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[6-6]-Closed versus [6-5]-Open Isomers of Imino- and Methanofullerenes: A Comparison with Pristine C_{60} and $(C_{59}N)^{\bullet}$

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Two sets of [6-6]-closed and [6-5]-open isomers, namely, those of a methano- and iminofullerene series, are probed in light of their excited state and electron acceptor properties. Steady-state emission, fluorescence, and phosphorescence indicate that the excited-state energy levels of the [6-5]-open (**2**) and [6-6]-closed (**1**) iminofullerene isomers follow a seemingly surprising, reverse trend relative to the [6-5]-open (**4**) and [6-6]-closed (**3**) methanofullerene isomers. Specifically, the [6-5]-open iminofullerene (**2**) reveals almost identical characteristics to that of the [6-6]-closed methanofullerene (**3**). On the other hand the [6-6]-closed iminofullerene (**1**) is observed to resemble the [6-5]-open methanofullerene (**4**). Transient absorption spectra, i.e., singlet−singlet, triplet−triplet, and π−radical anion absorption are in accord with the emission studies. These effects have been rationalized in terms of an efficient engagement between the nitrogen electron pair and the fullerene π-system. The [6-5]-open methanofullerene (**4**) is, therefore, considered to be a true isoelectronic analogue of pristine C_{60} (60 π-electrons). Although the [6-6]-closed iminofullerene (**1**), constitutes a quasi 60 π-electron system, it appears to bear only a weak resemblance with the former two. In contrast, the [6-6]-closed isomer (**3**) is characterized by a 58 π-electron system, and the [6-5]-open isomer (**2**) is characterized by a 62 π-electron system. In terms of optimizing the electron acceptor properties and photostability, the most promising monofunctionalized fullerene derivative for the design of multicomponent donor acceptor arrays is unequivocally the [6-6]-closed iminofullerene (**1**).

Introduction

The remarkable electronic properties of [60]fullerene, in its singlet ground state and also its photoexcited states, evoked a keen interest to employ them as 3-dimensional acceptor moieties in bimolecular electron and energy transfer reactions.[1−5] Relevant studies have primarily been performed in homogeneous solutions, at heterogeneous interfaces,[6,7] or, more recently, across biologically important membrane interfaces.[8,9] The first reduction potential of C_{60},[10] comparable to that of planar, 2-dimensional acceptor moieties, such as quinones and methyl viologen, is furthermore favored by an exceptionally low reorganization energy.[11] In essence, this combination points to the possible

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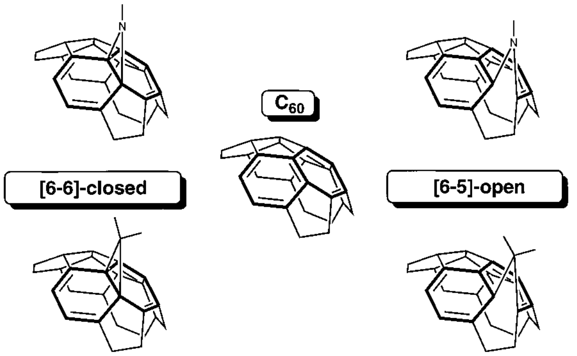


Figure 1. Structures of [6-5]-open and [6-6]-closed isomers.

key role of fullerenes as electron-transfer agents in more complex systems, such as artificial photosynthesis. Parallel to the development of various protocols with the modification of their polyfunctional structure as a scope, functionalized fullerenes emerged as promising building blocks in light-harvesting donor−acceptor arrays and advanced electronic devices.[2,12−18]

Usually, 1,2-additions are observed across a [6-6]-ring junction, which possesses a higher electron density than the [6-5]-ring junction. The driving force of addition reactions to C_{60} lies mainly in the relief of strain energy stemming from the curved fullerene surface and the deviation from planarity of the respective C_{60} double bonds. In particular, covalent attachment of a symmetrical carbene moiety to C_{60} can afford, in principle, up to four different isomeric products. Among those, the [6-5]-open and the [6-6]-closed isomers are by far the most important ones (see Figure 1).[2,12−18] The electronic structure of [6-5]-open isomers is very appealing because their fullerene core completely sustains the π-system of pristine C_{60} and still enables the attachment of virtually any functionalizing group. Unfortunately, most of the [6-5]-open derivatives undergo conversion, by thermal,[19−21] electrochemical,[22−24] and photochemical means,[25] into the thermodynamically more stable [6-6]-closed isomers. An important consequence is associated with this transformation; the fullerene core in these [6-6]-closed isomers is affected by a loss of 2 π-electrons, compared to pristine C_{60}.

Converting the fullerene core into such a 58 π-electron system subsequently leads to an alteration of the electron accepting properties of the resulting monofunctionalized fullerene derivatives.[26−29] For example, the reduction potentials of most of the studied derivatives reveal a shift to more negative values.[10] This trend seems not only to apply for their singlet ground states (~ -100 mV)[10] but also for their singlet (~ -300 mV) and triplet excited states (~ -150 mV).[27] As a direct consequence, the driving force for intra- and intermolecular electron-transfer processes experiences a significant impact relative to pristine C_{60}.[30]

Iminofullerenes have recently attracted considerable attention as novel starting materials for the synthesis of heterofullerenes, in which, for example, a nitrogen atom is incorporated into the fullerene structure.[31,32] The most interesting example has been the synthesis of $(C_{59}N)^{\bullet}$. Apart from a few electrochemical data,[33] very little information is available on the photophysical properties, including electron and energy transfer reactions. More importantly, the [6-5]-open structure gains some degree of stabilization over the methanofullerene series, although the [6-6]-closed configuration is still the thermodynamically more stable isomer.[34] In contrast to methanofullerenes, the [6-5]-open iminofullerene isomer does not isomerize upon extensive illumination, but rather exhibits conversion to a ring-opened ketolactam.[25,34]

