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Radical Reactivity of Aza[60]fullerene: Preparation of Monoadducts and Limitations

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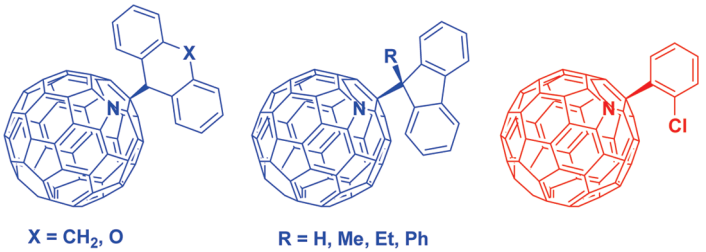

Six aza[60]fullerene monoadducts were synthesized by the thermal reaction between the azafullerene radical $C_{59}N^{\bullet}$ and 9-alkyl-substituted fluorenes, 9,10-dihydroanthracene, or xanthene. Unlike fluorenes, dihydroanthracene, and xanthene, the structurally related substituted diphenylmethanes, ethylbenzene, cumene, 1,2-diphenylethane, 5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene, 9-methylanthracene, and 9-benzylanthracene do not lead to the isolation of azafullerene monoadducts. Moreover, 1,2-dichlorobenzene, the most commonly utilized solvent for azafullerene reactions, reacts slowly with the azafullerenyl radical $C_{59}N^{\bullet}$ affording the corresponding aza[60]fullerene monoadduct.

Introduction

Heterofullerenes derive from the modification of the fullerene framework by replacing one or more carbon atoms by heteroatoms such as boron or nitrogen. For example, the mass spectroscopic detection of $C_{60-n}B_n$ clusters, generated by laser vaporization of graphite/boron nitride composites, has been reported in the literature since 1991;[1] however, the only heterofullerenes that have been synthesized and isolated in bulk quantities by "chemical procedures" are nitrogen heterofullerenes, that is, azafullerenes $(C_{59}N)_2$ and $(C_{69}N)_2$.[2,3] In particular, the synthesis of aza[60]fullerene dimer $(C_{59}N)_2$ (**1**, Figure 1), starting from an open-cage fullerene derivative,[4] was reported for the first time in 1995 by Wudl and co-workers.[2] According to that report, the initially formed azafullerenyl radical $C_{59}N^{\bullet}$ (**2**, Figure 1), which is isoelectronic to the $C_{60}^{-\bullet}$ radical anion, readily dimerizes to yield bisaza[60]fullerene **1**. The two $C_{59}N$ spheres in the dimer are connected through their sp^3 carbon atoms that are adjacent to the nitrogen atoms. The intradimer bond is relatively weak (18 kcal/mol)[5] and can be thermally or photolyticaly homolyzed giving back radical **2**.[6,7]

The first reported azafullerene functionalization methodology is based on the trapping of aza[60]fullerenyl radical (**2**, Figure 1). This trapping can be achieved either by a hydrogen atom, provided by a donor such as hydroquinone, leading to hydroaza[60]fullerene $C_{59}HN$ (**3**, Scheme 1),[6] or

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(1) (a) Guo, T.; Jin, C.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 4948–4950. (b) Chai, V.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, I.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564–7568.

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(3) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421–1422.

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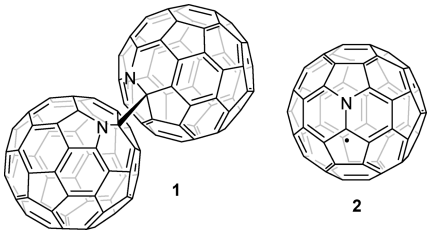
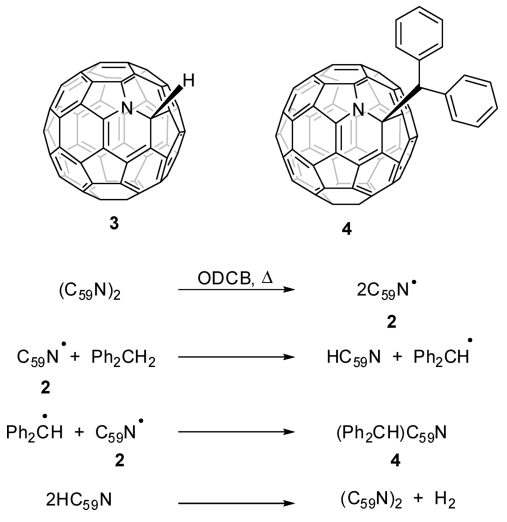


FIGURE 1. Azafullerene dimer $(C_{59}N)_2$ (**1**) and azafullerenyl radical $C_{59}N^{\bullet}$ (**2**).

