

Excited-State Properties of C₆₀ Fullerene Derivatives

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ABSTRACT

This Account reviews our main achievements in the field of excited-state properties of fullerene derivatives. The photosensitizing and electron-acceptor features of some relevant classes of functionalized fullerene materials are highlighted, considering the impact of functionalization on fullerene characteristics. In addition, the unique optimization in terms of redox potentials, water-solubility, and singlet oxygen generation is presented for several novel fullerene-based materials.

Introduction

The popularity of fullerenes in science is not merely due to aesthetics. Years of intense research activity have shown that C₆₀ can be considered as a powerful building block for use in materials science and medicinal chemistry.^{1,2} What makes fullerenes special is the combination of several interesting properties, particularly in terms of electron-acceptor capability, both in the solid state and in solution. For instance, the formation of charge-transfer salts with a number of donor groups or doping with metals has led to ferromagnetic³ or superconducting materials.⁴ Furthermore, an entirely new discipline, commonly called “fullerene chemistry”, has emerged in the past few years.^{5–7}

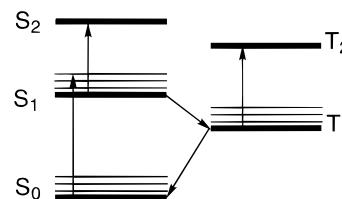
Original and well-established synthetic methodologies, applied to fullerenes, have produced a wide variety of novel derivatives, whose properties are continuously being investigated. One of the most exciting developments of

fullerene chemistry is related to their excited-state properties.^{8,9} Strong absorptions in the UV region and weaker but significant bands in the visible region characterize C₆₀, the most abundant representative of the fullerene family. When functionalized, C₆₀ retains the same basic characteristics but, in addition, the absorption of the derivatives extends further into the near-IR region. This implies that C₆₀ and its derivatives are very easily excited by low-energy light, which combined with the fullerenes' high electron affinities makes these materials appealing partners in photoinduced electron transfer^{10–12} and also for applications in medicinal chemistry.^{13–16} In this Account, we discuss some of our main achievements in this rapidly developing field and, in particular, the photophysical phenomena associated with the excited state of fullerenes. The photosensitizing features of some relevant classes of functionalized fullerene materials are surveyed, followed by a detailed description of their electron-acceptor features. In addition, after elucidation of the impact of functionalization on fullerene characteristics, the unique optimization in terms of redox potentials, water solubility, and generation of strongly oxidizing species is presented for several novel fullerene-based materials.

Excited States

Pumping of the fullerene ground state (S₀) with UV or visible light leads to the population of the singlet excited state (S₁, Scheme 1).^{8,17}

Scheme 1. Ground and Excited States of Fullerenes



The lifetime of this intermediate state is relatively short (low nanosecond regime), as C₆₀ and most of its derivatives convert rapidly to the much longer-lived triplet excited state (T₁, lifetime = tens to hundreds of microseconds) with nearly unit yield (eq 1).^{8,18} The process is a spin-forbidden intersystem crossing (ISC) with a high rate of $5.0 \times 10^8 \text{ s}^{-1}$ driven by an efficient spin-orbit coupling.

The spectral characteristics of these main excited states



for a model C₆₀ derivative, namely the *N*-methylfulleropyrrolidine, are shown in Figure 1a, where, for comparison, the ground-state absorption is also reported. Both the singlet and triplet excited states give rise to transient absorptions in the near-IR with characteristic maxima around 900 (S₁ → S₂, Scheme 1) and 700 nm (T₁ → T₂, Scheme 1), respectively.^{17,19–21} Perturbation of the fullerene π-system, which stems from removal of a C=C double bond upon functionalization, brings about noticeable blue

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Maurizio Prato obtained his Laurea in Chemistry in Padova (Italy) in 1978. He then joined the Faculty of Science and the Organic Chemistry Department of the University of Padova. In 1992 he moved to the University of Trieste, where he took a position as an Associate Professor of Organic Chemistry. He was promoted to Full Professor in 2000. He spent sabbatical terms at Yale University in 1986–1987 and at the University of California, Santa Barbara, in 1991–1992. He received the Federchimica Prize in 1995. His main research interests focus on synthesis and applications of novel functional materials and use of modified fullerenes in medicinal chemistry.