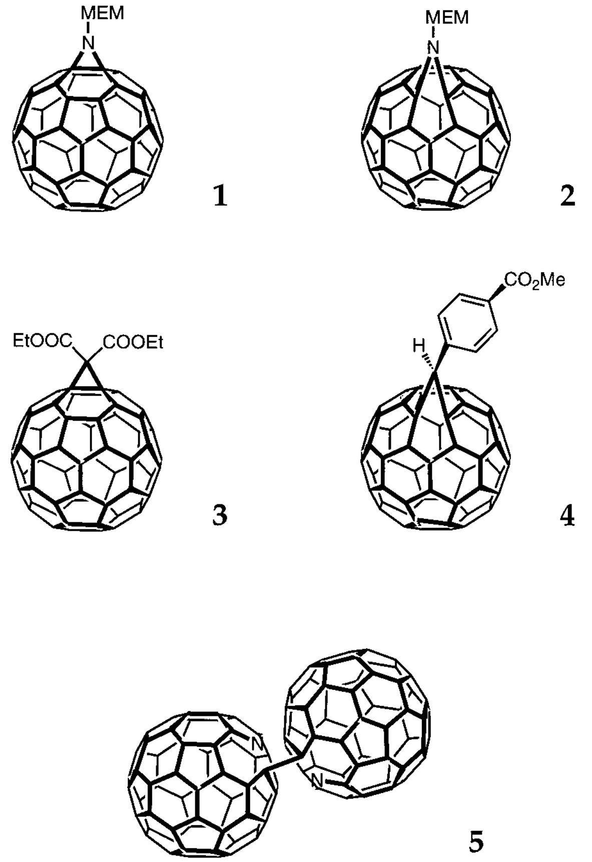


Figure 2. Compounds used in this study.

An important question that emerges is whether the [6-5] and [6-6] forms differ in their reactivity. In addition to the challenge of addressing this issue, it is of fundamental importance to determine the impact that a heteroatom, adjacent to the fullerene core (**1** and **2**), or even within the fullerene framework (**5**), has on the fullerene characteristics. Time-resolved techniques, such as flash photolysis and pulse radiolysis, offer powerful approaches that may help to shed light on aspects ranging from ground state and excited-state properties to electron-transfer reactions. In the current investigation, the excited and reduced states of the [6-6]- and [6-5]-iminofullerene isomers are, for the first time, compared with those of the corresponding methanofullerenes and also with $(C_{59}N)^{\bullet}$.

Experimental Section

Details regarding the synthesis of monofunctionalized fullerene derivatives (**1**−**4**) and $(C_{59}N)_2$ (**5**) are described elsewhere (Figure 2).[25,32,34] Pristine C_{60} was purchased from SES Research, Inc. (Houston, TX).

Pulse radiolysis experiments were performed using 50-ns pulses of 8 MeV electrons from a Model TB-8/16-1S electron linear accelerator. The basic details of the equipment and the data analysis have been described in a recent work.[35] Dosimetry is based on the $^{\bullet}OH$-induced oxidation of SCN^- to $(SCN)_2^{\bullet -}$ which, in N_2O-saturated aqueous solutions, takes place with $G \approx 6$ (G denotes the number of species generated per 100 eV, which is equivalent to an approximate micromolar concentration per 10 J of absorbed energy). The radical concentration generated per pulse was varied between 1×10^{-6} M and 3×10^{-6} M for all investigated systems. Apart from radical-induced reduction studies, pulse radiolysis has been further employed to generate and characterize triplet excited states of derivatives **1**−**5** in a nitrogen-saturated toluene solution containing 0.02

M biphenyl. Radiolysis yields the long-lived triplet excited state of biphenyl (^{3}BP). In the presence of fullerene derivatives **1**−**5**, intermolecular triplet−triplet energy transfer starting from the ^{3*}BP (E_T = 2.80 eV) to the lower lying triplets of **1**−**5** can be expected.[29,36]

For flash-photolysis studies, the fullerene concentrations were prepared to exhibit an optical density of at least 0.2 at 337 or 355 nm, the wavelength of irradiation. Picosecond laser flash photolysis experiments were carried out with 355-nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP ND:YAG laser system (pulse width ≈ 18 ps, 2−3 mJ/pulse). The white continuum picosecond probe pulse was generated by passing the fundamental output through a D_2O/H_2O solution. Nanosecond Laser Flash Photolysis experiments were performed with laser pulses from a Molectron UV-400 nitrogen laser system (337.1 nm, 8 ns pulse width, 1 mJ/pulse) in a front face excitation geometry. A Xe lamp was triggered synchronously with the laser. A monochromator (SPEX) in combination with either a Hamamatsu R 5108 photomultiplier or a fast InGaAs-diode was employed to monitor transient absorption spectra.

The molar extinction coefficients were determined by employing the comparative method, which enables the estimation of the molar extinction coefficients of the monofunctionalized fullerenes, in reference to a known standard such as pristine C_{60} ($\Phi_T \approx 1$, ϵ_t = 20 200 $M^{-1}cm^{-1}$).[37]

Absorption spectra were recorded with a Milton Roy Spectronic 3000 Array spectrophotometer. Emission spectra were recorded on a SLM 8100 Spectrofluorometer. Fluorescence spectra of derivatives **1**−**4** were measured in methylcyclohexane (5.0×10^{-5} M) which forms a clear, noncracking glass at liquid nitrogen temperature. A 570 nm long-pass filter in the emission path was used in order to eliminate the interference from the solvent and stray light. Long integration times (20 s) and low increments (0.1 nm) were applied. The slits were 2 and 8 nm. Each spectrum was an average of at least 5 individual scans.