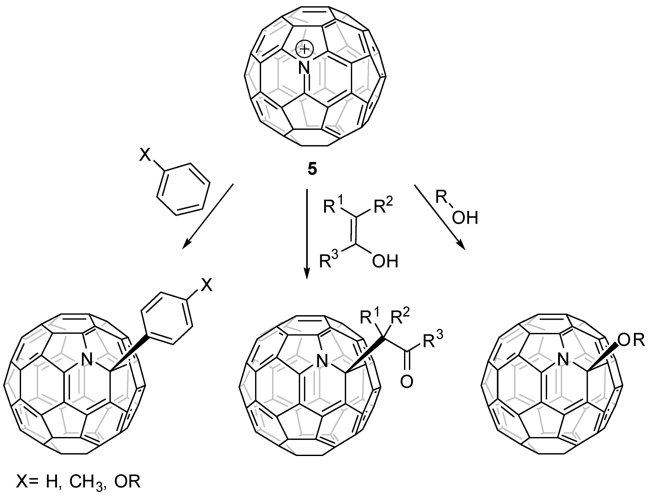
SCHEME 1. Aza[60]fullerene Monoadducts Derived from the Trapping of Aza[60]fullerenyl Radical and the Proposed Free Radical Chain Mechanism



by the diphenylmethane radical leading to $C_{59}(CHPh_2)N$ (**4**, Scheme 1).[7] Also, in a preliminary communication, we have reported the efficient trapping of radical **2** with 9-alkyl-substituted fluorenyl radicals.[8] The free radical chain mechanism that has been proposed for the production of these kinds of aza[60]fullerene monoadducts is presented in Scheme 1. More recently, we carried out a mechanistic study on the aza[60]fullerene radical reactivity.[9] The primary and secondary kinetic isotope effects in the aza[60]fullerenyl radical reaction with selectively deuterated diphenylmethanes and 9-methyl-9*H*-fluorenes provided strong evidence for a stepwise radical mechanism, in which the hydrogen atom abstraction is the rate-determining step, followed by a fast coupling of $C_{59}N^{\bullet}$ with the diphenylmethane or methylfluorene radicals.

However, the most promising procedure that has been hitherto developed for the synthesis of azafullerene monoadducts is based on the nucleophilic trapping of the azafullerene carbocation $C_{59}N^+$ (**5**, Scheme 2). $C_{59}N^+$ is typically produced by the thermal treatment of dimer $(C_{59}N)_2$ in the presence of air and excess toluene-*p*-sulfonic acid. Nucleophiles such as electron-rich aromatics,[10,11] enolizable carbonyl compounds,[12] as well as alcohols and olefins[13] have been successfully used to trap carbocation **5**, and several azafullerene adducts were isolated by utilizing this method (Scheme 2). $C_{59}N^+$ has been proposed to derive from the initially formed $C_{59}N^{\bullet}$ radical after oxidation with oxygen, whereas toluene-*p*-sulfonic acid is necessary in order to adjust the pH of this redox reaction and/or trap the reduced oxygen species.[10] The monomeric $C_{59}N^+$ cation also has been isolated as a carborane anion salt, via the oxidation of the sp^3-sp^3 C−C bond of **1** with the radical cation of hexabromo(phenyl)carbazole.[14]

SCHEME 2. Representative Aza[60]fullerene Monoadducts Derived from the Trapping of Aza[60]fullerene Carbocation



During the course of our earlier studies on the photochemical behavior of azafullerene carbocation $C_{59}N^+$, we have revealed another reaction sequence that aza[60]fullerene takes part in.[15] Hence, the photoinduced electron transfer reaction between **5** and benzyltrimethylsilane afforded aza[60]fullerene monoadduct **6** (Scheme 3) in 28% isolable yield. In the same study, we showed that, depending on the reaction conditions, $(C_{59}N)_2$ displays three different modes of reactivity toward benzyltrimethylsilane, i.e., radical, electrophilic aromatic substitution, and photoinduced electron transfer, leading to novel aza[60]fullerene monoadducts.

All existing methods for the functionalization of aza[60]fullerene were recently reviewed by Vostrowsky and Hirsch.[16] The majority of azafullerene adducts reported to date result from the trapping of azafullerene cation **5**, while publications referring to azafullerenyl radical **2** as the reactive intermediate are rather limited. In this paper, we report on the isolation and characterization of aza[60]fullerene monoadducts **8a**−**d** and **10a**,**b**, afforded by the reaction between **2** and arylalkanes **7a**−**d** and **9a**,**b** (Scheme 5), respectively, that follows a free radical chain mechanism similar to that presented in Scheme 1.

(8) Vougioukalakis, G. C.; Orfanopoulos, M. *Tetrahedron Lett.* **2003**, *44*, 8649–8652.
(9) Vougioukalakis, G. C.; Hatzimarinaki, M.; Lykakis, I. N.; Orfanopoulos, M. *J. Org. Chem.* **2006**, *69*, 829–832.
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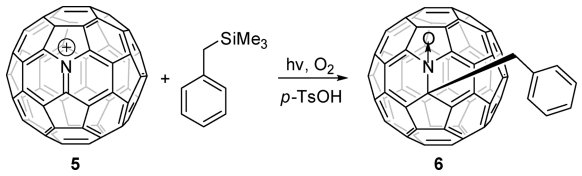
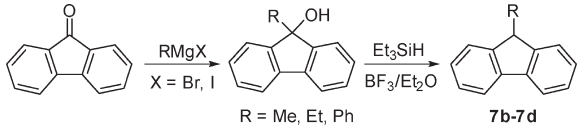
(15) Vougioukalakis, G. C.; Orfanopoulos, M. *J. Am. Chem. Soc.* **2004**, *126*, 15956–15957.
(16) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191–5207.

