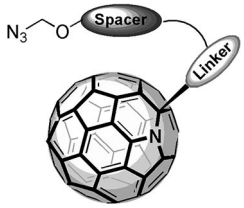

Figure 3. General representation of envisaged target structures as precursors for the formation of $C_{58}N_2$.

addition. Approach (4), presented in this contribution, is synthetically more demanding than all the other approaches, however. As such, at the beginning of the project we identified four important prerequisites for promising target structures; these are presented and discussed below:

(I) The synthesis of the $C_{59}N$ adduct must be reliable, which is why only Mannich-type[8c] or arylation functionalizations of $(C_{59}N)_2$ come into consideration.[6]

(II) Because of the mechanism of the last synthetic step shown in Scheme 1, an acid-labile functionality – more precisely, an analogue for the MEM or MOM protecting group – must be incorporated into the spacer chain. A convenient and mild procedure for the synthesis of an –O–CH_2–N_3 functionality must thus be found.

(III) Most azaheterofullerene derivatives prepared so far suffer from very low solubility once they are vigorously dried. If further reactions have to be carried out with the material, sufficient solubility either in 1,2-dichlorobenzene (ODCB) or in 1,2-tetrachloroethane (TCE) seems essential. The linker moiety should thus bear a powerful solubilizing group such as a triethylene glycol ether chain.[8e]

(IV) The regioselectivity of the decisive [3+2] addition will be highly dependant on the design of the spacer moiety. Consequently, extensive molecular modelling, using semi-empirical methods,[18] was carried out with various different spacer motifs. The main purpose of this was to identify spacer geometries that should favour the [3+2] addition in the two equatorial double bonds ^{C}e and ^{N}e of the heterofullerene core. Those two double bonds were chosen because they are the only ones that would lead to triazoline adducts with C_s symmetry. In order to do this, the total energies for possible isomeric triazoline products were calculated; the results of these calculations and a figure that clarifies the labelling of the different double bonds are given in the Supporting Information. Additionally, those "ring-closed" energy values were compared with the total energies of molecules in which a C–C bond in the spacer is opened. This strategy, which is closely related to Pople's concept of isodesmic equations,[19] helped us to estimate the amount of strain present in the different triazoline isomers.

Figure 4 shows three target structures that fulfill all the above requirements. In all three cases the linker is an aromatic ring that carries a triethylene glycol monoethyl ether chain *para* to the heterofullerene core, and with the spacer moiety bearing a terminal azidomethyl ether functionality in the *meta* position. While the spacer part of **9** is just an aliphatic chain, **10** and **11** have either an ester or amide moiety in the spacer motif. From a retrosynthetic point of view this makes compound **9** significantly different from **10** and **11**, since in the synthesis of **9** the azidomethoxy functionality must be introduced after the functionalization of $(C_{59}N)_2$ with the aromatic ring. The reason for this is that model studies have shown that the N_3–CH_2–O fragment would not survive the harsh conditions (150 °C, excess *p*-TsOH) that are required for the electrophilic substitution. Since the crucial two-step introduction of the azidomethoxy functionality has to be done after the convergent synthesis of the heterofullerene derivative, this synthetic strategy is referred to below as a divergent approach. The situation is different for **10** and **11**. The azidomethoxy functionality could be introduced into a small bifunctional molecule (only the spacer part) and subsequently coupled in only one final step to the carboxylic acid of a corresponding heterofullerene derivative. This strategy is therefore called the convergent approach.

Convergent Approach

As indicated above, the synthetic efforts in the context of the convergent approach can be divided into two parts: the synthesis of a small bifunctional molecule bearing both the azidomethoxy and an alcohol or amine group on the one hand, and the synthesis of a $C_{59}N$ derivative bearing a carboxylic acid functionality on the other. With regard to the latter, it has to be noted that so far no heterofullerene derivative bearing a carboxylic acid has been reported. In view of the relatively wide range of $C_{59}N$ derivatives that has been described so far,[6a] however, we saw no reason why

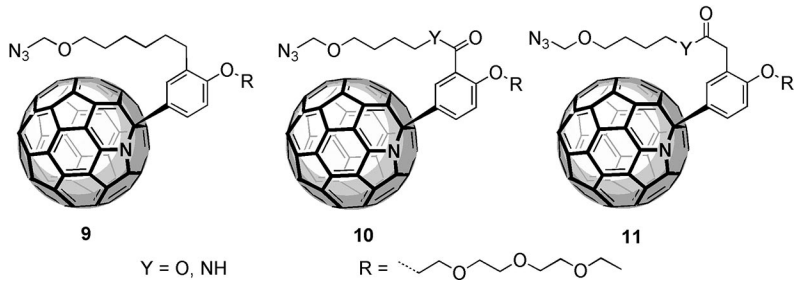

Figure 4. Target structures that, according to molecular modelling, should be able to perform regioselective [3+2] addition at the ^{C}e or ^{N}e double bonds. For reasons of convenient chemical functionalization, the arylation reaction seems more promising, which means that the linker moiety in Figure 2 should be an aromatic ring.

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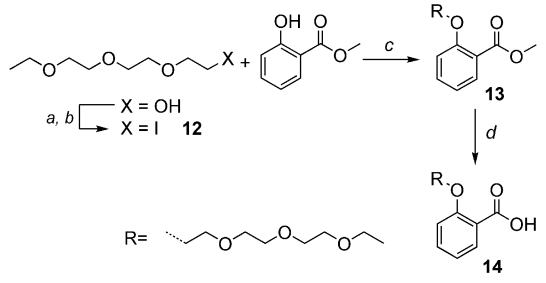
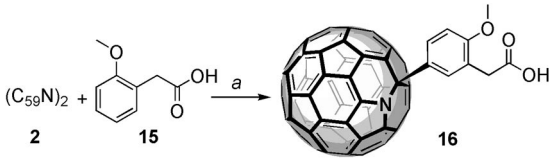
such a product could not be obtained. Another important aspect of this approach is that prior to our experiments it was not clear whether the synthesis of a compound such as **10**, in which the aromatic ring is substituted with both a strongly electron-donating and a strongly electron-withdrawing group, is generally possible. This, in fact, was the reason why **11** was considered as a "plan B", since the corresponding ring in **11** is electronically much more activated for electrophilic substitution reaction with the azafulleronium cation.

Scheme 2 shows the synthesis of the carboxylic acid precursor **14**. Subsequently, the synthesis of precursor compound **10** from **14** and the bi(azafullerenyl) **2** under standard conditions was attempted.[8a] After the usually required reaction times, however, no product was obtained, and with longer reaction times (more than 30 min) the decomposition of **2** to its bis(*N*-oxide) occurred. To confirm that this failure was due to the relatively low electron density of the aromatic ring of **14**, a model experiment with commercially available acid **15** was carried out. The successful synthesis of $C_{59}N$ derivative **16**, shown in Scheme 3, demonstrated that $C_{59}N$ derivatives of carboxylic acids can indeed be synthesized, if the aromatic ring is sufficiently activated. Furthermore, the experiment revealed that, as expected, the *para*-directing effect of the methoxy group is far stronger than the corresponding effect of the methylene unit, so that only one constitutional isomer is formed.



Scheme 2. Synthesis of **14**. Reaction conditions: (a) $SOCl_2$, toluene, 90 °C, 24 h, 57%; (b) NaI, acetone, reflux, 36 h, 94%; (c) DMF, K_2CO_3, room temp., 24 h, 99%; (d) NaOH, H_2O, MeOH, reflux, 20 h, 57%.



Scheme 3. Synthesis of the carboxylic acid $C_{59}N$ derivative **16**. Reaction conditions: (a) O_2, *p*-TsOH, ODCB, 150 °C, 18 min, 23%.