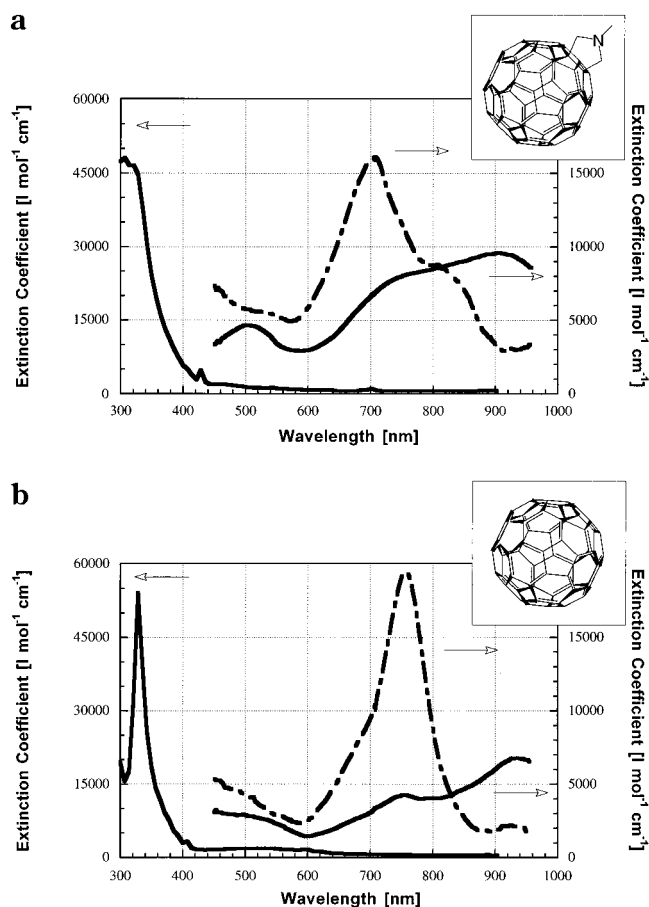


FIGURE 1. (a) Ground-state absorption spectrum (solid line), transient singlet excited-state spectrum (solid line), and transient triplet excited-state spectrum (dashed line) following picosecond flash photolysis (355 nm) of *N*-methylfulleropyrrolidine in oxygen-free toluene solution. (b) Ground-state absorption spectrum (solid line), transient singlet excited-state spectrum (solid line), and transient triplet excited-state spectrum (dashed line) following picosecond flash photolysis (355 nm) of C₆₀ in oxygen-free toluene solution.

shifts of the excited-state absorptions relative to those of C₆₀.^{19,20} The latter exhibits maxima at 920 nm for the singlet excited-state absorption and 750 nm for the triplet (Figure 1b).^{18,22}

The fluorescence spectrum of *N*-methylfulleropyrrolidine is in excellent agreement with the mirror imaged absorption features. This reflects the fact that the force constants of vibrational levels in the first singlet excited state resemble those in the singlet ground state (Figure 2).^{19,23} The good match of the two respective extreme lines (i.e., the longest-wavelength absorption and the shortest-wavelength emission) and the fact that they exhibit the highest oscillator strengths are convincing evidence for an assignment to 0 → 0 transition bands. Most importantly, the *0 → 0 emission (703 nm) and 0 → *0 absorption bands (701 nm) differ only very slightly, which suggests only small Stokes shifts and little, if any, need for the adjustment of the fullerene singlet excited state to the solvent environment.¹⁹ The minor Stokes shift, expressing a Franck–Condon instability energy of ~20 cm⁻¹, is well compatible with the highly symmetric and rigid structure of the fullerenes and their derivatives.

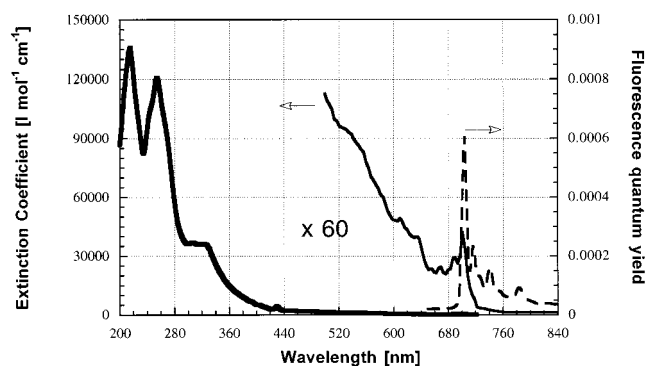


FIGURE 2. Ground-state absorption and fluorescence spectrum of *N*-methylfulleropyrrolidine in oxygen-free toluene solution at room temperature.