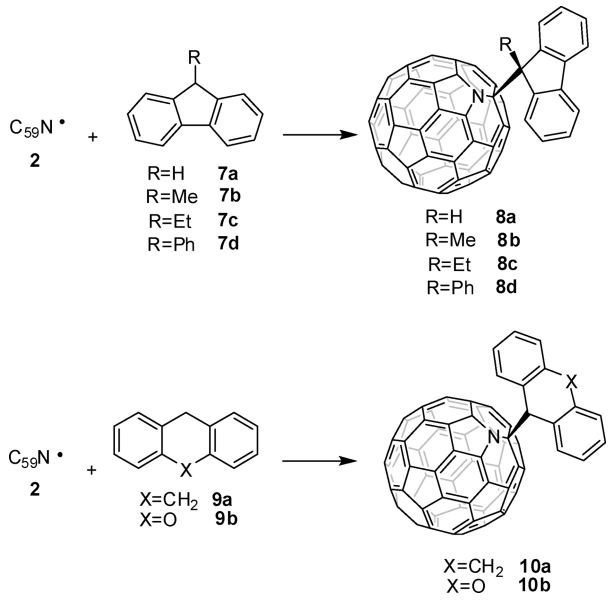
SCHEME 3. The Photoinduced Electron Transfer Reaction between $C_{59}N^+$ and Benzyltrimethylsilane



SCHEME 4. Preparation of Substituted Fluorenes 7b−d



SCHEME 5. Aza[60]fullerene Monoadducts 8a−d and 10a,b



Results and Discussion

Substituted fluorenes **7b−d** were quantitatively synthesized in two steps (Scheme 4) starting from 9-fluorenone: 9-Fluorenone reacted with the corresponding Grignard[17] reagent (MeMgI, EtMgI, or PhMgBr) to give the intermediate substituted fluorenol. This fluorenol was next converted into the corresponding fluorene by reduction with the etherated boron trifluoride−triethylsilane system.[18] Substrates **7a**, **9a**, and **9b** are all commercially available.

Substituted aza[60]fullerenes **8a−d** and **10a**,**b** were obtained by the reaction of aza[60]fullerene radical **2** with the corresponding arylalkane (Scheme 5). Specifically, aza[60]fullerene dimer **1** was dissolved in degassed 1,2-dichlorobenzene (ODCB), 300 equiv of the substituted arene was added, and the resulting mixture was heated to 160 °C for 3−9 h under argon. All reactions were monitored by removing small aliquots, which were subsequently analyzed via HPLC. Following the removal of ODCB by distillation under reduced pressure, the crude mixture was washed with acetonitrile and/or acetone in order to remove the remaining arene. Flash chromatographic purification afforded **8a−d** and **10a**,**b** as black solids (Table 1). All adducts were characterized by ^{1}H, ^{13}C, COSY, and HMQC NMR experiments, as well as with UV−vis, FT-IR spectroscopy, and mass spectrometry. The solutions of adducts **8a−d** and **10a**,**b** are all green, with their UV−vis spectra being identical with that of $(C_{59}N)_2$ in agreement with all the other aza[60]fullerene monoadducts reported thus far. All adducts have characteristic absorptions at 380, 450, 595, 730, and 817 nm. The FT-IR spectra of **8a−d** and **10a**,**b** are also very similar to that of $(C_{59}N)_2$, with strong characteristic absorptions at 524 and 1510 cm^{-1}.

TABLE 1. Reaction Times and Isolated Yields for Adducts 8a−d and 10a,b

adduct	R	X	yield (%)[a]	reaction time (h)
8a	H		41	9
8b	Me		30	8
8c	Et		35	6
8d	Ph		20	4
10a		CH_2	30	4
10b		O	24	3

[a]Based on the amount of isolated adduct.

It also has to be noted that aza[60]fullerenyl radical **2** reacts much slower with diphenylmethane than with fluorene **7a**. In this regard, after 48 h of heating at 180 °C the reaction with diphenylmethane affords adduct **4** (Scheme 1) in 42% yield,[7] whereas in the case of fluorene, **8a** (Scheme 5) is obtained in the same yield only after 9 h of heating at 160 °C.[8]

We also tried to functionalize aza[60]fullerene with substituted diphenylmethanes **11a−c**, ethylbenzene (**12**), cumene (**13**), arylalkanes **14a−c**, and substituted anthracenes **15** and **16** (Figure 2); however, our attempts to isolate or even in situ observe the formation of a monoadduct in these reactions, by trying several experimental conditions, failed (vide infra). Instead, progressive degradation of the aza[60]fullerene dimer **1** was observed by HPLC and no further investigation of its fate was attempted.

The dramatic change in reactivity upon going from substituted fluorenes **7b−d** to the structurally similar diphenylmethanes **11a−c** has to be related to the rigid, planar structure of fluorenes, compared to the free-to-rotate structure of diphenylmethanes. Thus, methine hydrogen abstraction to form the corresponding free radical occurs much easier for fluorenes **7b−d** than for diphenylmethanes **11a−c**, and this is because, in the latter, free rotation of the phenyl rings and substituent R sterically hinders the attack of the aza[60]fullerenyl radical to the benzylic hydrogen.