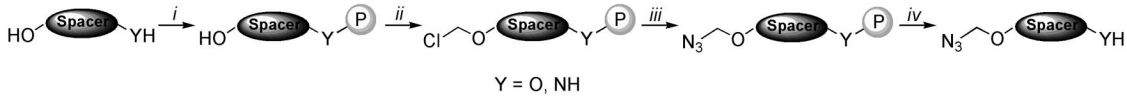
With this promising result in hand, the synthesis of the second moiety, intended for coupling to a compound such as **16**, was evaluated. Scheme 4 shows the general idea behind the synthesis of the desired molecules, which should bear both an azidomethoxy and an alcohol or amine group, separated by a spacer moiety. The first step (i) would be the monoprotection of the alcohol or amine with a protecting group[20] that must be suitably acid-stable to survive the next synthetic step. For the alcohol group, benzylic, TBDMS or TBDPS ethers were taken into consideration, and for the amine the Fmoc group. The second step (ii) would be the introduction of the chloromethyl ether moiety (i.e., a chloromethylation reaction). Particularly with respect to the stability of the protecting groups towards acid, this was expected to be the key step of the sequence. Because of the high reactivity towards nucleophiles and air moisture[21] (neighbouring group effect), as well as the toxicity[22] of the chloromethyl ether fragment, step (ii) would be directly followed by nucleophilic substitution with NaN_3 [step (iii)]. The final step (iv) should then be a preferably mild deprotection, leading to the alcohol or amine.

Chloromethylation of alcohols with dry HCl gas and *s*-trioxane (as a formaldehyde source) is the classical method[23] for the preparation of the important protecting group precursors MEM and MOM chloride.[24] Unfortunately, this procedure turned out to be incompatible with all three of the protecting groups described above. Although the reaction conditions were varied over a broad range, no chloromethyl ether or corresponding azidomethyl ether [(after step (iii)] were obtained. Subsequent control experiments confirmed that the failure of the reaction was a consequence of cleavage of the above protecting groups.

As a result of the described synthetic problems and the absolute necessity of the azidomethoxy fragment in this project, alternative conditions for the chloromethylation reaction [step (ii)] had to be found. Whereas one possible strategy using MEM chloride and BCl_3[25] did not seem very practical, a procedure published by Shipov et al. seemed very promising.[26] It made use of paraformaldehyde instead of *s*-trioxane, and of TMS chloride instead of HCl gas. In the original version the reactions were carried out neat in TMS chloride; more recently, however, the use of dry CCl_4 as solvent was reported.[27]

As is shown in Scheme 5, the use of this procedure led to the successful preparation of 4-(azidomethoxy)butan-1-ol (**20**).

The next step in the context of the convergent approach would have been the synthesis of a carboxylic acid $C_{59}N$ derivative more soluble than **16** and the *N*,*N*′-dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-[3-(dimethylamino)pro-



Scheme 4. Schematic representation of the alcohol/amine synthesis in the context of the convergent approach. Synthetic steps: (i) protection of the alcohol/amine with an acid-stable group; (ii) chloromethylation; (iii) introduction of the azidomethyl functionality; (iv) selective deprotection.

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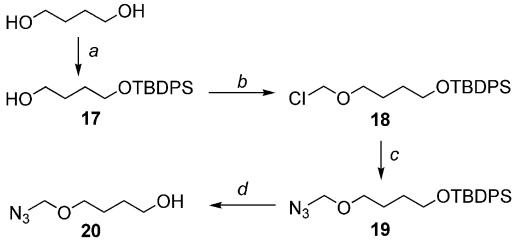
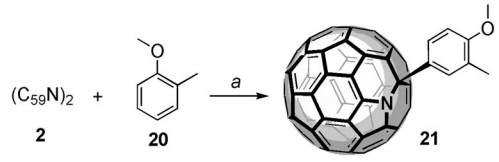


Scheme 5. Synthesis of bifunctional compound **20**. Reaction conditions: (a) TBDPS-Cl, DIPEA, DCM, room temp., 2 h, 83%; (b) paraformaldehyde, TMSCl, room temp., 2.5 h; (c) NaN_3, 18-crown-6, THF, room temp., 14 h, 50% (two steps); (d) TBAF, THF, room temp., 3 h, 57%.

pyl]carbodiimide (EDCI) coupling of alcohol **20** to this acid. However, the results of the divergent approach, described below, seemed to make further work on the convergent approach unnecessary.

Divergent Approach

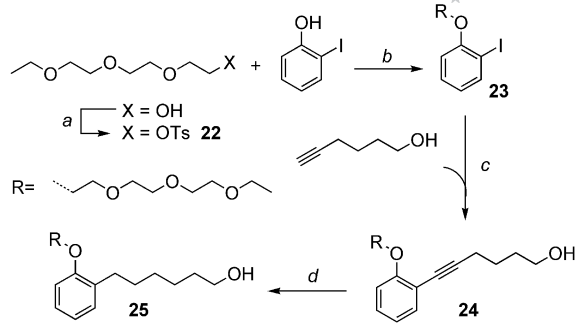
Firstly, model compound **21** was successfully synthesized (Scheme 6) to verify once more the general possibility and the regioselectivity of the reaction.



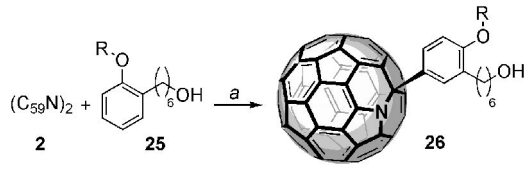
Scheme 6. Synthesis of model compound **21**. Reaction conditions: (a) O_2, *p*-TsOH, ODCB, 150 °C, 20 min, 24%.

Scheme 7 shows the synthesis of the important precursor **25**. For the introduction of the triethylene glycol monoethyl ether chain the higher-yielding route via the tosylate **22** was chosen this time. The key step was the C–C bond-forming Sonogashira reaction, which, despite rigorous exclusion of oxygen and some optimization efforts, gave high amounts of homo-coupled alkyne (Glaser reaction). Thanks to the high yields of all other synthetic steps in Scheme 7, however, an extensive optimization of the reaction conditions was not necessary. With the successful synthesis of a multigram amount of **25**, the next step was the preparation and full characterization of aza[60]fullerene derivative **26**. Scheme 8 shows the corresponding reaction sequence.

After purification by preparative HPLC, analytically pure **26** was obtained and fully characterized. The synthesis of **26** was accompanied by the formation of a remarkable side product during step (b) in Scheme 8. As previously reported,[4b] dimer **2** can react, via the intermediate azafulleronium cation, with an alcohol group to form a hemiaminal (S_N1 substitution). By HPLC we were even able to isolate and characterize this interesting compound **26a** (structure and ^1H NMR spectrum are given in the Supporting Information).

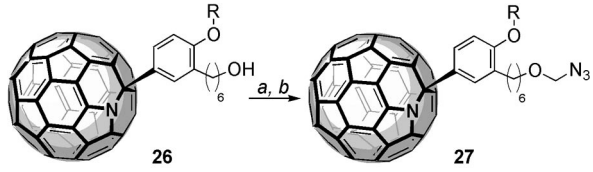


Scheme 7. Synthesis of precursor **25**. Reaction conditions: (a) *p*-TsCl, NEt_3, 0 °C to room temp. 5 h, 100%; (b) K_2CO_3, DMF, room temp., 48 h, 85%; (c) CuI, $Pd(Ph_3)_2Cl_2$, Et_2NH, THF, 0 °C to room temp. 24 h, 29%; (d) H_2, Pd/C, EtOH, room temp., 18 h, 85%.



Scheme 8. Synthesis of $C_{59}N$ derivative **26**. Reaction conditions: (a) O_2, *p*-TsOH, ODCB, 150 °C, 20 min, 24%; R = triethylene glycol monoethyl ether chain.

Subsequently, a convenient method for the introduction of the azidomethoxy functionality into $C_{59}N$ derivative **26** had to be found. Thanks to its successful application in the convergent approach, the chloromethylation described by Shipov et al.[26] was the method of choice. For **26** it turned out that 1,1,2,2-tetrachloroethane (TCE) proved to be the most suitable solvent for both reaction steps (a) and (b) in Scheme 9.