Results and Discussion

Absorption Spectra. The ground-state absorption characteristics of the [6-6]-closed iminofullerene (**1**) in methylcyclohexane, with λ_{max} at 330, 424, 499, 543, 602(sh), and 678 nm, follow closely the pattern noticed for the [6-6]-closed methanofullerene (**3**), e.g., 327, 428, 492, 547, 606(sh), and 689 nm (for illustration see Figure 3a). Both sets of absorption reflect the partially broken symmetry (C_{2v}) of the fullerene core, relative to pristine C_{60} (I_h). The spectroscopically important transition in the long wavelength region, e.g., around 680−690 nm, appears, nevertheless, to be much weaker in **1** (678 nm). Also, an overall blue-shift is noticed. The latter alteration is tentatively attributed to the higher electron donating ability of the adjacent nitrogen atom, relative to the analogous carbon atom, both of which are located at the three-membered ring. To reinforce this assignment, the absorption characteristics of the [6-6]-closed methanofullerene were compared with those of two other [6-6]-closed isomers, namely, a *N*-methylfulleropyrrolidine[12] and a cyclohexanone adduct. The ground-state absorption spectra of these derivatives should be governed by the electron withdrawing nature of the corresponding functionalizing addends, the pyrrolidine and the cyclohexanone group, respectively. Indeed, both absorption spectra exhibit red-shifted bands relative to the methanofullerene (**3**). Another noticeable difference between the two [6-6]-closed isomers, e.g., **1** and **3**, appears in the 430−500 nm region which, remarkably, exhibits a resolved minimum around 490 nm only in the case of methanofullerene (**3**).

On the other hand, the two [6-5]-open isomers, imino- (**2**) and methanofullerene (**4**), reveal strong resemblance to the isoelectronic core of pristine C_{60}, particularly the two dominant transitions in the VIS range at 405 and 536 nm.[37] A closer view of the two spectra discloses, however, a number of appreciable differences between the two derivatives and pristine C_{60}. The most important deviation, apart from some slightly shifted absorption bands, resides in the long wavelength absorption of the [6-5]-closed iminofullerene (**2**) with the low intensity maximum around 696 nm ($\epsilon_{696\ nm}$ = 190 M^{-1} cm^{-1}). It is safe to assume that the latter refers to the ($S_0 \rightarrow {}^*S_1$) transition which, in turn, characterizes the energy of the singlet excited state. In this spectral region, both pristine C_{60} (330, 405, 536, 600, and 620(sh)), due to its symmetry prohibition (I_h), and the [6-5]-open isomer (**4**) (335, 528, 545, 600, and 620(sh)) lack any noticeable absorption at all (see Figure 3 and Table 1). In essence, the herein described spectral features indicate some dramatic discrepancies in the electronic structure of the fullerene core in derivatives **1**−**4**.

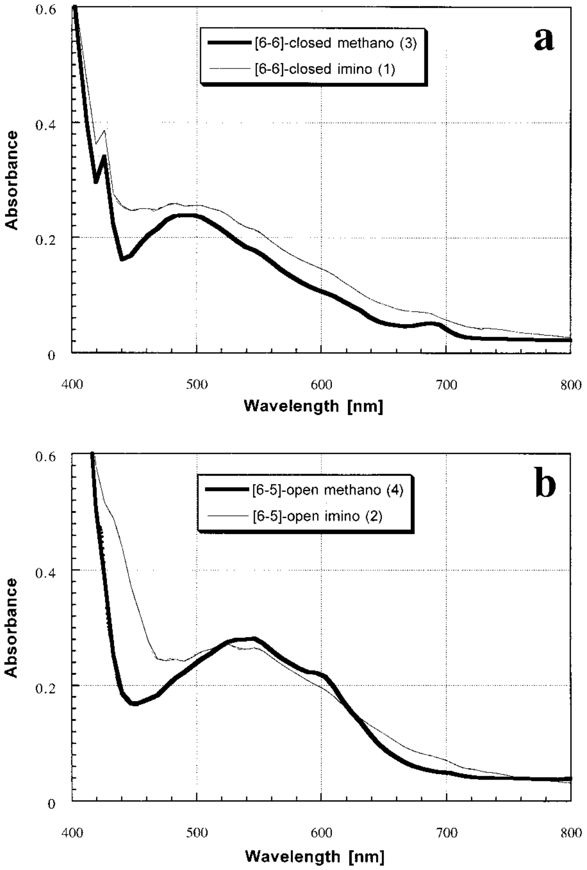
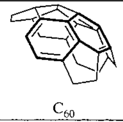
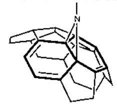
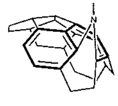
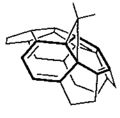
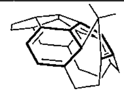


Figure 3. Ground-state absorption spectra of (a) [6-6]-closed isomers and (b) [6-5]-open isomers in methylcyclohexane solutions at room temperature.

An immediate consequence, which stems from lifting a carbon−carbon bond, located along a hexago*n*-pentagon junction, is that the 60 π-electron nature of the fullerene core is largely conserved in both [6-5]-open isomers. This leads to the hypothesis that these derivatives are effectively isoelectronic analogues of pristine C_{60}. The difference in absorption spectra, however, underlines the fundamental necessity of investigating these isomers in detail by means of steady-state and time-resolved photolytic and radiolytic techniques.

Emission Spectra. A logical extension of the ground-state characterization is to probe the excited-state behavior of the four isomers (**1**−**4**) and relate the resulting data to pristine C_{60}. The fluorescence spectra of the iminofullerene isomers, recorded in methylcyclohexane at 77 K, are virtually mirror images of

TABLE 1. Absorption Maxima and (*S$_1$ → S$_0$) Emission of C$_{60}$ and Fullerene Derivatives 1−4 in Methycyclohexane

Compound	Absorption maxima [nm]	(*S$_1$—>S$_0$) Emission [nm]
 C$_{60}$	330, 405, 536, 600, 620(sh)	620
 [6-6]-closed (**1**)	330, 424, 499, 543, 602(sh), 678	681
 [6-5]-open (**2**)	340, 430(sh), 520, 547, 605(sh), 700	725
 [6-6]-closed (**3**)	327, 428, 492, 547, 606(sh), 689	690
 [6-5]-open (**4**)	335, 528, 545, 600, 620(sh)	630

the corresponding ground-state spectra. Although the [6-6]-closed isomer (**1**) shows a strong (*S$_1$ → S$_0$) transition at 681 nm ($\Phi_{rel} = 4.9 \times 10^{-4}$) followed by a series of well-resolved emission bands (e.g., *2 → 0, *3 → 0, *4 → 0, etc.) (Figure 4 a/b), the fluorescence spectrum of the [6-5]-open isomer (**2**) gives rise to a substantially red-shifted emission around 725 nm ($\Phi_{rel} = 1.5 \times 10^{-4}$). The low emission quantum yields (Φ), associated with the singlet excited state, relate to the combination of a short singlet lifetime, a quantitative intersystem crossing and, finally, the symmetry-forbidden nature of the lowest-energy transition.