Moreover, it is well-known that radicals such as Me$^\bullet$, *t*-Bu$^\bullet$, Ph$^\bullet$, PhS$^\bullet$, and PhCH$_2^\bullet$, readily react with C_{60} leading to free radical mono- and multi-adducts.[19] For example, in the case of PhCH$_2^\bullet$, free radical fullerene species have been observed by ESR spectroscopy. These fullerene adducts result from the addition of three or five PhCH$_2^\bullet$ radicals to the [6,6] double bonds of C_{60}, with the unpaired electron localized within a pentagon ring, forming an "allylic" or a "cyclopentadienyl" radical, respectively.[20] Therefore, the

(17) Vogel's, *Textbook of practical Organic Synthesis*, 4th ed.; Longman: London, UK, 1978; p 366.
(18) Orfanopoulos, M.; Smonou, I. *Synth. Commun.* **1988**, *18*, 833–839.
(19) For a review on the addition of free radicals to C_{60} see: Morton, J. R.; Negri, F.; Preston, K. F. *Acc. Chem. Res.* **1998**, *31*, 63–69.
(20) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183–1185.

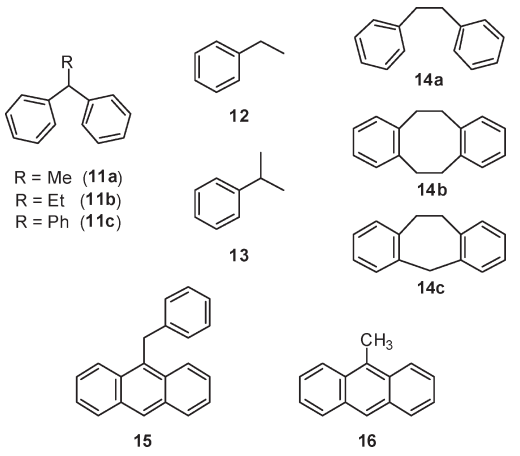


FIGURE 2. Arylalkanes that did not yield aza[60]fullerene monoadducts.

slow decomposition of aza[60]fullerene dimer **1**, when heated in the presence of arylalkanes **11a**−**c**, may be attributed to the rapid, multiple addition of the produced unstable (vide infra) and consequently highly reactive radicals (**17**, Figure 3) to the [6,6] double bonds of the aza[60]fullerene carbon shell. This explanation is even more compelling in the case of the monobenzylic radicals that are produced by a hydrogen atom abstraction from substrates **12**, **13**, and **14a**−**c**. The same undesirable side reaction is almost certainly operable with substrates **7a**−**d** as well. In this case, however, the enhanced stability of the intermediate arylalkane radicals (**18**, Figure 3) leads to an efficient radical coupling between **2** and **18**, providing the isolated monoadducts **8a**−**d** at a significant yield. The enhanced stability of the doubly benzylic radical intermediate, in the case of fluorenes (**18**, Figure 3), originates from the rigid structure of the molecule and the resulting efficient overlap between the p-orbital of the benzylic carbon and the π-system of both aromatic rings. This conjugation is only partial in the case of diphenylmethanes, and, hence, the corresponding intermediate radical **17** (Figure 3) is less stable due to the free rotation of the phenyl rings that does not allow efficient orbital overlap. In the case of substrates **9a**,**b** the situation is quite similar to that of **7b**−**d**, with the rotation of the phenyl rings being restricted, providing both easy access to the benzylic hydrogen and stabilization to the intermediate dibenzylic radical. Consequently, monoadducts **10a**,**b** were isolated in considerable yields. Finally, in the case of substrates **15** and **16** failure in isolating the corresponding monoadducts most probably originates from the existence of the anthracene moiety that sterically hinders the benzylic position and renders the azafullerenyl radical approach difficult.

Related to the discussion above, radical-type reactivity has been also observed in the thermal reaction of aza[60]fullerene **1** with benzyltrimethylsilane in the absence of oxygen (Scheme 6).[15] In this case, aza[60]fullerene adduct **19** is isolated in less than 10% yield. The mechanism that has been proposed to account for the formation of this aza[60]fullerene adduct is shown in Scheme 6. In brief, aza[60]fullerenyl radical $C_{59}N^{\bullet}$ attacks a methyl hydrogen of benzyltrimethylsilane rather than a benzylic one owing to the less hindered access to the methyl groups and the enhanced stability of the incipient benzyl radical at the transition state

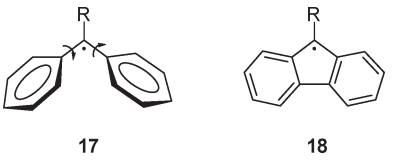
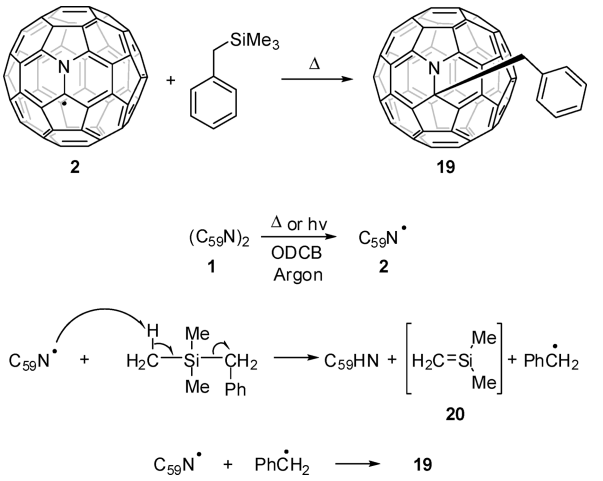


FIGURE 3. Disturbed conjugation in diphenylmethenyl radical **17** and the planar fluorenyl radical **18**.

