Fullerene Chemistry

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Pentaarylazafullerenes and their Triaryldihydro and Tetraarylmonohydro Precursors**

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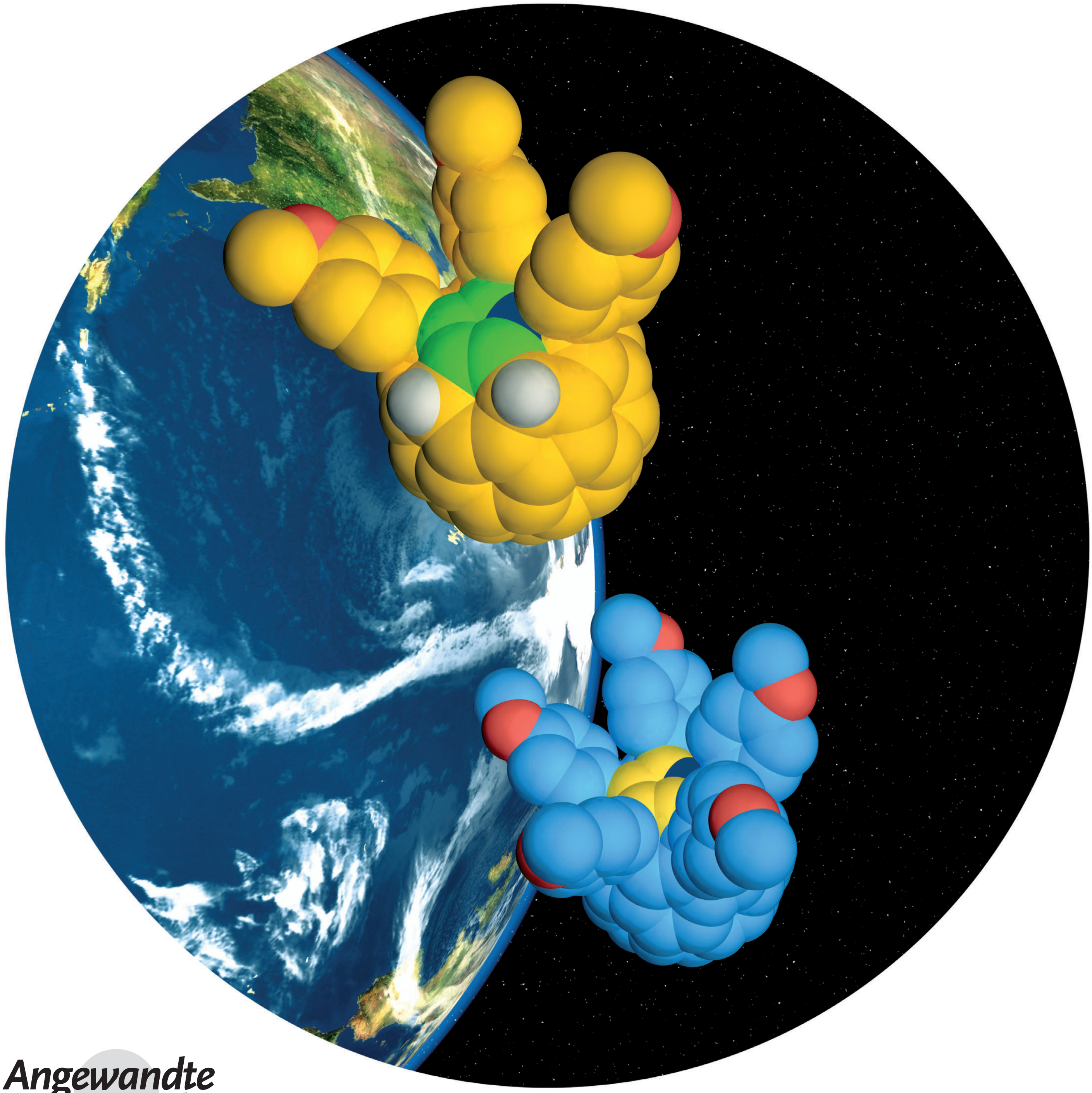