A correlation of the (*S$_1$ → S$_0$) emission with the long-wavelength (S$_0$ → *S$_1$) absorption shows a reasonable spectral overlap, suggesting an only small Stokes-shift in the singlet excited state of these isomers. This Stokes-shift is a sensitive measure of the energetic compensation associated with the adaptation of the molecule to a new solvent environment after population of the excited state. The emission spectra indicate that the singlet excited-state energy of the [6-6]-closed isomer **1** (1.82 eV), which is deduced from the corresponding (*S$_1$ → S$_0$) transitions, is actually closer in energy to pristine C$_{60}$ (1.99 eV)[37] than that of the [6-5]-open isomer **2** (1.68 eV).

To identify a possible intramolecular electron transfer in **1** and **2**, e.g., between the photoexcited fullerene and the nitrogen lone pair, the fluorescence behavior was probed in solvents of progressively increasing polarity. However, regardless of the solvent polarity, e.g., toluene ($\Phi_{rel} = 5.0 \times 10^{-4}$), CH_2Cl_2 ($\Phi_{rel} = 5.0 \times 10^{-4}$), and benzonitrile ($\Phi_{rel} = 5.5 \times 10^{-4}$), the fluorescence quantum yield of **1** remained nearly identical and, therefore, participation of an electron-transfer process can be ruled out. A similar conclusion can be drawn for **2**, which also showed no detectable changes in the fluorescence intensity upon variation of the solvent polarity.

The excited-state energies and properties of [6-6]-closed methanofullerenes have already been subjected to an extensive number of investigations and are very well understood.[1,27,28] On the other hand, no information is available concerning [6-5]-open isomers. As stated above, the combination of the isoelectronic nature of the fullerene core and the lack of a long-wavelength transition give rise to the expectation that both the [6-5]-open isomer (**4**) and the pristine C$_{60}$ should possess similar emission properties. Indeed, the fluorescence characteristics, e.g., a (*S$_1$ → S$_0$) transition around ca. 630 nm with an overall quantum yield of $\sim 2.0 \times 10^{-4}$ for this emissive process, are in reasonable agreement with those reported for C$_{60}$.[37] Upon comparing the *1 → 0 energy levels the following conclusion emerges: The singlet excited state of the [6-5]-open isomer **4** (1.96 eV) is energetically higher than the singlet excited state of the [6-6]-closed isomer **3** (1.79 eV) thus, reversing the trend noticed for the iminofullerenes **1** and **2**.

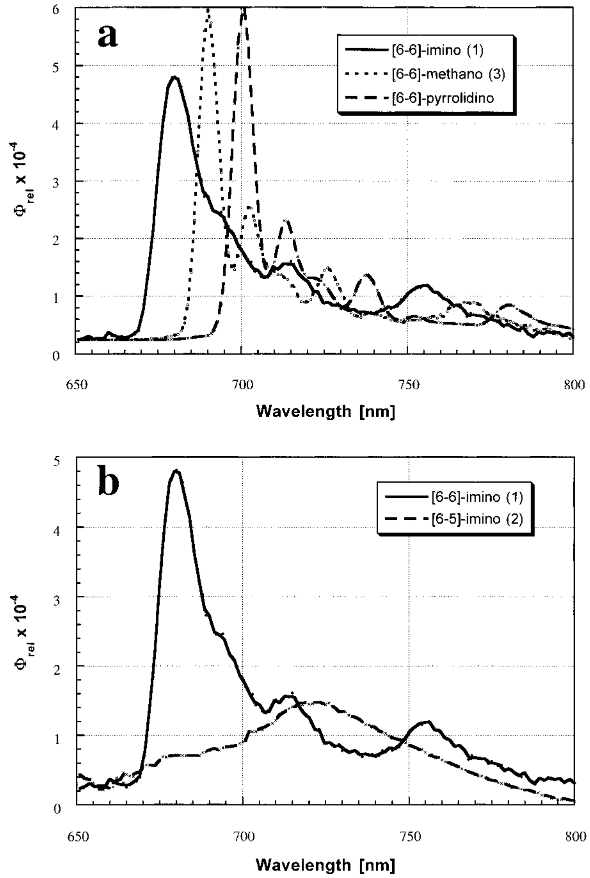


Figure 4. (a) Fluorescence spectra (Φ_{rel}) of [6-6]-closed iminofullerene **1** (solid line), [6-6]-closed methanofullerene (dotted line), and [6-6]-closed *N*-methyl fulleropyrrolidine (dashed line) in methylcyclohexane solution at 77 K (excitation wavelength 398 nm). (b) Fluorescence spectra (Φ_{rel}) of [6-6]-closed iminofullerene **1** (solid line), [6-5]-open iminofullerene **2** (dashed line) in methylcyclohexane solution at 77K (excitation wavelength 398 nm).

A parallel trend is found for the phosphorescence. These experiments make use of the heavy ion effect, e.g., by addition of ethyl iodide,[38] for a controlled acceleration of the ISC process between the fullerene singlet and triplet excited states. From the respective (T$_1$ → S$_0$) transitions the energies of the first triplet excited states (T$_1$) were estimated. Once again, the first triplet excited state of the [6-6]-closed iminofullerene (**1**) is clearly higher in energy than that of the corresponding isomeric [6-5]-open derivative (**2**). This clearly contrasts with the methanofullerene series, which shows a higher lying triplet excited state for the [6-5]-open (**4**) relative to its [6-6]-closed isomeric form (**3**).