While the moderate fluorescence quantum yield (1.0×10^{-4} and $\sim 6.0 \times 10^{-4}$ for pristine C₆₀²⁴ and for mono-functionalized fullerene derivatives,²⁵ respectively) guarantees assignment with relative ease and confidence, the insignificant phosphorescence yields (on the order of 10⁻⁶)²⁶ make their detection a challenging and often impossible task.

Redox Features

C₆₀ is an excellent electron acceptor in the ground state and can accept, reversibly, up to six electrons.²⁷ The first reduction potential, as measured by cyclic voltammetry, is -0.3 to 0.4 eV (vs SCE), with the exact value depending on the solvent polarity, type of supporting electrolyte, and temperature. In particular, a moderate HOMO–LUMO energy gap of about 1.8 eV separates a maximally degenerate and fully occupied HOMO (5-fold) from a degenerate LUMO (3-fold).²⁸

In contrast to reduction, oxidation of C₆₀ is more difficult.²⁷ Oxidation is usually limited to two one-electron steps, yielding the dication as the highest oxidation state.

The singly reduced fullerene, C₆₀^{•-}, has a characteristic near-IR absorption around 1080 nm ($\epsilon_{1080 \text{ nm}} = 15\,000 \text{ M}^{-1} \text{ cm}^{-1}$).²⁹ This experimental value is in excellent agreement with CNDO/S calculations regarding the electronic structure of C₆₀^{•-}.³⁰ In the case of methanofullerenes and fulleropyrrolidines, this maximum is slightly shifted to higher energies with maxima at 1040 ($\epsilon_{1040 \text{ nm}} = 10\,000 \text{ M}^{-1} \text{ cm}^{-1}$) and 1010 nm ($\epsilon_{1010 \text{ nm}} = 8000 \text{ M}^{-1} \text{ cm}^{-1}$), respectively (Figure 3).^{20,31} These fingerprint absorptions allow a clear identification of the one-electron reduced state and, also, an accurate analysis of electron-transfer (ET) dynamics by means of transient absorption spectroscopy (see below).

The redox features of the excited states are of great importance for photoinduced electron- and energy-transfer reactions. Population of the excited states (singlet, ~1.9 eV, or triplet, 1.5 eV) renders the fullerene both a better electron acceptor and an electron donor compared to the ground-state species (Scheme 2).²⁰ Both excited states readily react with many suitable reducing (for example, diazabicyclooctane, DABCO)³² and oxidizing (for example, tetracyanoquinodimethane, TCNQ)^{33,34} quenchers.

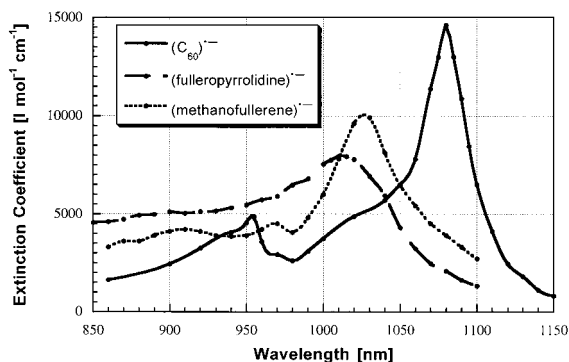


FIGURE 3. Differential absorption spectrum in the near-IR region of the π -radical anion of C_{60} (solid line), *N*-methylfulleropyrrolidine spectrum (dashed line), and methanofullerene spectrum (dotted line) obtained upon radiation-induced reduction in organic solvents (toluene, acetone, and 2-propanol in an 8:1:1 v/v ratio).

In summary, C_{60} displays very promising features as a three-dimensional electron acceptor, which, in principle, could be utilized as an electron accumulator and electron relay.