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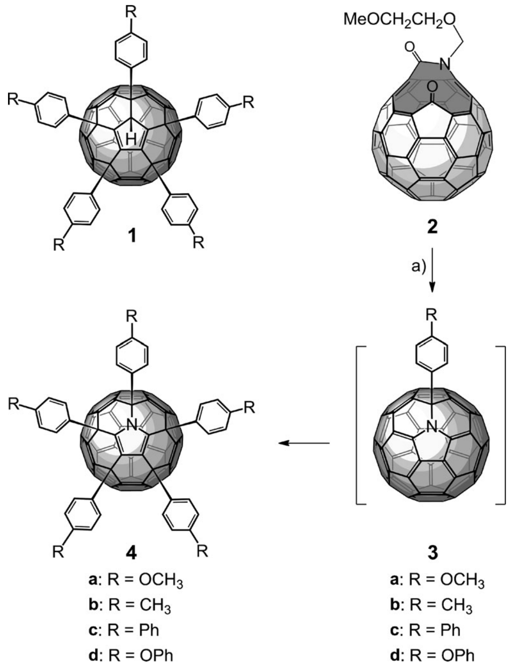

Scheme 1. Preparation of the pentaarylazafullerenes **4a–d** by the acid-catalyzed rearrangement of **2** to azafullerenes **3a–d** and subsequent pentaarylation reaction under the reaction conditions: a) *p*-TsOH, air, R-C_6H_5/*o*-DCB (1:5), 150°C, 6 h.

Azafullerenes are homologues of the corresponding all-carbon fullerenes obtained by replacement of one or more carbon atoms of the fullerene cage with nitrogen. The parent representative of this interesting class is the monoazafullerene radical $C_{59}N^{\bullet}$, which is isoelectronic to $C_{60}^{\bullet-}$, and can be isolated as the stable dimer $(C_{59}N)_2$.[1] Electrophilic arylation with electron-rich aromatic compounds affords monoadducts with the general formula $C_{59}NAr$ (**3**, Scheme 1), whereby arylation occurs in α position to nitrogen and at the corresponding [6,6]-ring junction.[2]

Higher adducts of azafullerenes[3] are still rare, in contrast to the rich variety of higher adducts of C_{60} and the corresponding patterns of addition. In particular, C_s-symmetric 6,9,12,15,18-pentaaryl-1-hydro[60]fullerenes (**1**, "pentaarylfullerenes", Scheme 1) belong to an unusual class of fullerene derivatives first prepared by Friedel–Crafts arylation of $C_{60}Cl_6$ in benzene,[4] and subsequently, by the versatile fivefold addition of organocopper reagents to C_{60}.[5] This addition motif is unique amongst the vast number of fullerene derivatives in that one of the five-membered rings of the C_{60} cage becomes formally isolated from the rest of the π-system, giving an embedded cyclopentadiene unit that can be complexed with a variety of transition metals after deprotonation. An additional and intriguing aspect of the 6,9,12,15,18-addition motif is that the corresponding derivatives can form supramolecular columnar stacks in the solid state or in solution by nestling the ball-shaped fullerene subunit of **1** into the cavity formed by the five aryl addends of an adjacent molecule.[6] This self-assembly propensity has been exploited in columnar liquid-crystalline materials,[6a] and more recently in bulk-heterojunction photovoltaic devices, where control of the phase-separation behavior between the electron-donating polymer and electron-accepting fullerene phases was achieved.[7]

In regard to higher azafullerene adducts, a pentaaddition pattern similar to that of C_{60} was first discovered in the Hirsch group after treatment of $C_{59}NAr$ adducts **3** with excess ICl, which affords tetrachlorinated aryladducts, $C_{59}NArCl_4$, having an isolated pyrrole substructure.[3b] A similar pentaaddition pattern of $C_{59}N$ was obtained by Zhang et al. through a complex sequence of reactions and rearrangements starting from a cage-opened oxafulleroid prepared from C_{60}.[3c] More recently, this pentaaddition pattern was obtained upon reaction of $(C_{59}N)_2$ with trifluoromethyl iodide where $C_{59}N(CF_3)_5$ was formed among other higher adducts and characterized by X-ray single-crystal analysis.[3d]

Overall, however, general synthetic access to pentaaryl azafullerenes **4** has been lacking. We report here that adducts **4a–d** can be efficiently prepared by acid-catalyzed rearrangement of ketolactam **2** to $C_{59}N^+$, which reacts in situ with an electron-rich arene present in the reaction in a Friedel–Crafts manner. Interestingly, the unexpected triaryldihydro[$C_{59}N$]fullerene adducts $C_{59}NAr_3H_2$ (*rac*-**5a**, **6a**, **7a**, and *rac*-**8a**; Scheme 2) and tetraarylmonohydro[$C_{59}N$]fullerene adducts $C_{59}NAr_4H$ (*rac*-**9a** and *rac*-**10a,d**) were also isolated as intermediates. The latter finding provides invaluable insight into the mechanism of the overall pentaarylation reaction of azafullerene dimer $(C_{59}N)_2$.