Scheme 9. Two-step introduction of the azidomethoxy functionality. Reaction conditions: (a) paraformaldehyde, TMS-Cl, TCE, room temp., 2.5 h; (b) NaN_3, 18-crown-6, TCE, room temp., 14 h; R = triethylene glycol monoethyl ether chain.

Although the formation of product **27** could be confirmed by thin layer chromatography (TLC) and in particular by IR spectroscopy, chromatographic purification appeared to be impossible, due to the instability of the azidomethoxy fragment. Consequently, for the proof of concept, towards which this contribution is directed, further one-pot experiments concerning $C_{58}N_2$ were carried out with crude **27**.

Except for the presence of TCE as co-solvent, the chosen reaction conditions were exactly the same as in the introduction of the first nitrogen atom into the fullerene frame-

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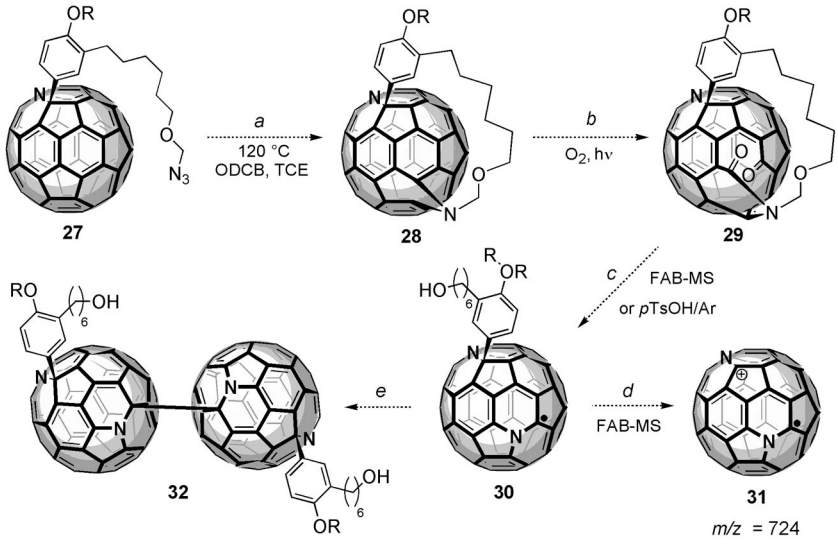

Scheme 10. One-pot semisynthetic approach towards $C_{58}N_2$. The molecular processes for the formation of only one, presumably preferred, isomer (^{C}e) during the [3+2] addition are shown. The reaction conditions (a) and (b) are the same as those shown in Scheme 1; R = triethylene glycol monoethyl ether chain.

work (Scheme 1). Scheme 10 depicts the molecular processes believed to happen during this sequence when the [3+2] addition occurs in the ^{C}e position (as predicted by molecular modelling).

The first step is the [3+2] addition, which, after nitrogen extrusion, leads to the spacer-bridged [5,6] adduct **28**. Photooxygenation [step (b)] of the sample should then lead to the $C_{59}N$-oxo-lactam **29**, which, analogously to the C_{60}-oxo-lactam **7**, should fragment under the conditions of FAB mass spectrometry to the diazaheterofullerene compound **30** and further to the $C_{58}N_2$ radical cation **31** (*m*/*z* = 724).

Since it would have been unlikely, even in the case of a fully regioselective [3+2] addition step, that the presence of a $C_{58}N_2$ species would be observable by NMR spectroscopy, the analysis of the samples treated as shown in Scheme 10 was mainly based on FAB mass spectrometry. Figure 5 shows a typical FAB mass spectrum obtained immediately after the two-step reaction sequence directed towards species **29** (Scheme 10). The zoom on the region between *m*/*z* = 700 and 850 (Figure 5a) reveals that the major peak clearly still belongs to a $C_{59}N$ species (*m*/*z* = 722). Furthermore, the signal-to-noise ratio appears to be very good, so that an analysis of the isotopic pattern is legitimate.

An analysis of the intensities of the peaks between *m*/*z* = 722 and 726 is shown in Figure 5b. A comparison with the calculated isomeric distribution for pure $C_{59}N$ derivatives given in Figure 6a shows that the experimentally observed values for *m*/*z* = 724 and 725 are significantly enhanced. It is important to note that the intensities of the isomeric patterns for all other $C_{59}N$ derivatives synthesized during this work were much closer to the ideal, as shown in Figure 6a. Figure 6b shows the calculated intensity distribution for a sample with a ratio of 4:1 between $C_{59}N$ and $C_{58}N_2$ species, which is in good agreement with the experimental result shown in Figure 5b.

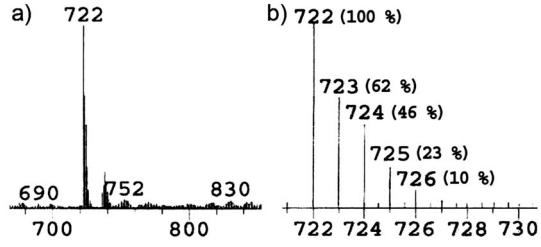

Figure 5. (a) FAB mass spectrum of a crude sample of **27** treated as is shown in Scheme 10. (b) Zoom on the decisive region, with the relative intensities of the corresponding peaks shown in parentheses.

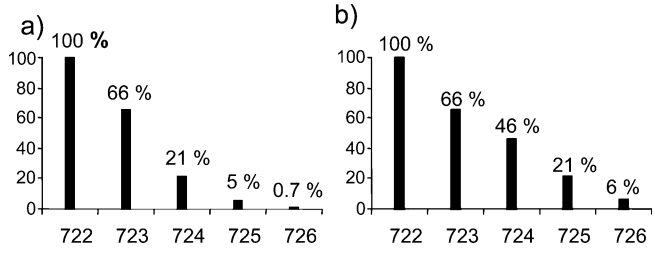

Figure 6. Calculated isotopic patterns with peak intensities in %: (a) for a sample of a pure $C_{59}N$ species; (b) for a sample containing both a $C_{59}N$ and a $C_{58}N_2$ species in a ratio of 4:1.

Considering that the procedure was carried out in a one-pot manner, a conversion of 20% of the material into a $C_{58}N_2$ species seems quite realistic.

Encouraged by these results, we now intend to move on, on the basis of the findings presented in this paper, to design new precursors and experiments with the ultimate goal of isolating preparative amounts of a member of the diazafullerene ($C_{58}N_2$) family.

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Conclusions and Outlook

The evaluation of a new fundamental approach towards the synthesis of the $C_{58}N_2$ family is presented. With the aid of extensive molecular modelling, two general synthetic routes towards suitably functionalized $C_{59}N$ derivatives were designed and executed. For the introduction of the mechanistically essential azidomethoxy functionality, a mild chloromethylation procedure, using TMSCl instead of HCl gas, proved to be successful. Subsequent one-pot experiments were carried out, each of them making use of the same conditions as previously used for the introduction of the first nitrogen atom into the fullerene framework. Immediate analysis by FAB mass spectrometry indicated that samples with contents of up to 20% of a $C_{58}N_2$ species were obtained. This represents the first strategic chemical synthesis of a $C_{58}N_2$ derivative. Although isolation of the corresponding material was not possible in this case, this work has to be seen as a major step forward in the ongoing quest for $C_{58}N_2$, and we are confident that a related strategy will lead to its isolation in the near future.