Reorganization Energy

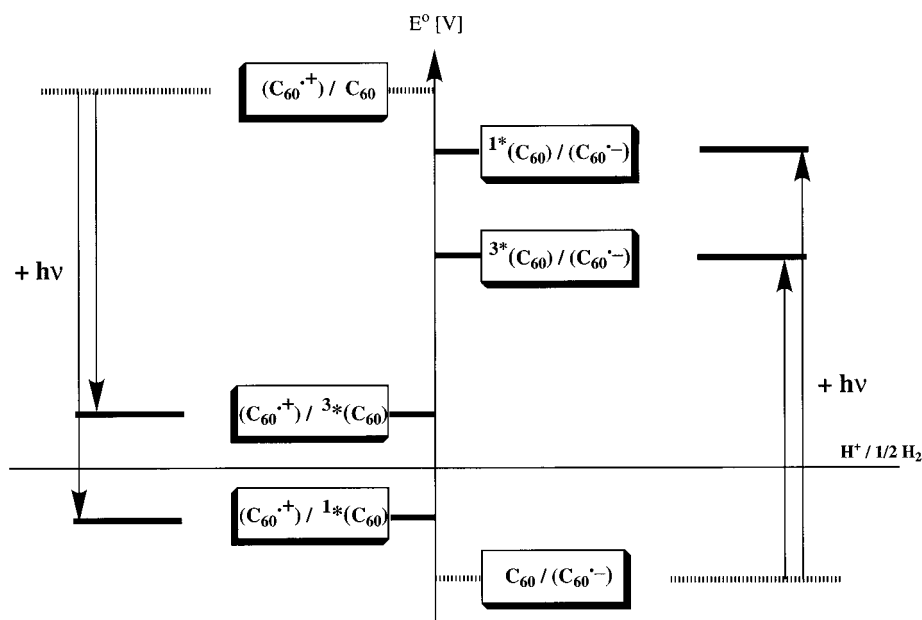
One of the most intriguing aspects of ET theories is the characteristic parabolic dependence of the corresponding rate constants on the free energy changes of the reaction.³⁵ Hereby, the electronic coupling (V) between donor and acceptor states and, foremost, the reorganization energies (λ) of the latter two dominate the absolute rate constant. V is dependent on the separation distance and nature of the intervening spacer, while λ includes components from the vibrations of the molecules (λ_{vib}) and polarization changes in the solvent environment (λ_{sol}). Since these parameters attain different values before and after ET occurs, the energy associated with these rearrangements defines λ , which for fullerenes is very low.^{36,37}

Ideally, the rate constant of an ET first increases with increasing thermodynamic driving force ($-\Delta G^\circ < \lambda$) in the “normal region” of the parabolic relationship. When the driving force becomes of the same magnitude as the reorganization energy ($-\Delta G^\circ \sim \lambda$), the reaction rate is governed mostly by the electronic coupling between the donor and acceptor. Upon passing this thermodynamic maximum, the highly exothermic region ($-\Delta G^\circ > \lambda$) is entered, in which an increase of the free energy results in lowering the rate of the process. The latter range is generally referred to as the Marcus “inverted region”.

Variation of λ and V is the key to modulating the shape and the maximum of the Marcus parabola. Most importantly, it is possible to influence the associated reaction dynamics: In principle, donor–acceptor systems with smaller λ values give faster ET (small $-\Delta G^\circ$) and slower back electron transfer (BET, large $-\Delta G^\circ$) compared to those having larger λ values.

One of the first experimental demonstrations that provided evidence for small λ in a fullerene-based donor–acceptor dyad was given by the photoinduced ET rates in a π -stacked ZnTPP– C_{60} dyad.³⁸ In particular, the π – π stacking between the two redox-active moieties mediates an efficient ET to yield the charge-separated radical pair, namely, $\text{ZnTPP}^{+\bullet} - C_{60}^{\bullet-}$, even in nonpolar toluene. By increasing the solvent polarity to polar benzonitrile, the energy of the charge-separated state could be lowered, while keeping that of the precursor state unaffected. The dependence of the BET rate on the free energy changes revealed stabilizing effects for the charge-separated state at higher $-\Delta G^\circ$ values, especially in solvents of low polarity.³⁸ Slower rate constants at increasing $-\Delta G^\circ$ values resemble the key features for BET in the Marcus “inverted region”. From the best fit of the Marcus parabola, with ET and BET rates being in the “normal region” and

Scheme 2. Schematic Diagram Showing the Difference in the Redox Properties of the Ground-State C_{60} $\{E^\circ[(C_{60})/(C_{60}^{\bullet-})]/E^\circ[(C_{60}^{+\bullet})/(C_{60})]\}$ and the Excited 1^*C_{60} and 3^*C_{60} States



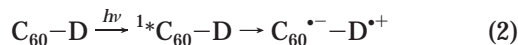
“inverted region”, respectively, we derived a total reorganization energy of 0.86 eV.