SCHEME 6. Radical Reaction between $C_{59}N^{\bullet}$ and Benzyltrimethylsilane



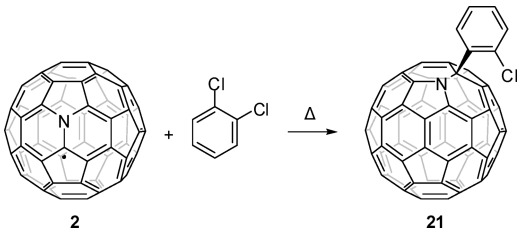
of the concerted mechanism. During this procedure, formation of the highly reactive intermediate **20** (dipolar or biradical)[21] is assumed, which could account for the low isolated yield of **19** as it can multiply add to the aza[60]fullerene cage. Indeed, the slow degradation of **1** and the formation of unidentified aza[60]fullerene multiadducts that were observed by HPLC can be explained by the existence of the intermediate **20**. An alternative mechanism, involving the attack of $C_{59}N^{\bullet}$ on the benzyl-Si(Me)$_3$ bond, cannot be excluded as it would directly afford adduct **19** and the relatively stable TMS radical; nevertheless, due to the increased steric hindrance of the corresponding transition state we are not in favor of such a mechanism.

Another remarkable observation, which came up during our present studies, is that ODCB slowly reacts with aza[60]fullerenyl radical **2** toward the production of aza[60]fullerene monoadduct **21** (Scheme 7). To date, ODCB was believed to be inactive toward **2**; however, monoadduct **21** was identified as a byproduct during the prolonged reaction of **1** with diphenylmethane in ODCB. Further experiments showed that when aza[60]fullerene and ODCB are heated under Ar, at 180 °C for 2 days, **21** is obtained in ~10% isolated yield. The mechanism for this intriguing reaction has not been clarified yet. Note that ODCB is the most commonly utilized solvent in fullerene radical reactions due to its hypothetical inertness toward the intermediate radical species and the high solubility of fullerenes in it.

The shorter reaction times together with the lower temperature used for the radical reactions between **1** and substrates **7a**−**d** and **9a**,**b**, compared to the diphenylmethane reaction,[7] make the purification of adducts **8a**−**d** and **10a**,**b**

(21) Gusel'Nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529–557.

SCHEME 7. The Isolated Byproduct 21 from the Thermal Reactions of Aza[60]fullerene in ODCB



easier and the use of preparative HPLC unnecessary. It turns out that the most important reason is the absence of byproduct **21**, which is impossible to separate from the desired products solely by flash chromatography.

Conclusions

A detailed study on the reactivity of azafullerenyl radical $C_{59}N^{\bullet}$ toward aromatic compounds bearing benzylic or dibenzylic hydrogen atoms was carried out. Only substrates that can give a planar dibenzylic radical intermediate led to well-defined aza[60]fullerene monoadducts. The efficiency of these reactions is proposed to originate from the convenient abstraction of the dibenzylic hydrogen and the enhanced stability of the produced intermediate radical that permits coupling with $C_{59}N^{\bullet}$. Nonplanar dibenzylic radicals and (mono)benzylic radicals are not stable enough, resulting in nonregiospecific multiple additions onto the fullerene skeleton, leading to the formation of several multiadducts that are impossible to identify. It was also found that under high temperatures and prolonged reaction times ODCB reacts with $C_{59}N^{\bullet}$, forming the corresponding aza[60]fullerene monoadduct.

Functionalization of $(C_{59}N)_2$ has thus far proven to be a trickier task than that of parent fullerene C_{60}. The most profound reason is the lower symmetry of the $C_{59}N$ framework (C_s) when compared with the highly symmetric C_{60} (I_h). On the other hand, incorporating a nitrogen heteroatom into the all-carbon framework of C_{60} endows a molecule with interesting physicochemical properties such as enhanced electron affinity. In this context, the preparation of covalently linked heterofullerene−porphyrin conjugates, exhibiting long-lived intramolecular charge separation, was recently achieved.[22] These preliminary studies could lead to molecular systems with potential applications in material science and biology.

Experimental Section

Synthesis of Aza[60]fullerene $(C_{59}N)_2$ (1). a. 2-Methoxyethoxymethylazide (MEM-N_3). A mixture of NaN_3 (2.08 g, 32 mmol), MEM-Cl (1.82 mL, 16 mmol), and dry CH_3CN (50 mL) was placed in a dry, two-necked round-bottomed 150 mL flask, which was then heated to reflux under an Ar atmosphere for 3 h. The reaction mixture was subsequently cooled to room temperature and 50 mL of diethyl ether was added. This solution was transferred to a separating funnel and was extracted with saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and then the solvent was removed with a rotary evaporator to give 1.66 g (79%) of MEM-N_3, as pale yellow oil. This product was subsequently used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 2H), 3.76 (m, 2H), 3.58 (m, 2H), 3.39 (s, 3H).