Experimental Section

General: All starting materials were, if not otherwise specified, purchased from commercial sources. All solvents were distilled prior to use. 1,2-Dichlorobenzene (ODCB) and 1-chloronaphthalene were distilled from calcium hydride. Ethyl acetate, dichloromethane and toluene were distilled from potassium carbonate. The bulk of the C_{60} used was provided by Aventis as a C_{60}/C_{70} mixture, which was subsequently purified by plug filtration.[28] Pure C_{60} was purchased from Job Joint srl. Reactions were monitored by thin layer chromatography (TLC) on silica 60 F_{254} TLC aluminium foils (Merck). Products were isolated by flash column chromatography (FC; silica gel 60M, 0.04–0.063 mm/230–400 mesh ASTM, Macherey–Nagel and MP Ecochrom Silica, 32–63, 60 Å, MP Biomedicals). NMR spectra were recorded with Jeol JNM EX 400, Jeol JNM GX 400 or Bruker Avance 300 NMR spectrometers. Chemical shifts are indicated in ppm in relation to the particular internal standard (^{1}H NMR: δ = 7.27 ppm for $CDCl_3$, δ = 5.98 ppm for $C_2D_2Cl_4$; ^{13}C NMR: δ = 77.00 ppm for $CDCl_3$, δ = 73.70 for $C_2D_2Cl_4$). Signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) or combinations thereof. Unresolved signals are labelled br. (broad). Mass spectra were recorded with a Micromass Zabspec spectrometer [FAB mode, matrix: 3-nitrobenzyl alcohol (NBA)]. For the EI spectra a Varian MAT 311A spectrometer was used. IR spectra were recorded neat with an ASI-ReactIR 1000 spectrometer. Elemental analyses were carried out with an EA 1110 CHNS machine from CE Instruments. Optical spectra were recorded with a Specord® S 600 simultaneous high-performance diode-array UV/Vis spectrophotometer (Analytic Jena AG). Analytical and preparative high performance liquid chromatography (HPLC) was performed with Shimadzu Corporation and Analytical Instruments Division instruments. Solvents were purchased from Acros Organics and VWL in HPLC quality. For the columns, Cosmosil (Buckyprep Waters 4.6 × 250 mm, Nacalai Tesque) and Nucleosil (200 × 4 mm, 5 μm, Macherey–Nagel) phases were used.

Syntheses

(2-Methoxyethoxy)methyl Azide [MEM-azide] (4): In a 500 mL round-bottomed flask, MEM chloride (22.6 mL, 24.9 g, 188 mmol, 1.0 equiv.) was dissolved in THF (350 mL). 18-Crown-6 (1.49 g, 5.6 mmol, 0.03 equiv.) and sodium azide (37 g, 564 mmol, 3.0 equiv.) were added to this solution. The solution was stirred at room temperature for 24 h. The solid sodium azide residue was removed by filtration, and the solvent was evaporated. Vacuum distillation (40 °C, 0.2 mbar, ***shield!***) produced a clear, colorless liquid. Yield: 24.54 g (99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.70 (s, 2 H), 3.76 (m, 2 H), 3.57 (m, 2 H), 3.39 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.4 MHz): δ = 83.07, 71.44, 68.61, 58.97 ppm. IR (neat): $\tilde{\nu}$ = 2930, 2891, 2822, 2119, 1776, 1455, 1390, 1366, 1282, 1227, 1200, 1096, 1069, 1023, 988, 930, 872, 699 cm^{-1}.

Optimized Synthesis of 1,6-Aza[N-MEM]homo[60]fullerene (6): In a 2 L round-bottomed flask with a reflux condenser, C_{60} (**3**) (5.0 g, 6.94 mmol) was dissolved in ODCB (1000 mL). After the solution had been heated at 180 °C overnight, MEM-azide (**4**) (450 μL, 461 mg, 3.52 mmol) was added, and the purple solution was stirred for 60 min. After quick cooling to room temperature, approximately 700 mL of the solvent were removed under reduced pressure. The products of the reaction were obtained by flash column chromatography (8 × 15 cm, 240 g of SiO_2, toluene). Firstly, C_{60} (**3**) (violet, $R_f \approx 1$), followed by 1,6-aza[N-MEM]homo[60]fullerene (**6**) (grey-brown, R_f = 0.49) and 1,2-dihydro[N-MEM]aziridino[60]-fullerene (pink, R_f = 0.46) were consecutively eluted. After the elution of a small quantity of undecomposed triazoline **5** (brown) the eluent could be switched to toluene/ethyl acetate (9:1) to isolate the bis(adduct) **8** (R_f = 0.1) as a broad, brown band. After evaporation of the solvents, each product can be further purified by dissolving it in a minimum amount of CS_2, precipitation from *n*-pentane and repeated washing with *n*-pentane, together with drying at high vacuum. It turned out, however, to be advisable to convert the isolated 1,6-aza[N-MEM]homo[60]fullerene (**6**) directly (i.e., without further purification) into oxo-lactam **7**, since the dry product was only minimally able to re-dissolve in organic solvents after a certain period of time. The eluted C_{60} fraction was thoroughly freed from toluene and ODCB in a rotary evaporator. The recovered C_{60} (**3**) (appr. 4 g) was transferred to a frit and was successively washed with THF (50 mL) and *n*-pentane (50 mL). After drying in high vacuum, the C_{60} (**3**) can be reused for the synthesis of **6** as outlined above. Brown-black solid; yield not determined at this step. ^{1}H NMR ($CS_2/CDCl_3$, 400 MHz): δ = 5.27 (s, 2 H), 4.17 (t, ^3J = 4.8 Hz, 2 H), 3.70 (t, ^3J = 4.8 Hz, 2 H), 3.41 (s, 3 H) ppm. ^{13}C NMR ($CS_2/CDCl_3$, 100.4 MHz): δ = 147.57, 144.71, 144.53, 144.41, 144.19, 144.07, 143.92, 143.78, 143.61, 143.38, 143.28, 143.18, 142.98, 142.84, 142.80, 142.67, 142.52, 142.43, 141.47, 140.57, 140.28, 139.09, 138.29, 138.23, 138.03, 137.55, 136.76, 136.15, 135.60, 133.33, 83.69, 72.00, 68.25, 58.74 ppm. IR (neat): $\tilde{\nu}$ = 2976, 2953, 2914, 2866, 2807, 1557, 1509, 1460, 1428, 1391, 1371, 1340, 1307, 1266, 1227, 1200, 1172, 1104, 1020, 932, 850, 804, 768, 644, 629, 593, 581, 570, 559, 541, 525, 489, 480, 444 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 262, 332, 428, 545 nm. MS (FAB, NBA): *m*/*z* = 823 $[M]^+$, 720 $[C_{60}]^+$.

Optimized Synthesis of C_{60}-N-MEM-oxo-lactam 7: In a 250 mL Schlenk tube 1,6-aza[N-MEM]homo[60]fullerene (**6**) was dissolved in ODCB (150 mL). The tube was immerged in a basic, aqueous solution of potassium chromate, which served as a light filter and had to be vigorously stirred and kept at a constant 5 °C by means of a cryostat. The reaction mixture was stirred and irradiated with two halogen flood lights (500 W) while a steady, slow stream of oxygen (gas bottle) was passed through the solution. The progress of the reaction was monitored by TLC (silica gel, toluene/ethyl acetate, 9:1). After approximately 6 h, the formation of the C_{60}-N-MEM-oxo-lactam **7** was almost complete, and the reaction mixture was purified by flash column chromatography (silica gel, 5 × 6 cm,

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35 g of SiO_2, toluene, toluene/ethyl acetate, 9:1). After elution of traces of C_{60}, unconverted reactant **6** was eluted with pure toluene. Subsequently, the eluent was switched to toluene/EtOAc (9:1), and C_{60}-N-MEM-oxo-lactam **7** was obtained as a red-brown band. After evaporation of the solvents under reduced pressure, the red-brown solid was reprecipitated from *n*-pentane and dried in high vacuum. R_f = 0.53 (toluene/ethyl acetate, 9:1); yield: 354 mg (15.1% corresponding to MEM-azide **4**). ^{1}H NMR (CS_2/$CDCl_3$, 400 MHz): δ = 6.30 (d, ^2J = 11.0 Hz, 1 H), 5.93 (d, ^2J = 11.0 Hz, 1 H), 3.97 (m, 2 H), 3.55 (m, 2 H), 3.30 (s, 3 H) ppm. ^{13}C NMR (CS_2/$CDCl_3$, 100.4 MHz): δ = 196.69, 162.11, 149.63, 148.96, 147.45, 146.99, 146.84, 146.52, 146.34, 146.29, 145.99, 145.79, 145.73, 145.70, 145.64, 145.49, 145.38, 144.99, 144.94, 144.79, 144.62, 144.46, 144.09, 143.92, 143.85, 143.77, 143.74, 143.59, 143.45, 143.39, 143.23, 143.03, 142.41, 141.30, 140.74, 140.71, 140.16, 139.95, 139.78, 139.42, 139.11, 138.99, 138.34, 137.61, 136.29, 135.64, 135.52, 135.32, 135.29, 133.79, 133.50, 132.60, 132.24, 131.45, 127.87, 80.20, 71.52, 69.85, 58.54 ppm. IR (neat): $\tilde{\nu}$ = 2957, 2910, 2880, 2806, 1725, 1687, 1559, 1513, 1494, 1444, 1420, 1393, 1370, 1254, 1197, 1100, 1073, 1046, 1023, 992, 938, 838, 803, 768, 745, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 259, 327, 429, 464, 692 nm. MS (FAB, NBA): *m*/*z* = 855 [M]$^+$, 781 [M – CH_3OCH_2-CH_2OH]$^+$, 720 [C_{60}]$^+$.