While monoarylated azafullerenes $C_{59}NAr$ (**3a–d**) are usually prepared from $(C_{59}N)_2$, they can also be prepared directly from precursor **2**, although with considerably reduced yields.[2a] Surprisingly, however, when ketolactam **2** was heated under similar conditions (*p*-TsOH, 6 h, *ortho*-dichlorobenzene) with an excess of anisole, toluene, biphenyl, or diphenyl ether, pentaarylazafullerene derivatives $C_{59}NAr_5$ (**4a–d**) were isolated as the main products. During the course of the reaction, the color of the mixture changed from dark

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Supporting information for this article, including detailed descriptions of the synthesis, spectroscopic, and crystallographic details of the presented compounds, is available on the WWW under http://dx.doi.org/10.1002/anie.201206878.

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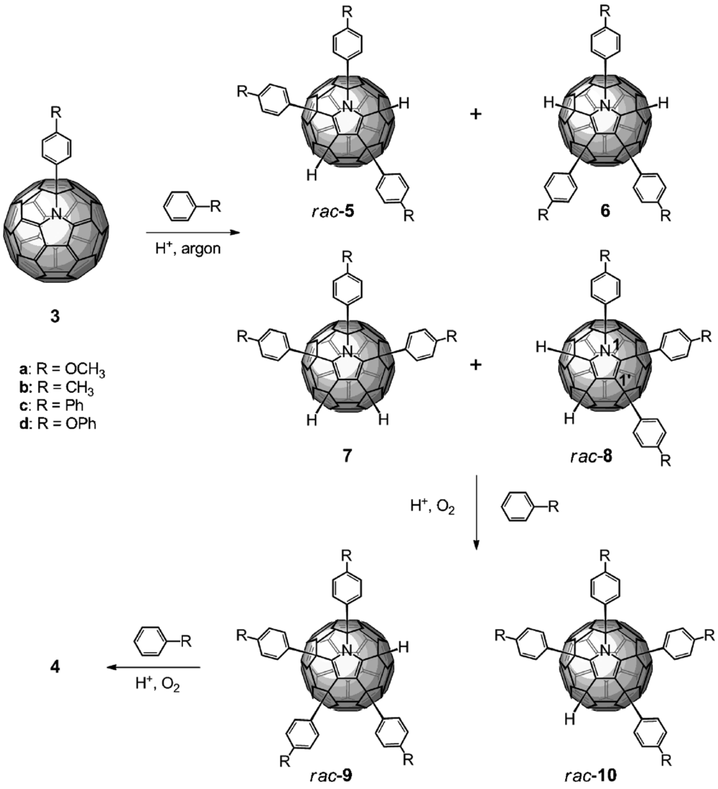

Scheme 2. Formation of pentaarylazafullerenes **4a–d** from monoadducts **3a–d** via the triaryldihydro intermediates *rac*-**5a–d**, **6a–d**, **7a—d**, and *rac*-**8a–d**. The latter are formed under the exclusion of air as exemplified by the isolation of the anisyl adducts **5a–8a** ($R=OCH_3$). Subsequent formation of tetraarylmonohydro[$C_{59}N$]fullerene adducts *rac*-**9a–d** and *rac*-**10a–d** requires the presence of air.

brown to red, indicating the formation of the characteristic red–orange-colored pentaarylazafullerenes **4a–d**.

The efficient but unexpected formation of $C_{59}NAr_5$ **4a–d** made us wonder about the mechanistic pathway for the entire conversion. Fortunately, we were able to isolate and fully characterize a number of intermediates (Scheme 2) providing valuable insight into the nature of the reaction sequence. It is reasonable to assume that $C_{59}N^+$ is first formed in situ from ketolactam **2**, as reported by Wudl and co-workers.[1a] Subsequently, $C_{59}N^+$ reacts with an electron-rich arene such as anisole to form the monoadduct **3a** through electrophilic aromatic substitution (Scheme 1). As noted above, the formation of monoadducts **3a–d** by electrophilic aromatic substitution is well-established.[2a,b,8] The very efficient fivefold arylation leading to **4a** takes place when either ketolactam **2** or monoadduct **3a** is heated with 20 equiv of *p*-TsOH and an excess of anisole in *o*-dichlorobenzene while air is bubbled through the solution for 6 h. We recognized that only electron-rich aromatic compounds react under these conditions and that the substitution takes place exclusively in the *para* position of the arene.