In summary, steady-state fluorescence and phosphorescence studies demonstrate that the excited-state energy levels of the [6-5]-open and [6-6]-closed iminofullerene isomers follow a

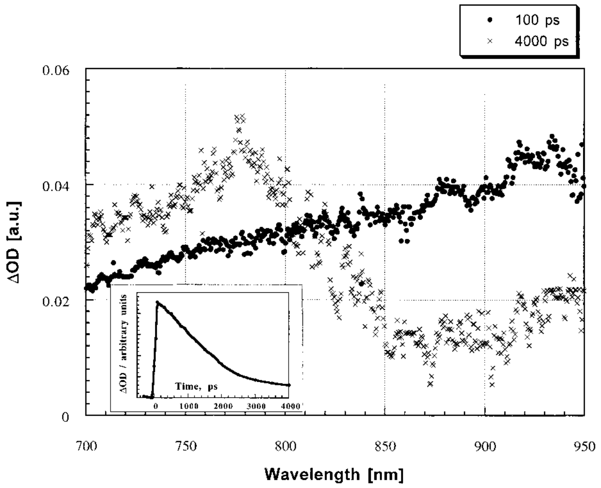


Figure 5. Transient absorbance changes observed following picosecond flash photolysis (●) 100 ps and (×) 4000 ps after 355 nm laser pulse (pulse width 18 ps, 1.6 mJ) excitation. The differential absorption spectra were recorded following excitation of [6-6]-closed iminofullerene **1** (2.0×10^{-5} M) in deaerated methylcyclohexane. The inset displays the kinetic time trace at 930 nm.

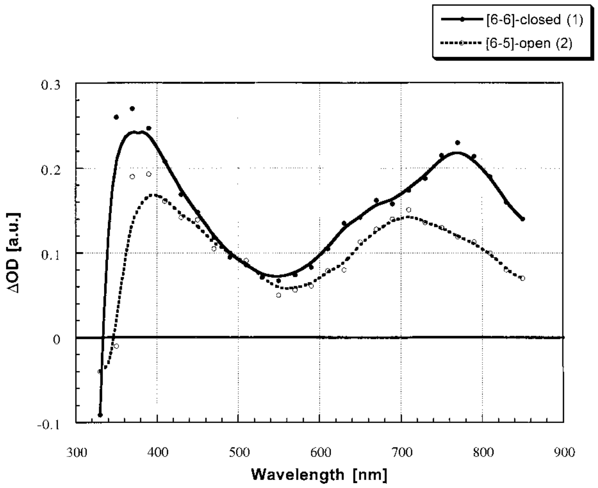


Figure 6. Differential absorption spectra obtained upon flash photolysis at 337 nm of 2.0×10^{-5} M [6-6]-closed iminofullerene **1** (●) and [6-5]-open iminofullerene **2** (○) in nitrogen saturated methylcyclohexane solution.

reverse trend than that observed for the analogous methanofullerene isomers. Furthermore, the [6-5]-open iminofullerene (**2**) reveals almost superimposable characteristics to the [6-6]-closed methanofullerene (**3**), and a similar resemblance is noted between the [6-6]-closed iminofullerene (**1**) and [6-5]-open methanofullerene (**4**). To understand this surprising behavior, it should be noted that the only meaningful difference between the methanofullerene and iminofullerene series is the nature of the bridging atom. The presence of a nitrogen atom with its free electron pair will afford a different electronic perturbation of the fullerene π-system. This leads to the following postulate: The difference in excited-state energies arises from an electronic interaction between the nitrogen lone pair and the fullerene core.

Singlet and Triplet Excited-State Absorption. To provide additional evidence in support of the above hypothesis, the excited-state behavior of **1**−**4** was probed by time-resolved differential absorption spectroscopy. Considering the dominant fullerene ground-state absorption in the 250−350 nm range, a 355 nm excitation wavelength was chosen. Differential absorption spectra, recorded after admission of a 18 ps laser pulse, to the [6-6]-closed iminofullerene **1** (2.0×10^{-5} M) in methylcyclohexane, reveal the immediate formation of the excited singlet state with λ_{max} around 930 nm (Figure 5). It should be noted that the latter is slightly red-shifted, relative to pristine C_{60} (920 nm).[39] The intersystem crossing in photoexcited **1** can be followed by the decay of the singlet excited state at 930 nm (see inset to Figure 5) and simultaneous growth of the triplet excited state at 775 nm.

$$(C_{60}) + h\nu \rightarrow {}^{1*}(C_{60}) - \text{ISC} \rightarrow {}^{3*}(C_{60}) \qquad (1)$$

Similarly, picosecond resolved excitation of the [6-5]-open iminofullerene (**2**) (3.0×10^{-5} M) in methylcyclohexane gives rise to a ${}^*S_1 \rightarrow {}^*S_n$ absorption at 917 nm. The decay of ${}^*S_1 \rightarrow {}^*S_n$ (7.1×10^8 s^{-1}), following clear first-order kinetics, occurs simultaneously to the formation of a sharp absorption around 710 nm, which is attributed to a $T_1 \rightarrow T_n$ transition originating from the energetically lower lying triplet excited state. The spectral shifts associated with the formation of the triplet excited states imply a rather strong effect of the [6-5]- or [6-6]-isomeric forms on the fullerene core. Typically, the rates for the forbidden intersystem crossing (ISC) in **1**−**4** are 5.3×10^8 s^{-1}, in reasonable agreement with that noticed for pristine C_{60}.[39] This suggests that the nitrogen electron pair exerts little impact on the formation and fate of the fullerene singlet excited state. However, the magnitude of the rate constant in these 3-dimensional systems, which is orders of magnitudes faster than those known for 2-dimensional aromatic hydrocarbons, can best be interpreted in terms of a large spin−orbit coupling.

To confirm and complement the above picosecond experiments, some nanosecond flash photolysis was also carried out. Excitation with 337 nm pulses (8 ns) of the [6-6]-closed iminofullerene **1** (2.0×10^{-5} M) in methylcyclohexane resulted in differential absorption changes, which are depicted in Figure 6. An immediate bleaching is observed of the ground-state absorption in a spectral region below 335 nm, due to the conversion of the singlet ground state to the triplet excited state. This bleaching is accompanied by the generation of two strong absorption maxima located at 360 and 775 nm and is in excellent agreement with the picosecond experiments. Likewise, two maxima, i.e., at 380 and 710 nm, were observed for the [6-5]-open iminofullerene **2**.