Optimized Synthesis of Bi(azafullerenyl) ($C_{59}N)_2$ (2): In a 50 mL round-bottomed flask with nitrogen inlet and reflux cooler, under argon, C_{60}-N-MEM-oxo-lactam **7** (60 mg, 70.2 μmol, 1 equiv.) was dissolved in thoroughly degassed and argon-saturated ODCB (30 mL). *p*-TsOH (400 mg, 2.11 mmol, 30 equiv.) was added to this solution, and the reaction mixture was stirred in a preheated oil bath at 150 °C for 1.5 h. During this period a slow, steady argon stream was passed over the solution. In the course of the reaction, the solution turned from brown to olive-green. The reaction can be monitored by TLC (silica gel, toluene/ethyl acetate, 9:1) or analytical HPLC (Cosmosil, toluene, 1.0 mL min^{-1}, t_R = 15.0 min). After quick cooling to room temperature, the reaction mixture was immediately purified by flash column chromatography (5 × 8 cm, 50 g of SiO_2, toluene). The bi(azafullerenyl) **2** was eluted in a broad, green band at the solvent front-line. The solution was concentrated to dryness in a rotary evaporator. If isolation of $(C_{59}N)_2$ (**2**) was intended, the residue was dissolved in a minimum amount of ODCB and reprecipitated from *n*-pentane. The black precipitate was washed five times with *n*-pentane and subsequently dried in high vacuum. If further conversion of the material was intended, the reprecipitation step was usually omitted. Analysis of the purity of the bi(azafullerenyl) **2** was possible by analytical HPLC (Cosmosil, 1.0 mL min^{-1} toluene, t_R = 15.0 min). Brown-black solid; R_f = 1.0 (toluene); yield: 38 mg (75%). ^{13}C NMR (CS_2/$CDCl_3$, 100.4 MHz): δ = 156.15, 148.43, 147.84, 147.42, 146.63, 146.58, 146.31, 145.81, 145.18, 144.59, 144.35, 144.00, 143.28, 142.88, 142.21, 141.86, 141.77, 141.39, 141.04, 140.04, 137.82, 136.15, 130.23, 127.30, 124.87, 80.10 ppm. IR (KBr): $\tilde{\nu}$ = 1583, 1551, 1510, 1455, 1424, 1363, 1342, 1326, 1289, 1237, 1215, 1186, 1172, 1092, 1034, 963, 844, 817, 762, 746, 683, 578, 568, 557, 524, 504, 481, 469 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 259, 328, 441, 590 nm. MS (EI): *m*/*z* = 722 [$C_{59}N$]$^+$, 696 [$C_{59}N$ – CN]$^+$, 672 [$C_{59}N$ – -C_2-CN]$^+$, 648 [$C_{59}N$ – -C_2-C_2-CN]$^+$, 624 [$C_{59}N$ – -C_2-C_2-C_2-CN]$^+$, 600 [$C_{59}N$ – -C_2-C_2-C_2-C_2-CN]$^+$.

2-[2-(2-Ethoxyethoxy)ethoxy]ethyl Iodide (12): In a dry 500 mL round-bottomed flask with reflux cooler and addition funnel, triethylene glycol monoethyl ether (71.32 g, 400 mmol, 1.0 equiv.) was dissolved in dry toluene (350 mL) under inert gas. A solution of thionyl chloride (44 mL, 600 mmol, 1.5 equiv.) in dry toluene (50 mL) was slowly added to this solution with constant stirring. Subsequently, the solution was stirred at 90 °C for 24 h. The remaining thionyl chloride and the toluene were distilled off at normal pressure, and the crude chloride was purified by vacuum distillation (90 °C, 0.05 mbar). In a dry 250 mL round-bottomed flask with reflux cooler, 2-[2-(2-ethoxyethoxy)ethoxy]ethyl chloride (10.00 g, 50.8 mmol, 1.0 equiv.) was dissolved in acetone (150 mL), which had been previously dried with $MgSO_4$ and molecular sieves (4 Å). Upon the addition of sodium iodide (22.86 g, 153 mmol, 3.0 equiv.), the solution was heated at reflux for 36 h. After the mixture had cooled to room temperature, water (100 mL) was added, and the mixture was extracted three times with diethyl ether (150 mL). The combined organic phases were washed with saturated NaCl solution (100 mL), dried with $MgSO_4$ and filtered. After evaporation of the solvents and drying in high vacuum, a yellow-orange oil of low viscosity was obtained. Yield: 13.79 g (54% two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.76 (t, ^3J = 6.8 Hz, 2 H), 3.67 (m, 8 H), 3.26 (t, ^3J = 6.8 Hz, 2 H), 3.53 (q, ^3J = 7.1 Hz, 2 H), 1.22 (t, ^3J = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 71.95, 70.72, 70.58, 70.19, 69.79, 66.61, 15.07, 2.81 ppm. IR (neat): $\tilde{\nu}$ = 2972, 2868, 1737, 1602, 1455, 1378, 1351, 1293, 1247, 1104, 1038, 996, 942, 845, 757, 687 cm^{-1}. MS (FAB, NBA): *m*/*z* = 289 [M + H]$^+$.

Methyl 2-{2-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}benzoate (13): In a dry 250 mL round-bottomed flask with nitrogen inlet, **12** (5.16 g, 17.9 mmol, 1.2 equiv.) and methyl salicylate (2.27 g, 14.9 mmol, 1.0 equiv.) were dissolved in DMF (100 mL, extra dry). Upon addition of potassium carbonate (2.48 g, 17.9 mmol, 1.2 equiv.), the suspension was stirred at room temperature for 24 h. After the addition of a saturated, aqueous NH_4Cl solution (100 mL), the reaction mixture was extracted three times with dichloromethane (50 mL). The combined organic phases were washed with water (100 mL), dried with $MgSO_4$ and filtered, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography (8 × 12 cm, 250 g of SiO_2, DCM/EtOAc, 4:1). Clear, light yellow oil. Yield: 4.60 g (99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (dd, ^3J = 7.9, ^4J = 1.8 Hz, 1 H), 7.44 (m, 1 H), 6.99 (m, 2 H), 4.21 (t, ^3J = 5.0 Hz, 2 H), 3.91 (t, ^3J = 5.0 Hz, 2 H), 3.88 (s, 3 H), 3.78 (t, ^3J = 4.8 Hz, 2 H), 3.69–3.58 (m, 6 H), 3.52 (q, ^3J = 7.0 Hz, 2 H), 1.21 (t, ^3J = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 166.86, 159.37, 133.43, 131.66, 120.57, 113.81, 111.99, 70.97, 70.65, 70.63, 70.60, 69.78, 68.89, 66.57, 51.86, 15.04 ppm. IR (neat): $\tilde{\nu}$ = 2976, 2946, 2930, 2872, 1729, 1602, 1490, 1451, 1351, 1305, 1247, 1189, 1100, 1050, 950, 923, 834, 757, 706, 663 cm^{-1}. MS (FAB, NBA): *m*/*z* = 313 [M + H]$^+$.