Significantly, if monoadduct **3a** is treated under the same conditions, but under the exclusion of air, pentaaryl adduct **4a** does not form. Instead, all four possible isomers of the intermediate triaryldihydro[$C_{59}N$]fullerene (*rac*-**5a**, **6a**, **7a** and *rac*-**8a**) (Scheme 2) can be isolated and separated by preparative HPLC. Structural characterization was confirmed by high-resolution APPI-TOF mass spectrometry as well as by ^{1}H and ^{13}C NMR spectroscopy, and NOE experiments, and especially by single-crystal X-ray diffraction on compound *rac*-**8a**. The particularly remarkable features of these compounds are the H atoms attached to the $C_{59}N$ core. Their ^{1}H NMR resonances appear around 5.6 ppm either as one singlet for the symmetrical compounds **6a** and **7a** or as two singlets for the unsymmetrical substituted compounds *rac*-**5a** and *rac*-**8a**. In particular, these signals for *rac*-**8a** appear as two doublets at 5.64 and 5.60 ppm with a characteristic $^{5}J_{H,H}$ coupling constant of 4.8 Hz. These chemical shifts and coupling constants are typical for H atoms attached to the fullerene core.[9] The UV/Vis spectra of all four regioisomers have similar absorption features owing to the similarity of their addend pattern, and accordingly, their fullerenyl π-system.

The X-ray diffraction analysis of a single crystal of triaryldihydro[$C_{59}N$]fullerene *rac*-**8a**, grown at −30 °C from a mixture of $CDCl_3$ and CS_2, represents the first crystallographic characterization of a hydroazafullerene derivative (Figure 1).[10] The binding of both aryl addends and H atoms is accompanied by a considerable increase in pyramidalization of the corresponding C atoms because of sp^3 rehybridization. The N atom is disordered between two equivalent positions (1 and 1′, shown in Scheme 2).[11] Figure 1 a shows one of the two enantiomers, and Figure 1 b presents their partially stacked, "feather-in-cavity" arrangement[6b] in the packing structure.

When triaryldihydro[$C_{59}N$]fullerenes (*rac*-**5a–d**, **6a–d**, **7a—d**, and *rac*-**8a–d**) are exposed to air while all other parameters are held constant, the reaction proceeds further and provides the tetraarylmonohydro[$C_{59}N$]fullerenes (*rac*-**9a–d** and *rac*-**10a–d**) and the pentaaryl adducts (**4a–d**) by replacement of the H atoms of the triaryldihydro adducts with one or two aryl addends. The presence of O_2 causes

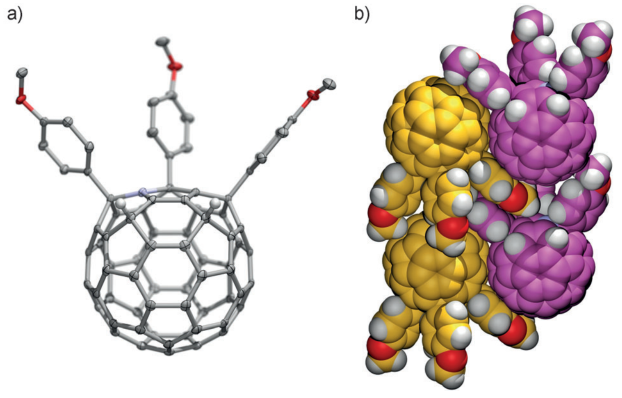

Figure 1. Single-crystal structure of *rac*-**8a**: a) ORTEP representation with ellipsoids at the 50% probability level (C gray, N blue, O red, H white spheres, hydrogen atoms on the substituents are omitted for clarity) and b) space-filling representation of the packing motif (C violet/yellow, N blue, O red, H white). Solvent molecules are omitted for clarity.