At first glance, the location of the maxima of **2**, especially the one at 710 nm, is surprising because they resemble, at least in part, those of the [6-6]-closed methanofullerene (**3**) (720 nm). In addition, another close resemblance was noted with the spectra of the cited cyclohexanone adduct (710 nm)/*N*-methyl fulleropyrrolidine (705 nm) in aprotic media.[40] On the other hand, the isoelectronic [6-5]-open methanofullerene (**4**) reveals, like pristine C_{60} (747 nm), a strong $T_1 \rightarrow T_n$ transition at 745 nm. These superimposing features clearly substantiate the similarity of the π-electron distribution in C_{60} and derivative **4**.

Kinetic analyses of both bleaching and formation profiles reveals an exponential recovery of the transient absorption to the original baseline. Specifically, in deoxygenated solutions, the triplet excited states of **1**−**4** decayed typically with half-lives on the order of 12 μs, much shorter than for planar aromatic hydrocarbons.[36] The half-lives measured in our present systems are in good agreement with those found for pristine fullerenes. The close analogy with other fullerene triplet excited states leads to the assumption that the free electron pair of the nitrogen lacks an active role in a photoinduced quenching reaction.

Similar $T_1 \rightarrow T_n$ spectra, with maxima at 745 (**4**), 720 (**3**), 710 (**2**), and 775 nm (**1**), were obtained upon bimolecular energy

TABLE 2. Photophysical Properties of C_{60}, $C_{59}N$, [6-5]-open, and [6-6]-closed Monofunctionalized Fullerene Isomers

compound	$*S_1 \rightarrow *S_n$ [nm]	$T_1 \rightarrow T_n$ [nm]	$E_{singlet}$ ($*S_1 \rightarrow S_0$) [eV]	$E_{triplet}$ ($T_1 \rightarrow S_0$) [eV]	$\epsilon_{triplet}$ [$M^{-1}cm^{-1}$]	ISC [s^{-1}]	π-Radical anion [nm]	$k_{quenching}$ (DABCO) [$M^{-1}s^{-1}$]	$k_{quenching}$ (O_2) [$M^{-1}s^{-1}$]
C_{60}	920	747	1.99	1.57	20 200	4.1×10^8	1080	2.5×10^9	1.9×10^9
[6-6]-closed (**1**)	930	775	1.82	1.55	10 900	5.6×10^8	1060	0.32×10^9	2.1×10^9
[6-5]-open (**2**)	917	710	1.68	1.51	7200	5.4×10^8	1000	0.149×10^9	1.8×10^9
[6-6]-closed (**3**)	920	720	1.79	1.50	13 500	5.3×10^8	1040	0.077×10^9	2.5×10^9
[6-5]-open (**4**)	920	745	1.96	1.55	[a]	7.1×10^8	1080	0.59×10^9	2.4×10^9
$(C_{59}N)_2$ (**5**)	940	690	1.78	1.51	[a]	[a]	985	0.1×10^9	[a]

[a] not measured.

transfer from a radiolytically excited biphenyl sensitizer in degassed toluene solutions. This radiation-chemical route provides an elegant method for forming triplet excited states of the fullerene without generating the initial singlet excited state. Additionally, these data serve as an independent confirmation for the photolytically generated triplet spectra.

$$^{3*}(\mathrm{BP}) + \mathrm{fullerene} \rightarrow \mathrm{BP} + {}^{3*}(\mathrm{fullerene}) \qquad (2)$$

Again, from a direct comparison of the iminofullerenes with the analogous methanofullerene isomers, a similar trend is observed to the above emission studies, namely, a reversed dependence, with a reasonably good agreement between derivatives **1**/**4** and between derivatives **2**/**3**, respectively.

It is also interesting to note that the energies of the second triplet excited state (T_2) of the methanofullerene (3.21 and 3.22 eV for the [6-5]-open (**4**) and [6-6]-closed isomer (**3**), respectively) and iminofullerene isomers (3.25 and 3.16 eV for the [6-5]-open (**2**) and [6-6]-closed isomer (**1**), respectively) are almost identical. Furthermore, the former reveal a nice similarity with C_{60} (3.22 eV) and two different monofunctionalized fullerene derivatives, namely *N*-methylfulleropyrrolidine (3.25 eV) and a cyclohexanone adduct (3.24 eV).

Intermolecular Transfer Processes. The excited state, which is primarily involved in bimolecular electron-transfer reactions, is the lower lying first triplet excited state (T_1) (ranging from 1.50 to 1.57 eV). In line with the emission studies (see above), it is expected that the photoexcited states of **1**−**4** may vary in their redox reactivity. To test this expectation, the electron-transfer processes evolving from triplet excited **1**−**4** with a sacrificial electron donor, such as diazabicyclooctane (DABCO), were probed by monitoring the lifetime of the $T_1 \rightarrow T_n$ absorption as a function of the quencher concentration. Addition of DABCO in the range of $(0.5-2.6) \times 10^{-3}$ M to deoxygenated fullerene solutions ($\sim 2.0 \times 10^{-5}$ M) resulted in accelerated decays of the excited triplet state absorption with the observed rates ($k_{obs} = \ln 2/\tau_{1/2}$) being linearly dependent on the DABCO concentration. The underlying process can thus be attributed to a reductive quenching of the triplet excited state. From the slopes of the k_{obs} versus [DABCO] plots, $k_{quenching}$ values between 2.5×10^9 $M^{-1}s^{-1}$ and 0.077×10^9 $M^{-1}s^{-1}$ were determined (see Table 2).

$$^3(\mathrm{C_{60}}) + \mathrm{DABCO} - k_{obs} \rightarrow [\mathrm{C_{60}}^{\bullet-} \cdots \mathrm{DABCO}^{\bullet+}] \rightarrow (\mathrm{C_{60}}^{\bullet-}) + (\mathrm{DABCO}^{\bullet+}) \qquad (3)$$