2-{2-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}benzoic Acid (14): In a 250 mL round-bottomed flask, **13** (3.55 g, 11.4 mmol, 1.0 equiv.) was dissolved in methanol (100 mL). A solution of sodium hydroxide (1.37 g, 34.2 mmol, 3.0 equiv.) in water (10 mL) was added, and the mixture was heated at reflux for 20 h. After the addition of water (50 mL), the mixture was neutralized with HCl (2 M) and extracted five times with dichloromethane (50 mL). The combined organic phases were washed with water, dried with $MgSO_4$ and filtered, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography (4 × 18 cm, 150 g of SiO_2, DCM/EtOAc/acetic acid, 66:33:1). Clear, light yellow oil. Yield: 2.04 g (57%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.01 (s, 1 H), 8.16 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H), 7.54 (m, 1 H), 7.18–7.03 (m, 2 H), 4.37 (t, ^3J = 4.6 Hz, 2 H), 3.93 (t, ^3J = 4.5 Hz, 2 H), 3.75–3.55 (m, 8 H), 3.51 (q, ^3J = 7.0 Hz, 2 H), 1.19 (t, ^3J = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 165.70, 157.44, 134.78, 133.68, 122.50, 118.61, 113.38, 70.74, 70.65, 70.50, 69.67, 69.08, 68.59, 66.54, 51.86, 15.04 ppm. IR (neat): $\tilde{\nu}$ =

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3277, 2976, 2872, 1729, 1602, 1486, 1455, 1347, 1293, 1239, 1100, 1038, 926, 842, 818, 757, 687 cm^{-1}. MS (FAB, NBA): *m/z* = 299 $[M + H]^+$.

1-[3′-(Carboxymethyl)-4′-methoxyphenyl]hydroazafullerene (16): In a dry 100 mL round-bottomed flask with nitrogen inlet and reflux condenser, the bi(azafullerenyl) **2** obtained from C_{60}-N-MEM-oxo-lactam **7** (120 mg, 140.4 μmol, 1.0 equiv.) was dissolved in ODCB (60 mL). (2-Methoxyphenyl)acetic acid (117 mg, 0.70 mmol, 5.0 equiv.) and *p*-TsOH (538 mg, 1.4 mmol, 20 equiv.) were added to this solution, and the mixture was stirred at 150 °C for 18 min, while a slow stream of oxygen was passed over the reaction mixture. The progress of the reaction was monitored by analytical HPLC (Cosmosil, toluene, 1.0 mL min^{-1}) or TLC (toluene/MeOH, 9:1, R_f = 0.16). After the mixture had cooled to room temperature, the product was obtained by flash column chromatography (6 × 15 cm, 100 g of SiO_2, toluene/MeOH, 9:1). For further purification, the black solid was dissolved in a minimum amount of CS_2, precipitated from *n*-pentane, washed several times with water (to remove any residue of the reactant) and *n*-pentane and dried in high vacuum. To avoid solubility problems, however, purification of the material by means of preparative HPLC (Nucleosil, toluene/MeOH, 98:2, 40 mL min^{-1}, t_R = 4.2 min), rather than by reprecipitation, was carried out. Brown, amorphous, solid. Yield: 21 mg (17% relative to **7**). HPLC (Nucleosil, toluene/MeOH, 95:5, 1.0 mL min^{-1}): t_R = 4.4 min. ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz): δ = 8.79 (dd, ^3J = 8.6, ^4J = 2.4 Hz, 1 H), 8.67 (d, ^4J = 2.4 Hz, 1 H), 7.29 (d, ^3J = 8.6 Hz, 1 H), 4.08 (s, 3 H), 4.04 (s, 2 H) ppm. The low solubility of this product in all conventional deuterated solvents did not allow a ^{13}C NMR spectrum to be recorded. IR (neat): $\tilde{\nu}$ = 2949, 2914, 2837, 1706, 1602, 1498, 1440, 1420, 1293, 1247, 1177, 1116, 1207, 926, 853, 815, 753, 679 cm^{-1}. UV/Vis (toluene): λ_{max} = 289, 326, 443 nm. MS (FAB, NBA): *m/z* = 722 $[C_{59}N]^+$, 888 $[M]^+$, 904 $[M + O]^+$.

4-(*tert*-Butyldiphenylsilyloxy)butan-1-ol (17): *tert*-Butyldiphenylsilyl chloride (5 mL, 18 mmol, 0.3 equiv.) was added dropwise at room temperature to a solution of butane-1,4-diol (5.0 g, 55 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) and DIPEA (10 mL, 1.06 equiv.). The solution was stirred for 2 h, concentrated in vacuo and purified by flash column chromatography (8 × 25 cm, 300 g of SiO_2, hexanes/EtOAc, 8:2). Clear, colorless oil. Yield: 4.49 g (83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (dd, ^3J = 7.7, ^4J = 1.9 Hz, 4 H), 7.42 (m, 6 H), 3.71 (m, 4 H), 2.09 (t, ^3J = 5.5 Hz, 1 H), 1.70 (m, 4 H), 1.08 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 135.62, 133.69, 129.69, 127.70, 63.97, 62.76, 29.74, 29.18, 26.76, 19.06 ppm. IR (neat): $\tilde{\nu}$ = 3323, 3073, 2934, 2860, 1471, 1428, 1390, 1363, 1189, 1108, 1061, 822, 791, 741, 699 cm^{-1}. MS (FAB, NBA): *m/z* = 329 $[M]^+$.

[4-(Azidomethoxy)butoxy](*tert*-butyl)diphenylsilane (19): In a dry 10 mL round-bottomed flask, under argon, **17** (1.0 g, 3.04 mmol, 1.0 equiv.) was dissolved in trimethylsilyl chloride (1.54 mL, 12.2 mmol, 4.0 equiv.), and paraformaldehyde (105 mg, 3.35 mmol, 1.1 equiv.) was added. The solution was stirred at room temperature for 2.5 h, during which the insoluble paraformaldehyde was successively consumed. The excess trimethylsilyl chloride was removed under reduced pressure. Because of the high reactivity, as well as toxicity (!),[22] of the chloromethyl ether, the crude material was used without further purification. Under argon, the crude chloromethyl ether was dissolved in dry THF (6 mL). Sodium azide (594 mg, 9.13 mmol, 3.0 equiv.) and 18-crown-6 (40 mg, 0.15 mmol, 0.05 equiv.) were added, and the reaction mixture was stirred at room temperature overnight. The excess sodium azide was filtered off, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5 × 25 cm, 150 g of SiO_2, hexanes/EtOAc, 95:5). Clear, colorless oil. Yield: 583 mg (50% two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (dd, ^3J = 7.9, ^2J = 1.6 Hz, 4 H), 7.43 (m, 6 H), 4.65 (s, 2 H), 3.72 (t, ^3J = 6.1 Hz, 2 H), 3.63 (t, ^3J = 6.4 Hz, 2 H), 1.75 (m, 2 H), 1.67 (m, 2 H), 1.08 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 135.62, 133.98, 129.61, 127.67, 82.88, 69.69, 63.41, 28.97, 26.77, 25.93, 19.12 ppm. IR (neat): $\tilde{\nu}$ = 3073, 2934, 2860, 2119, 1471, 1428, 1390, 1363, 1227, 1104, 938, 867, 822, 741, 699 cm^{-1}. MS (FAB, NBA): *m/z* = 311 $[M - N_3CH_2O]^+$, 384 $[M]^+$, 406 $[M + Na]^+$, 341 $[M - N_3]^+$.

4-(Azidomethoxy)butan-1-ol (20): In a dry 10 mL round-bottomed flask, **19** (400 mg, 1.04 mmol, 1.0 equiv.) was dissolved in a solution of TBAF in THF (1.0 M, 3.13 mL, 3.13 mmol, 3.0 equiv.). The light yellow solution was stirred at room temperature for 3 h, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (3 × 20 cm, 60 g of SiO_2, DCM, DCM/EtOAc, 1:1). Clear, colorless oil. Yield: 86 mg (57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.62 (s, 2 H), 3.61 (t, ^3J = 6.1 Hz, 2 H), 3.60 (t, ^3J = 6.1 Hz, 2 H), 2.48 (s, 1 H), 1.64 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 82.72, 69.51, 62.10, 29.14, 25.77 ppm. IR (neat): $\tilde{\nu}$ = 3339, 2945, 2876, 2115, 1475, 1447, 1378, 1274, 1224, 1104, 1058, 1000, 957, 934, 869, 703 cm^{-1}.