b. [5,6]-*N*-MEM-azafulleroid. A solution of C_{60} (1.44 g, 2 mmol) in ODCB (100 mL) was added in a dry, two-necked round-bottomed 250 mL flask, which was placed in an ultrasound bath for 15 min. To remove oxygen traces from the solvent, the solution was degassed through five vacuum−Ar cycles. Next, MEM-N_3 (0.656 g, 5 mmol) was added to the flask and the mixture was heated to reflux under an Ar atmosphere for 4 h. After cooling at ambient temperature, the product was purified by column chromatography, using silica gel and toluene. Separation of [5,6]-MEM-azafulleroid from [6,6]-MEM-aziridinofullerene[23] was completely achieved in most of the cases. [5,6]-MEM-azafulleroid comes out from the column first and [6,6]-MEM-aziridinofullerene elutes second. After evaporation of the solvent with a rotary evaporator, the solid was washed several times with Et_2O and dried under vacuum for 12 h. [5,6]-*N*-MEM-azafulleroid (0.295 g, 18%) was isolated as a black powder. ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 5.36 (s, 2H), 4.25 (m, 2H), 3.79 (m, 2H), 3.50 (s, 3H).

c. *N*-MEM-ketolactam. [5,6]-*N*-MEM-azafulleroid (0.206 g, 0.25 mmol) was added in a round-bottomed 500 mL flask and dissolved, using a magnetic stirring rod, in ODCB (400 mL). After a homogeneous solution was obtained, toluene (100 mL) was added and the resulting solution was placed in an ultrasound bath for 15 min. Next, O_2 was passed through the mixture and the solution was irradiated with a Xe 300 W lamp as the light source. A water cooling system, in order to maintain the reaction temperature close to room temperature, and a $K_2Cr_2O_7$ 1% (w/w) aqueous solution as a filter was placed between the lamp and the flask. Reaction progress was monitored by HPLC analysis and it was typically completed in 20 h. The desired product was purified by column chromatography, using silica gel and toluene/EtOAc 9:1. After evaporation of the solvent, using a rotary evaporator, the solid was washed several times with Et_2O and dried under vacuum for 12 h. *N*-MEM-ketolactam (0.150 g, 70%) was isolated as a black powder. ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 6.38 (d, J = 10 Hz, 1H), 6.00 (d, J = 10 Hz, 1H), 4.03 (m, 2H), 3.60 (m, 2H), 3.36 (s, 3H).

d. Aza[60]fullerene $(C_{59}N)_2$ (1). *N*-MEM-ketolactam (0.160 g, 0.187 mmol) and ODCB (160 mL) were added to a dry, round-bottomed 250 mL flask, which was placed into an ultrasound bath for 10 min. Next, in order to remove oxygen traces from the solvent, the solution was degassed through five vacuum−Ar cycles and a reflux condenser was attached to the flask. The flask was heated to 150 °C under an Ar atmosphere. As soon as the reaction mixture reached 150 °C, *p*-toluenesulfonic acid monohydrate (0.544 g, 2.8 mmol) was added and the mixture was heated at 150 °C for 2 h. The product was purified by column chromatography, using silica gel and toluene ($(C_{59}N)_2$ comes down first as an olive-green band). After the evaporation of the solvents with a rotary evaporator, the remaining solid was washed several times with Et_2O and dried under vacuum for 12 h. $(C_{59}N)_2$ (0.103 g, 75%) was isolated as black powder. ^{13}C NMR (125 MHz, ODCB-d_4) δ 156.42, 149.01, 148.27, 148.13, 147.98, 147.85, 147.10, 147.04, 146.76, 146.30, 146.26, 145.62, 145.44, 145.31, 145.10, 144.80, 144.44, 143.70, 143.30, 142.64, 142.29, 142.17, 141.80, 141.47, 141.39, 140.54, 138.33, 136.76, 125.34, 90.66.

General Procedure for the Synthesis of Substituted Fluorenes 7b−d. 1. Substituted Fluorenols. A solution of 9-fluorenone (4.50 g, 25 mmol) in dry THF (40 mL) was added to a stirred

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solution of the appropriate Grignard reagent (MeMgI, EtMgI, or PhMgBr, 30 mmol), in dry Et_2O (100 mL), at 0 °C. The reaction was stirred overnight at room temperature and then cooled at 0 °C before being quenched with 3 mL of 1 N aqueous NaOH solution. After being washed with brine, the organic phase was dried over anhydrous $MgSO_4$ and concentrated (rotary evaporator) to afford the desired alcohol as a yellow solid (88−92% yield). All substituted fluorenols were subsequently used without any further purification.

9-Methyl-9-fluorenol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.40 (m, 2H), 7.35 (m, 2H), 2.06 (s, 1H), 1.77 (s, 3H).

9-Ethyl-9-fluorenol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.34 (m, 2H), 7.33 (m, 2H), 2.22 (q, J = 7.5 Hz, 2H), 2.00 (s, 1H), 0.58 (t, J = 7.0 Hz, 3H).

9-Phenyl-9-fluorenol: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.39 (m, 6H), 7.28 (m, 5H), 2.50 (s, 1H).

2. Substituted Fluorenes 7b−d. Each substituted fluorenol (23 mmol) was dissolved in dry CH_2Cl_2 (40 mL), together with triethylsilane (5.37 g, 46 mmol). After the reaction mixture was cooled at 0 °C, etherated boron trifluoride was added at one time (6.56 g, 46 mmol). The reaction mixture was kept at 0 °C for 1 h and quenched with the addition of aqueous saturated Na_2CO_3 (10 mL). Following the addition of Et_2O (120 mL), the organic layer was washed with brine, dried over $MgSO_4$, and purified by column chromatography (hexanes) to afford the desired 9-substituted fluorene in high yields (70−85%).