These quenching rates can be correlated with the associated reduction potentials $E°(^3C_{60}/C_{60}^{\bullet-})$. The latter can be expressed as the sum of the ground-state reduction potential ($C_{60}/C_{60}^{\bullet-}$) and the excited-state energy ($T_1 \rightarrow S_0$) (see eq 4). Figure 7 depicts the semilogarithmic plot of these calculated reduction potentials versus the quenching rate constants. In conclusion, from these kinetic results the same reversed trend emerges as observed for other parameters of the two sets of isomeric fullerene derivatives. These quenching data show that the triplet excited state of the [6-6]-closed iminofullerene (**1**) exhibits better electron acceptor properties than the corresponding [6-5]-open isomer (**2**), whereas in the methanofullerene series, the [6-5]-open (**4**) clearly outperforms the [6-6]-closed derivative (**3**) in this respect.

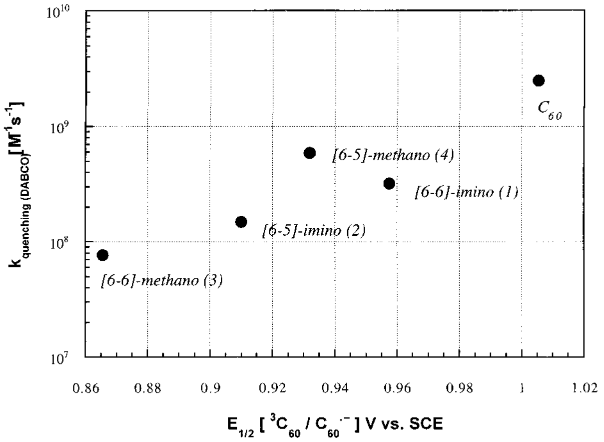


Figure 7. Semilogarithmic plot of ln($k_{QUENCHING}$) for the bimolecular quenching of the triplet states of various [6-5]-open and [6-6]-closed fullerenes by diazabicycolooctane (DABCO) versus the redox potential of the first reduction step of the triplet excited-state $E°(^3C_{60}/C_{60}^{\bullet-})$.

$$E°(^3\mathrm{C_{60}}/\mathrm{C_{60}}^{\bullet-}) = E°(\mathrm{C_{60}}/\mathrm{C_{60}}^{\bullet-}) + E(\mathrm{T_0} \rightarrow \mathrm{S_0}) \qquad (4)$$

Despite showing unambiguous quenching of the triplet state, the use of toluene as solvent to provide spectral evidence for the formation of a charge-separated radical pair and thus directly substantiate an electron-transfer process failed. In particular, recording the differential absorption changes in the NIR region, a wavelength range diagnostic for one-electron reduced fullerene π-radical anions,[41] yielded no appreciable absorption, which could be assigned to a charge-separated radical pair. Employing, however, a solvent with a higher dielectric constant, such as benzonitrile, prevented the fast-occurring charge recombination within the contact pair, as observed in toluene, which in turn resulted in a significantly increased stability of the charge separated radical pair, ($C_{60}^{\bullet-}$) and ($DABCO^{\bullet+}$). The similarity between the photolytically generated π-radical anion absorption and those bands noticed upon pulse radiolytic reduction (see below) corroborates the successful generation of the radical pair as a product of bimolecular excited triplet state quenching of the fullerenes by DABCO. On the microsecond time scale, these radical pairs were subject to a second-order back electron transfer with rate constants typically around 9.0×10^9 $M^{-1}s^{-1}$.

$$(\mathrm{C_{60}}^{\bullet-}) + (\mathrm{DABCO}^{\bullet+}) \rightarrow \mathrm{C_{60}} + \mathrm{DABCO} \qquad (5)$$

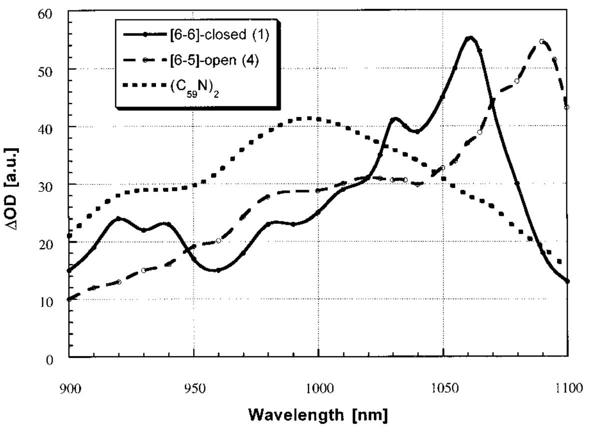


Figure 8. Differential absorption spectra of the π-radical anion of [6-6]-closed iminofullerene **1** (●), [6-5]-open methanofullerene **4** (○), and $(C_{59}N)_2$ (■), obtained upon pulse radiolysis of 4.0×10^{-5} M fullerene derivative in N_2-saturated toluene/acetone/2-propanol solution (8:1:1 v/v); 10 μs after the electron pulse.

Another remarkable property of fullerenes that promoted a lively interest toward their application as photosensitizers is the biologically important production of singlet oxygen ($^1O_2$),[37] in high yields. It should be noted, however, that the energy transfer reaction to molecular oxygen is only insignificantly affected by the functionalization, affording rate constants between 1.8×10^9 $M^{-1}s^{-1}$ and 2.5×10^9 $M^{-1}s^{-1}$ (see Table 2).

$$^3(C_{60}) + O_2 \rightarrow C_{60} + (^1O_2) \qquad (6)$$

Pulse Radiolytic Reduction. Finally, another set of sensitive parameters, which may provide further support for the key function of the nitrogen free electron pair, focuses on the NIR π-radical anion absorption of one-electron reduced fullerene moieties. These differential absorption changes basically confirm the generation of ($C_{60}^{\bullet -}$) which evolves from a photoinduced electron transfer with DABCO. π-Radical anions of fullerenes can most conveniently be studied by radiation-induced reduction in N_2-saturated toluene/2-propanol/acetone (8:1:1 v/v).[41] The reducing species, generated under these conditions, are $(CH_3)_2{}^{\bullet}C(OH)$ radicals, i.e., the radicals formed by hydrogen abstraction from 2-propanol and from electron capture of acetone followed by a subsequent protonation.