1-(4′-Methoxy-3′-methylphenyl)hydroazafullerene (21): In a dry 100 mL round-bottomed flask with nitrogen inlet and reflux condenser, the bi(azafullerenyl) **2** obtained from C_{60}-N-MEM-oxo-lactam **7** (60 mg, 70.2 μmol, 1.0 equiv.) was dissolved in ODCB (30 mL). 2-Methylanisole (171 mg, 1.4 mmol, 20 equiv.) and *p*-TsOH (269 mg, 1.4 mmol, 20 equiv.) were added to this solution, which was stirred at 150 °C for 20 min, while a slow stream of oxygen was passed over the reaction mixture. The progress of the reaction was monitored by analytical HPLC (Cosmosil, toluene, 1.0 mL min^{-1}). After the mixture had cooled to room temperature, the product was obtained by flash column chromatography (4 × 15 cm, 50 g of SiO_2, toluene). For further purification the black solid was dissolved in a minimum amount of CS_2, precipitated from *n*-pentane, washed five times with *n*-pentane and dried in high vacuum. Brown, amorphous, solid. Yield: 21 mg (18% corresponding to **7**). HPLC (Cosmosil, toluene, 1.0 mL min^{-1}): t_R = 4.92 min. ^{1}H NMR (CS_2/$CDCl_3$, 300 MHz): δ = 8.61 (m, 2 H), 7.30 (s, 1 H), 4.09 (s, 3 H), 2.58 (s, 3 H) ppm. The low solubility of this product in all conventional deuterated solvents did not allow a ^{13}C spectrum to be recorded. IR (neat): $\tilde{\nu}$ = 2914, 1710, 1691, 1606, 1556, 1498, 1440, 1417, 1243, 1116, 1096, 1073, 1046, 1027, 988, 938, 757, 679 cm^{-1}. UV/Vis (toluene): λ_{max} = 290, 325, 443 nm.

2-[2-(2-Ethoxyethoxy]ethoxy]ethyl 4-Methylbenzenesulfonate (22): In a 250 mL round-bottomed flask, triethylene glycol monoethyl ether (25 mL, 143 mmol, 1.0 equiv.) was dissolved in triethylamine (100 mL, 720 mmol, 5.0 equiv.), and the mixture was cooled to 0 °C. After addition of *para*-toluenesulfonyl chloride (30 g, 157 mmol, 1.1 equiv.), the mixture was allowed to warm slowly to room temperature and stirred for further 5 h. Subsequently, the reaction mixture was carefully added to a stirred mixture of concentrated hydrochloric acid (150 mL) and crushed ice (200 g). The mixture was extracted three times with diethyl ether (100 mL), and the combined organic phases were washed successively with brine (100 mL) and a saturated solution of sodium hydrogen carbonate. The organic phases were dried with $MgSO_4$ and filtered, and the solvents were removed under reduced pressure. Clear, colorless oil. Yield: 47.78 g (100%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, ^3J = 8.3 Hz, 2 H), 7.35 (d, ^3J = 8.3 Hz, 2 H), 4.17 (t, ^3J = 4.9 Hz, 2 H), 3.69 (t, ^3J = 4.9 Hz, 2 H), 3.63–3.56 (m, 8 H), 3.52 (q, ^3J =

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7.1 Hz, 2 H), 2.45 (s, 3 H), 1.21 (t, ^3J = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 144.76, 132.97, 129.79, 127.98, 70.73, 70.68, 70.50, 69.77, 69.22, 68.65, 66.61, 21.63, 15.14 ppm. IR (neat): $\tilde{\nu}$ = 2976, 2872, 1598, 1451, 1355, 1293, 1247, 1177, 1096, 1015, 919, 815, 772, 663 cm^{-1}. MS (FAB, NBA): *m*/*z* = 333 $[M]^+$.

1-{2-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}-2-iodobenzene (23): In a dry 250 mL round-bottomed flask with nitrogen inlet, 2-iodophenol (10.0 g, 45.5 mmol, 1.0 equiv.) and **22** (15.1 g, 45.5 mmol, 1.0 equiv.) were dissolved in DMF (120 mL, extra dry). Following the addition of potassium carbonate (37.7 g, 69.83 mmol, 6.0 equiv.), the suspension was stirred at room temperature for 48 h. The solvent was then evaporated, and water (50 mL) was added. The mixture was neutralized with HCl (1 M, pH = 5) and extracted three times with dichloromethane (80 mL). The combined organic phases were washed with water, dried with $MgSO_4$ and filtered, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography (8 × 24 cm, 400 g of SiO_2, DCM/EtOAc, 95:5). Clear, light yellow oil. Yield: 14.78 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 1 H), 7.28 (m, 1 H), 6.84 (dd, ^3J = 8.0, ^4J = 1.3 Hz, 1 H), 6.71 (td, ^3J = 7.7, ^4J = 1.3 Hz, 1 H), 4.17 (t, ^3J = 5.2 Hz, 2 H), 3.93 (t, ^3J = 5.2 Hz, 2 H), 3.82 (m, 2 H), 3.69 (m, 4 H), 3.60 (m, 2 H), 3.53 (q, ^3J = 7.1 Hz, 2 H), 1.21 (t, ^3J = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 157.55, 139.51, 129.46, 122.74, 112.45, 86.65, 71.18, 70.71, 70.66, 69.79, 69.46, 68.95, 66.58, 15.06 ppm. IR (neat): $\tilde{\nu}$ = 2972, 2868, 1583, 1475, 1440, 1374, 1351, 1278, 1247, 1108, 1054, 1019, 930, 845, 749, 706 cm^{-1}. MS (FAB, NBA): *m*/*z* = 381 $[M + H]^+$.

6-(2-{2-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}phenyl)hex-5-yn-1-ol (24): In a dry 100 mL round-bottomed flask with nitrogen inlet, **23** (8.72 g, 22.9 mmol, 0.9 equiv.), copper(I) iodide (243 mg, 1.27 mmol, 0.05 equiv.) and bis(triphenylphosphane)palladium(II) chloride (536 mg, 0.76 mmol, 0.03 equiv.) were dissolved in diethylamine (10 mL, 102 mmol, 4.0 equiv.) and dry THF (50 mL). The solution was cooled to 0 °C and stirred for 10 min, after which hex-5-yn-1-ol (2.88 mL, 25.5 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h and quenched with aqueous NH_4Cl (20 mL). Extraction with Et_2O (3 × 60 mL), washing with brine, drying with $MgSO_4$, filtration and evaporation of the solvent gave a yellow crude product, which was purified by repeated flash column chromatography (8 × 35 cm, 400 g of SiO_2, DCM/EtOAc, 1:1, 11 × 25 cm, 550 g of SiO_2, EtOAc/hexanes, 8:2). Clear, colorless oil. Yield: 2.30 g (29%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36 (dd, ^3J = 7.6, ^4J = 1.6 Hz, 1 H), 7.22 (td, ^3J = 7.9, ^4J = 1.6 Hz, 1 H), 6.87 (m, 2 H), 4.18 (t, ^3J = 5.2 Hz, 2 H), 3.94 (t, ^3J = 5.2 Hz, 2 H), 3.80 (m, 2 H), 3.72–3.63 (m, 6 H), 3.58 (m, 2 H), 3.52 (q, ^3J = 7.0 Hz, 2 H), 2.50 (t, ^3J = 6.6 Hz, 2 H), 2.01 (s, 1 H), 1.83–1.65 (m, 4 H), 1.21 (t, ^3J = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 159.36, 133.34, 128.84, 120.72, 113.81, 112.21, 94.12, 70.91, 70.74, 70.70, 69.82, 69.69, 68.33, 66.63, 62.35, 31.92, 24.88, 19.47, 15.12 ppm. IR (neat): $\tilde{\nu}$ = 3343, 2934, 2872, 1725, 1598, 1494, 1447, 1262, 1100, 1058, 938, 753 cm^{-1}. MS (FAB, NBA): *m*/*z* = 351 $[M]^+$.