oxidative dehydrogenation of these triaryldihydro-$[C_{59}N]$fullerene and tetraaryl monohydro$[C_{59}N]$fullerene adducts. A similar dehydrogenative alkylation has been observed previously during the addition of ketene silyl acetals to C_{60}.[12] The oxidative dehydrogenation of the triaryldihydro or tetraarylmonohydro adducts activates the fullerene core for subsequent electrophilic aromatic substitution. We were able to isolate and characterize the tetraarylmonohydro adducts *rac*-**9a** and *rac*-**10a**,**d** formed together with the pentaaryl adducts **4a**–**d**. In particular, compound *rac*-**9a** was synthesized selectively from **6a**.[11] Interestingly, when a mixture of both isomers *rac*-**9a** and *rac*-**10a** was subjected to further arylation, only *rac*-**9a** was converted to the pentaaryl adduct **4a**, whereas *rac*-**10a** was recovered from the reaction mixture. We also isolated **10d** from the corresponding reaction cascade starting from **2** when diphenyl ether served as the arene. The ^{13}C NMR spectra of both regioisomers *rac*-**9a** and *rac*-**10a**,**d** display the expected C_1 symmetry of these compounds. The structural assignment of regioisomers *rac*-**9a** and *rac*-**10a**,**d** is based on the comparison of the experimental and calculated ^{13}C NMR spectra and based on the NMR chemical shifts for the four $C(sp^3)$ atoms connected to the addends.[11] The fact that only the regioisomers *rac*-**10a** and **10d** could be isolated from the reaction mixture leads to the conclusion that *rac*-**9a**–**d** is considerably more reactive than *rac*-**10a**–**d** towards another arylation reaction, leading to pentaaryl adducts **4a**–**d**.

The ^1H and ^{13}C NMR data for the pentaaryl $[C_{59}N]$fullerene derivatives **4a**–**d** corroborate their depicted C_s symmetry. The *ortho* aromatic protons appear at about 7.6 ppm as three resolved doublets with an integration ratio of 2:1:2. The *meta* protons correspond to overlapping doublets around 7.0 ppm. Compound **4b** shows a particularly well-resolved splitting of the ^1H NMR signals for the protons in *meta* position at 6.99 ppm, 6.98 ppm, and 6.95 ppm, with the expected integration ratio of 1:2:2, respectively. The methoxy groups appear also as three separate singlets at 2.35 ppm, 2.34 ppm, and 2.33 ppm with an integration ratio of 1:2:2. Additionally, the ^{13}C NMR data for compounds **4a**–**d** show the same signal pattern with 1:2:2 intensities for the carbon atoms of the addends. Importantly, three signals with intensities of 1:2:2 for the five sp^3-hybridized carbons of the $C_{59}N$ core of compounds **4a**–**d** can be found at roughly 74 ppm, 60 ppm, and 58 ppm. A total of 26 signals are observed between 120–160 ppm for the residual 54 sp^2-hybridized carbons of the $C_{59}N$ cage, with 24 having double intensity and 2 having single intensity. Comparing the ^{13}C NMR data of the pentaaryl adducts **4a**–**d** reveals that the signals of the carbon atoms for the embedded pyrroles appear around 137 ppm (for the two α-C atoms) and at 128 ppm (for the two β-C atoms). In the UV/Vis spectra, all compounds including the pentaaryl adducts **4a**—**d** and triaryldihydro (*rac*-**5a**, **6a**, **7a** and *rac*-**8a**) and tetraarylmonohydro adducts (*rac*-**9a** and *rac*-**10a,d**) have similar absorptions at 238, 260, 276, 357, 444, 478, and 533 nm owing to their identical addition pattern.