$$C_{60} + (CH_3)_2{}^{\bullet}C(OH) \rightarrow (C_{60}{}^{\bullet -}) + (CH_3)_2CO + H^+ \quad (7)$$

Reduction of fullerene derivatives **1**−**4** via reaction 7, under these conditions, takes place with rate constants of $\sim 8 \times 10^8$ $M^{-1}s^{-1}$. Figure 8 selectively displays the π-radical anion spectra of the [6-6]-closed iminofullerene **1** (1060 nm) and [6-5]-open methanofullerene **4** (1080 nm) because they reveal, despite all differences in structural parameters, the strongest spectral resemblance to pristine C_{60} (1080 nm).[41] The same similarity, incidentally, holds for $(C_{59}N)^{\bullet}$ (see further below). In contrast, the corresponding spectra of the [6-5]-open iminofullerene (**2**) and [6-6]-closed methanofullerene (**3**) radical anions are strongly blue-shifted with maxima at 1000 and 1040 nm, respectively. It is interesting to note, that λ_{max} of the π-radical anion absorption seems to follow the same trend as noticed for the $T_1 \rightarrow T_n$ absorption, $^*S_1 \rightarrow S_0$ emission, and $T_1 \rightarrow S_0$ emission. Specifically, a reasonably good agreement exists between **1**/**4** on one hand and, on the other hand, **2**/**3**.

In summary, the spectroscopic properties and kinetic data lead unequivocally to the conclusion that the electron pair on the nitrogen may, indeed, engage with the delocalized π-electrons. A number of important consequences, regarding the electronic structure of the various fullerene derivatives, emerge from this assumption. The [6-5]-open methanofullerene (**4**), for example, is beyond any doubt a true isoelectronic analogue of the 60 π-electron containing core of pristine C_{60}. In sharp contrast, the [6-6]-closed isomer (**3**) is, following this consideration, best represented by a 58 π-electron system. On the basis of the present experimental data, the scenario for the corresponding iminofullerene isomers is quite different. Considering the free electron pair, located at the nitrogen atom, it is safe to postulate that the [6-6]-closed isomer (**1**) comprises a quasi 60 π-electron system, 2 of them deriving, at least partially, from the nitrogen lone pair and the remaining 58 from the functionalized fullerene core. Therefore, **1** becomes comparable to pristine C_{60} and also with **4**. The fact that **1** differs from C_{60} more significantly than **4** (see Table 2), can be rationalized by examining the computed HOMO−LUMO separations in the compounds. Density Functional Theory calculations,[42] with the B3LYP functional[43] and a small split-valence basis set (3-21G)[44] predict this gap to be 170 meV narrower in **1** than in pristine C_{60}, where the computed gap is 3.10 eV. In **4**, a similar computation results in a value of 70 meV for the corresponding difference. Last, the [6-5]-open isomer (**2**), which a priori was assumed to be an another isoelectronic analogue of pristine C_{60}, carries, in fact, 62 π-electrons and should thus, indeed, exhibit distinctly different electronic properties.

To confirm the validity of the proposed hypothesis, it was deemed important to extend the current investigation to another heteroatom-containing fullerene derivative, namely, $(C_{59}N)_2$ (**5**), the first isolated heterofullerene.[32] The latter has per se 61 π-electrons in each fullerene unit and, consequently, should be isoelectronic with the π-radical anion of C_{60}, namely, ($C_{60}^{\bullet -}$). An important characteristic of the $(C_{59}N)_2$ dimer is that its excitation leads to the generation of $(C_{59}N)^{\bullet}$ which recombines qualitatively to the educt (($(C_{59}N)_2$ dimer).[45,46]In this context, it must be recognized though, that isolation of long-lived pure monomer $(C_{59}N)^{\bullet}$ is hampered unless further stabilization is provided by additional functionalization. It is, however, possible to generate $(C_{59}N)^{\bullet}$ sufficiently stable for the current investigations, by means of photolysis.

$$(C_{59}N)_2 - h\nu \rightarrow (C_{59}N)^{\bullet} \rightarrow (C_{59}N)_2 \qquad (8)$$

The photophysical properties of $(C_{59}N)^{\bullet}$ are summarized in Table 2. Most importantly, it appears that the $E(^*S_1 \rightarrow S_0)$ energy of the singlet excited-state resembles those of the [6-6]-closed iminofullerene (**1**) and [6-5]-open methanofullerene (**4**). In contrast, the first triplet excited-state energies cannot hold the similarity with **1** and **4**. Nevertheless, the energy level of the second triplet excited state (T_2) (3.3 eV) is in close accord to those of **1**−**4**.

Finally, the differential absorption spectrum (see Figure 8) recorded upon radiation-induced reduction of $(C_{59}N)^{\bullet}$, affording ($C_{59}N^-$), shows a maximum at 985 nm flanked by a shoulder at 930 nm. Despite a noticeable red-shift, these features nicely resemble the spectrum of (C_{60}^{2-}) with λ_{max} at 950 nm and a shoulder at 830 nm. Unfortunately, the electronic spectra of the two-electron reduced forms of **1**−**4** are not available yet, preventing any further correlation beyond that just made.

Conclusion

Although the [6-5]-open methanofullerene (**4**) reveals the best electron accepting properties, its photoinstablity makes it, however, a rather ineffective target molecule for photoinduced electron-transfer processes. In contrast, the [6-6]-closed iminofullerene (**1**) is characterized, similar to **3**, by a high photostability, and in light of the current data, appears to be the most promising monofunctionalized fullerene derivative with respect to electron-transfer processes.

Currently, the investigation of the respective oxygen derivatives is under way with emphasis on the comparison of its properties with the carbon and nitrogen analogues described above.

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