9-Methyl-9*H*-fluorene (7b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.41 (m, 2H), 7.36 (m, 2H), 3.98 (q, J = 8.0 Hz, 1H), 1.57 (d, J = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.00, 140.53, 126.93, 126.92, 124.01, 119.85, 42.44, 18.18; MS, m/z (relative abudance) 180 (M^+, 59), 165 (100), 139 (4), 89 (16), 82 (21), 76 (11), 63 (4).

9-Ethyl-9*H*-fluorene (7c): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.47 (m, 2H), 7.41 (m, 2H), 4.06 (t, J = 5.6 Hz, 1H), 2.19 (m, 2H), 0.83 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.72, 141.84, 127.37, 127.30, 124.81, 120.26, 48.98, 26.22, 10.26; MS, m/z (rel abudance) 194 (M^+, 67), 178 (20), 165 (100), 139 (9), 115 (6), 94 (6), 82 (17), 63 (6).

9-Phenyl-9*H*-fluorene (7d): ^{1}H NMR (500 MHz, $CDCl_3$):δ 7.84 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.32 (m, 7H), 7.13 (d, J = 6.8 Hz, 2H), 5.09 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.90, 141.60, 141.01, 128.68, 128.34, 127.30, 126.83, 125.33, 119.87, 54.44; MS, m/z (rel abundance) 242 (M^+, 100), 215 (5), 165 (21), 119 (25), 106 (4).

General Procedure for the Synthesis of Substituted Azafullerenes 8a−d and 10a,b. A 300 equiv sample of the substituted arylalkane was added to a degassed (5 vacuum/argon cycles) solution of **1** (20 mg, 13.8×10^{-3} mmol) in HPLC grade ODCB (40 mL). The mixture was heated at 160 °C for 4−9 h under argon and the reaction was monitored by HPLC at 326 nm. After distillation of ODCB at 55 °C under reduced pressure, the crude mixture was washed 4−6 times with acetonitrile and/or acetone (centrifugation at 1500 c/min) in order to remove the remained substituted arylalkane. Chromatographic purification, using hexane as eluent (the remaining azafullerene dimer elutes first, followed by the more polar, green azafullerene monoadduct), afforded **8a−d** and **10a**,**b** as black solids (20−40% yield).

9-Azafullerenyl-9*H*-fluorene (8a): mp >360 °C; IR (KBr) ν (cm^{-1}) 2914, 1510, 1446, 1421, 1183, 1091, 1021, 806, 738, 576, 523; UV−vis (CS_2) λ_{max} (nm) 378, 450, 595, 730, 817; MS (FAB) m/z 888 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.47 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 7.6 Hz, 2H), 7.65 (m, 2H), 7.55 (m, 2H), 6.13 (s, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 156.29, 150.74, 148.52, 148.49, 148.39, 147.95, 147.87, 147.18, 147.09, 146.84, 146.30, 145.67, 145.51, 144.82, 144.58, 143.69, 143.59, 143.35, 142.69, 142.39, 141.70, 141.50, 139.74, 138.03, 135.18, 129.46, 128.64, 127.74, 126.44, 125.17, 121.04, 85.38, 58.44.

9-Azafullerenyl-9-methylfluorene (8b): mp >360 °C; IR (KBr): ν (cm^{-1}) 2920, 1510, 1441, 1422, 1185, 1083, 983, 761, 740, 672, 577, 524, 483; UV−vis (CS_2) λ_{max} (nm) 379, 450, 593, 730, 816; MS (FAB) m/z 902 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.30 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 7.60 (m, 2H), 7.53 (m, 2H), 2.95 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 156.62, 148.89, 148.32, 148.07, 147.94, 147.93, 147.72, 147.12, 147.03, 146.99, 146.80, 146.45, 146.25, 145.62, 145.48, 144.82, 144.76, 143.69, 143.34, 142.68, 142.41, 141.89, 141.49, 141.34, 139.34, 137.90, 135.23, 129.41, 127.86, 127.23, 125.22, 121.04, 88.91, 59.80, 20.05.

9-Azafullerenyl-9-ethylfluorene (8c): mp >360 °C; IR (KBr): ν (cm^{-1}) 2917, 1510, 1443, 1423, 1185, 1088, 1007, 965, 841, 761, 742, 679, 577, 523, 483; UV−vis (CS_2) λ_{max} (nm) 384, 451, 596, 731, 817; MS (FAB) m/z 916 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.24 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.6 Hz, 2H), 7.61 (m, 2H), 7.54 (m, 2H), 3.89 (q, J = 6.9 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 156.59, 148.17, 147.90, 147.70, 147.12, 146.46, 146.24, 145.63, 145.50, 144.78, 144.76, 144.53, 143.54, 142.44, 141.89, 141.51, 141.40, 141.34, 137.86, 129.38, 127.82, 127.30, 121.11, 89.04, 65.27, 26.02, 9.32.