X-ray diffraction analysis of compound **4a** was performed on two single crystals, one grown from a toluene solution, and the second grown from a mixture of $CDCl_3$ and CS_2.[10] The results of the two X-ray structure determinations are very similar, and only one structure (**4a** from toluene) is discussed here. The data for the second (**4a** from $CDCl_3/CS_2$) can be found in the Supporting Information. The X-ray structure of pentaaryl adduct **4a** confirms its C_s-symmetrical pentaaddition pattern and an isolated pyrrole subunit within the azafullerene core (Figure 2). The N atom is disordered over the five equivalent positions of the isolated pentagon owing to the overlap of five molecules rotated by 72° relative to each other. The same feature was observed in the single-crystal structure of $C_{59}N(CF_3)_5$.[3d] The average bond lengths within the pyrrole ring, at 1.40 Å, are comparable to the average bond length of 1.38 Å in pyrrole.[13] The pyrrole unit exhibits an almost planar arrangement within the azafullerene core. The dihedral angle (N-C-C-C) of the pyrrole plane is about 0.6°. The crystal packing of pentaaryl adduct **4a** exhibits an interdigitated dimeric motif (Figure 2b). The substituents of two molecules face each other and form a cavity with a distance of 8.9 Å between the two azafullerene cores. This cavity is occupied by a slightly disordered toluene molecule.[10] This interesting dimeric packing behavior has also been observed for related 6,9,12,15,18-pentaaryl-1-hydro[60]-fullerenes derivatives, showing that the crystal-packing motif depends mainly on the nature of the substituent and the crystallization solvent, and not on the shape of the fullerene core.[6b]

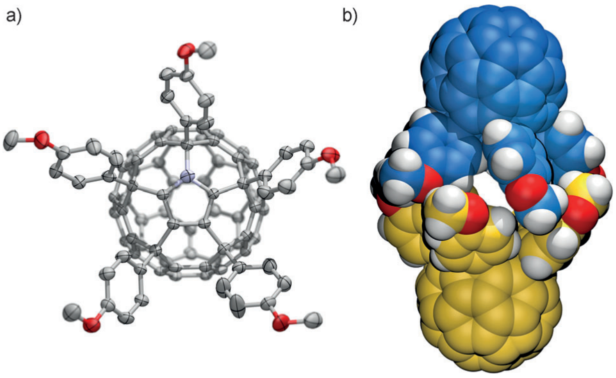

Figure 2. Single-crystal structure of **4a**: a) ORTEP representation with ellipsoids at the 50% probability level (C gray, N blue, O red, hydrogen atoms on the substituents are omitted for clarity) and b) space-filling representation of the dimeric motif (C blue/yellow, N blue, O red, H white); the disordered toluene molecule inside the cavity is omitted for clarity.

Compounds **4a**–**d** were also characterized by cyclic voltammetry. They all show two reversible reduction waves,[11] as is also the case for the similar pentaaryl[60]fullerene derivatives.[14] The first reduction potential for pentaarylazafullerenes **4a**–**d** appears at around −1.49 V with respect to the Fc^+/Fc redox couple (Table 1), which is about 10 mV more negative than for the pentaaryl[60]fullerene derivatives recorded in THF by Nakamura.[14] Our result reflects the electronegative influence of the nitrogen atom in $C_{59}N$.

In conclusion, we have found an efficient, versatile, and entirely regioselective synthesis of pentaaryl-$[C_{59}N]$azafullerenes. The C_s-symmetrical addition pattern

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Table 1: Redox potentials of pentaarylazafullerenes **4a–d** and C_{60} for comparison.[a]

	4a	**4b**	**4c**	**4d**	C_{60}
E^1_{red} [V]	−1.49	−1.49	−1.47	−1.49	−1.10
E^2_{red} [V]	−1.95	−1.95	−1.92	−1.95	−1.51

[a] Values versus Fc^+/Fc. The cyclic voltammograms were recorded in anhydrous *o*-DCB using Bu_4NBF_4 (0.1 M) as the supporting electrolyte and a scan rate of 100 mV s^{-1}. Reference electrode: Ag wire; working electrode: glassy carbon; counterelectrode: Pt wire.

was confirmed by X-ray crystal structure analysis of **4a**. We were also able to isolate and characterize a number of tri- (**5a**–**8a**) and tetraaryl[$C_{59}N$] adducts (*rac*-**9a**, *rac*-**10a**, and *rac*-**10d**) involving the same addition pattern but containing one or two H atoms instead of aryl rings as addends. These remarkable molecules represent the first examples of multihydroheterofullerenes that are intermediates in the pentaarylation cascade. Cyclic voltammetry measurements (Table 1) show that the pentaaryl derivatives **4a–d** have essentially identical redox potentials across the series. Thus, the reduction potentials of the pentaaryl adducts are independent of the nature of the aryl addends. The exploration of further chemical and physical properties of this new family of heterofullerenes is currently under way in our laboratories.

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[10] CCDC 895558 (*rac*-**8a**) 896086 (**4a** from toluene) und 895559 (**4a** from $CDCl_3/CS_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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