6-(2-{2-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}phenyl)hexan-1-ol (25): In a 50 mL round-bottomed flask with nitrogen cap, **24** (1.94 g, 5.53 mmol, 1.0 equiv.) was dissolved in EtOH (15 mL). Palladium/charcoal catalyst (10%, 194 mg, 0.18 mmol, 0.033 equiv.) was added, and the suspension was stirred under hydrogen under standard conditions for 18 h. The reaction mixture was filtered through Celite (30 g, 535 coarse), and the filter cake was thoroughly rinsed with ethanol. Evaporation of the solvents gave the crude product, which was purified by flash column chromatography (8 × 25 cm, 350 g of SiO_2, EtOAc/hexanes, 4:1). Clear, colorless oil. Yield: 1.67 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.13 (m, 2 H), 6.88 (td, ^3J = 7.4, ^4J = 1.1 Hz, 1 H), 6.83 (d, ^3J = 8.1 Hz, 1 H), 4.12 (t, ^3J = 5.2 Hz, 2 H), 3.88 (t, ^3J = 5.2 Hz, 2 H), 3.75 (m, 2 H), 3.70–3.57 (m, 8 H), 3.53 (q, ^3J = 6.9 Hz, 2 H), 2.61 (t, ^3J = 8.1 Hz, 2 H), 1.80 (s, 1 H), 1.58 (m, 4 H), 1.38 (m, 4 H), 1.21 (t, ^3J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 156, 131.44 (1 C, 14), 129.85 (1 C, 13), 126.76 (1 C, 11), 120.54 (1 C, 12), 111.34, 70.75, 70.62, 69.84, 69.73, 67.49, 66.56, 62.77, 32.56, 30.00, 29.63, 29.11, 25.41, 14.98 ppm. MS (FAB, NBA): *m*/*z* = 355 $[M]^+$. IR (neat): $\tilde{\nu}$ = 3435, 2930, 2860, 1602, 1494, 1451, 1351, 1243, 1108, 1054, 934, 845, 753 cm^{-1}. $C_{20}H_{34}O_5$ (354.49): calcd. C 67.76, H 9.67, O 22.57; found C 67.51, H 9.68.

1-[4′-{2-[2-(2-Ethoxyethoxy)ethoxy]ethoxy}-3′-(6-hydroxyhexyl)-phenyl]hydroazafullerene (26): In a dry 100 mL round-bottomed flask with nitrogen inlet and reflux condenser, the bi(azafullerenyl) **2** obtained from C_{60}-N-MEM-oxo-lactam **7** (120 mg, 140.4 μmol, 1.0 equiv.) was dissolved in ODCB (80 mL). Compound **25** (248 mg, 0.7 mmol, 5.0 equiv.) and *p*-TsOH (538 mg, 2.8 mmol, 20 equiv.) were added to this solution, which was stirred at 150 °C for 20 min, while a slow stream of oxygen was passed over the reaction mixture. The progress of the reaction was monitored by analytical HPLC (Cosmosil, toluene, 1.0 mL min^{-1}) or TLC (toluene/MeOH, 9:1, R_f = 0.3). After the mixture had cooled to room temperature, the product was obtained by flash column chromatography (4 × 15 cm, 60 g of SiO_2, toluene, toluene/MeOH, 9:1). For further purification, the black solid was dissolved in a minimum amount of CS_2, precipitated from *n*-pentane, washed five times with *n*-pentane and dried in high vacuum. To avoid solubility problems, however, purification of the material by means of preparative HPLC, rather than by reprecipitation, was carried out. Brown, amorphous solid. Yield: 21 mg (18% corresponding to **7**). HPLC (Nucleosil, toluene/MeOH, 98:2, 1.0 mL min^{-1}): t_R = 5.5 min. ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz): δ = 8.61 (m, 2 H), 7.32 (d, ^3J = 8.6 Hz, 1 H), 4.37 (t, ^3J = 4.7 Hz, 1 H), 4.01 (t, ^3J = 4.7 Hz, 2 H), 3.82 (m, 2 H), 3.71–3.59 (m, 8 H), 3.52 (q, ^3J = 7.1 Hz, 2 H), 2.94 (t, ^3J = 7.8 Hz, 2 H), 1.85 (m, 2 H), 1.65–1.46 (m, 6 H), 1.22 (t, ^3J = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($C_2D_2Cl_4$, 100.5 MHz): δ = 157.68, 154.48, 149.15, 147.79, 147.60, 147.58, 147.30, 147.15, 146.57, 146.34, 146.16, 145.83, 145.60, 144.98, 144.96, 144.44, 144.22, 143.95, 143.05, 142.66, 141.98, 141.73, 141.51, 141.30, 140.88, 140.80, 139.65, 137.56, 133.25, 133.15, 132.91, 128.65, 125.93, 124.04, 112.21, 82.62, 70.63, 70.33, 70.29, 69.54, 69.45, 67.75, 66.34, 62.71, 32.54, 30.63, 29.68, 29.30, 25.37, 15.03 ppm. IR (neat): $\tilde{\nu}$ = 3258, 2910, 2868, 2806, 1725, 1687, 1559, 1509, 1444, 1420, 1393, 1370, 1278, 1251, 1231, 1197, 1073, 1046, 1023, 992, 938, 919, 838, 803, 764, 741, 706, 679 cm^{-1}. UV/Vis (toluene): λ_{max} = 285, 324, 443 nm. MS (FAB, NBA): *m*/*z* = 722 $[C_{59}N]^+$, 1076 $[M]^+$, 1092 $[M + O]^+$.

1-{3′-[6-(Azidomethoxy)hexyl]-4′-(2-[2-(2-ethoxyethoxy)ethoxy]-ethoxy)phenyl}hydroazafullerene (27) and One-Pot Experiments Directed Towards $C_{58}N_2$: In a dry 2 mL flask with nitrogen inlet, **26** (21 mg, 24.9 μmol, 1.0 equiv.) was dissolved under nitrogen in tetrachloroethane (0.5 mL), and trimethylsilyl chloride (7.9 μL, 62.3 μmol, 2.5 equiv.) and paraformaldehyde (0.8 mg, 27.4 μmol, 1.1 equiv.) were added at room temperature. The solution was stirred at room temperature for 2 h, during which the insoluble paraformaldehyde was successively consumed. The excess trimethylsilyl chloride was removed under reduced pressure (appr. 100 mbar). Because of the high reactivity, as well as toxicity (!),[22] of the chloromethyl ether, the crude material was used without further purification. Under nitrogen, sodium azide (594 mg, μmol, 3.0 equiv.) and 18-crown-6 (40 mg, 0.15 μmol, 0.05 equiv.) were added to the crude chloromethyl ether, and the reaction mixture

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was stirred at room temperature for 2 h. The progress of the reaction was monitored by TLC (toluene/methanol, 9:1, R_f = 0.6) and IR spectroscopy (characteristic N_3 valence band at 2120 cm^{-1}). The crude azide was filtered through a syringe filter, and ODCB (1 mL) was added. The solution was heated in an oil bath at 180 °C for 60 min. After quick cooling to room temperature, the flask was immerged in a basic, aqueous solution of potassium chromate, which served as a light filter and had to be vigorously stirred and kept at a constant 5 °C by means of a cryostat. The reaction mixture was stirred and irradiated with two halogen flood lights (500 W), while a steady, slow stream of oxygen (gas bottle) was passed through the solution. After 6 h, the reaction mixture was immediately subjected to FAB mass spectrometry (see Figure 5).

Supporting Information (see footnote on the first page of this article): Results of the molecular modelling and ^1H NMR spectra of compounds **25**, **26** and **26a**.

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