9-Azafullerenyl-9-phenylfluorene (8d): mp > 360 °C; IR (KBr) ν (cm^{-1}) 2915, 1490, 1449, 1421, 1186, 1091, 1080, 903, 845, 737, 696, 581, 524, 482; UV−vis (CS_2): λ_{max} (nm) 384, 450, 595, 728, 813; MS (FAB) m/z 964 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.68 (d, J = 7.6 Hz, 2H), 8.62 (d, J = 7.5 Hz, 2H), 7.98 (d, J = 7.7 Hz, 2H), 7.58 (m, 7H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 156.71, 147.66, 147.53, 147.03, 147.01, 146.75, 146.46, 146.45, 146.24, 145.48, 144.81, 144.47, 143.70, 143.36, 142.86, 142.73, 142.50, 141.83, 141.54, 141.34, 138.92, 137.65, 130.56, 129.94, 129.57, 129.25, 128.57, 127.83, 121.04, 30.53.

9-Azafullerenyldihydroanthracene (10a). 9,10-Dihydroanthracene (748 mg, 4.15 mmol) was added to a degassed (5 vacuum/argon cycles) solution of **1** (20 mg, 13.8×10^{-3} mmol) in HPLC grade ODCB (40 mL). The mixture was heated at 160 °C for 4 h under argon and the reaction was monitored by HPLC at 326 nm. After distillation of ODCB at 55 °C under reduced pressure, the crude mixture was washed and centrifuged 6 times with acetonitrile in order to remove the remained tetrahydroanthracene. Chromatographic purification, using hexane as eluent (the crude reaction mixture was loaded with CS_2), afforded **10a** as a black solid (3.7 mg, 30% yield). mp > 360 °C; IR (KBr) ν (cm^{-1}) 2914, 1510, 1449, 1419, 1184, 1091, 1004, 953, 881, 744, 725, 649, 577, 523, 484, 448; UV−vis (CS_2) λ_{max} (nm) 386, 452, 599, 739, 827; HRMS (ESI) calcd for $C_{73}H_{11}N$ 901.0897, found 901.0902; MS (FAB) m/z 902 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.06 (m, 2H), 7.57 (m, 2H), 7.51 (m, 4H), 6.13 (s, 1H), 4.59 (d, J = 20 Hz, 1H), 4.28 (d, J = 20 Hz, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 155.83, 149.24, 148.41, 148.22, 148.12, 147.89, 147.80, 147.20, 147.02, 146.81, 146.46, 146.25, 145.64, 145.51, 144.90, 144.82, 144.59, 143.64, 143.30, 142.63, 142.32, 141.93, 141.60, 141.39, 141.37, 139.74, 138.71, 138.09, 134.94, 133.51, 132.21, 129.17, 128.62, 126.91, 125.00, 58.92, 37.35.

9-Azafullerenylxanthene (10b). Xanthene (756 mg, 4.15 mmol) was added to a degassed (5 vacuum/argon cycles) solution of **1** (20 mg, 13.8×10^{-3} mmol) in HPLC grade ODCB (40 mL). The mixture was heated at 160 °C for 3 h under argon and the reaction was monitored by HPLC at 326 nm. After distillation of ODCB at 55 °C under reduced pressure, the crude mixture was washed and centrifuged 6 times with acetonitrile in order to remove the remained xanthene. Chromatographic purification, using hexane as eluent (the crude reaction mixture was loaded with CS_2),

afforded **10b** as a black solid (3.0 mg, 24% yield). Mp >360 °C; IR (KBr) ν (cm^{-1}) 2953, 2917, 2846, 1510, 1475, 1456, 1421, 1252, 1177, 1091, 1084, 898, 857, 746, 719, 690, 650, 577, 523, 482; UV−vis (CS_2) λ_{max} (nm) 448, 596, 741, 824; HRMS (ESI) calcd for $C_{72}H_9NO$ 903.0690, found 903.0679; MS (FAB) m/z 904 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.01 (m, 2H), 7.54 (m, 2H), 7.37 (m, 4H), 6.09 (s, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 155.89, 154.53, 148.37, 148.25, 148.20, 147.82, 147.19, 147.04, 146.43, 145.46, 144.86, 144.80, 143.31, 142.63, 141.91, 141.47, 141.44, 141.40, 139.76, 138.09, 135.21, 132.29, 130.20, 124.83, 123.88, 119.49, 117.62, 87.78, 52.82.

1-Azafullerenyl-2-chlorobenzene (21). A degassed (5 vacuum/argon cycles) solution of **1** (10 mg, 6.9×10^{-3} mmol) in HPLC grade ODCB (20 mL) was heated at 180 °C for 48 h under argon and the reaction was monitored by HPLC at 326 nm. After distillation of ODCB at 55 °C under reduced pressure, the crude mixture was washed and centrifuged 6 times with acetonitrile in order to remove solvent traces. Chromatographic purification, using toluene as eluent (the crude reaction mixture was loaded with CS_2), afforded **21** as a black solid (~10% isolated yield). Mp > 360 °C; UV−vis (CS_2) λ_{max} (nm) 256, 321, 440, 585, 720, 800; HRMS (MALDI-TOF) calcd for $C_{65}H_4ClN$ 833.003, found 833.111; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.87 (dd, J_1 = 7.50 Hz, J_2 = 1.50 Hz, 1H), 7.92 (dd, J_1 = 7.50 Hz, J_2 = 1.00 Hz, 1H), 7.76 (m, 1H), 7.70 (m, 1H).

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, FT-IR, and MS spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.