This study on intramolecular ET complements our earlier pulse-radiolytic study on ET from C₇₆ and C₇₈ to a series of radiolytically generated arene radical cations with varying oxidation potentials. In particular, it provided a striking example of an “inverted region” in intermolecular ET and gave rise to a total reorganization energy of 0.6 eV in dichloromethane.³⁷

Donor–Acceptor Systems

By far the largest number of C₆₀-based donor–acceptor systems studied to date rely on porphyrins as the donor chromophores to ensure an efficient light harvesting in the visible region of the spectrum. In these cases, the fullerene core operates solely as an electron acceptor and remains in its singlet ground state. This aspect has already been reviewed^{10–12,39} and is, therefore, not further discussed in this Account. In this section, we will consider dyads in which the C₆₀ unit is excited, either exclusively or predominantly, by light irradiation while the donor remains in its ground state: leading examples are ferrocene (Fc)²⁵ or tetrathiafulvalene (TTF).^{40–42}

The relatively high singlet excited-state energy of a variety of fullerene derivatives, such as methanofullerenes (1.796 eV) or fulleropyrrolidines (1.762 eV), makes intramolecular ET from the covalently attached donor to the fullerene moiety very easy. In general, irradiation results in the formation of a charge-separated state (eq 2).

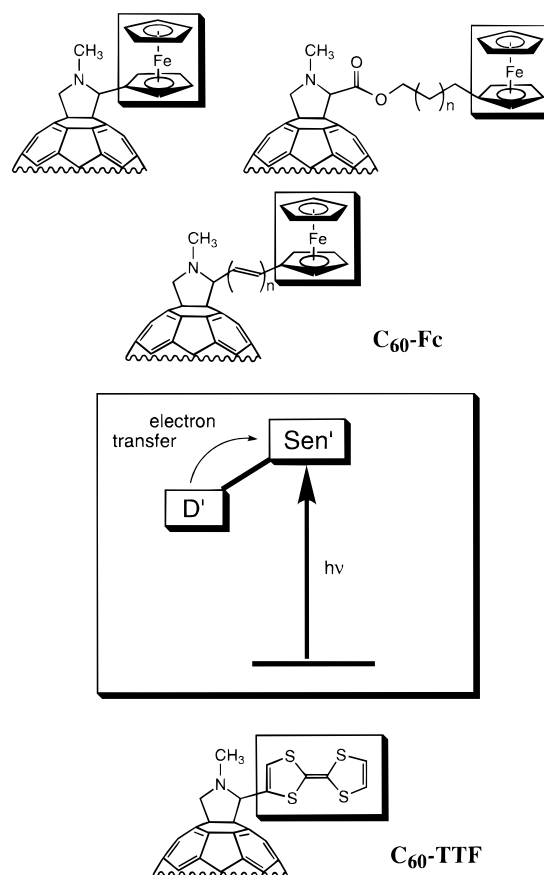


Electron transfer between a donor and an acceptor can occur, in principle, “through-bond” or “through-space” (exciplex route). To answer this fundamental question, we have pursued the strategy of using structurally diverse fullerene–ferrocene dyads.^{25,43} This was made possible by employing different spacer blocks, e.g., rigid vinylene units or flexible alkyl chains of variable length (Scheme 3).

Formation of charge-transfer (CT) complexes or exciplexes between C₆₀ in its ground or excited state, respectively, and adequate electron donors is one of the key steps in determining the rate and efficiency of photoinduced ET reactions.⁴⁴ Rigid donor–acceptor bridges lack the freedom of conformational changes, which are imperative for the formation of an intramolecular CT complex in the ground state or an exciplex upon photoexcitation. Consequently, a through-bond pathway is the only possibility in these donor–acceptor dyads.^{25,43}

The situation is quite different in the case of flexible spacers, whose length (i.e., 10 σ bonds) renders a through-bond mechanism energetically unfavorable. In principle, the flexible nature of the hydrocarbon bridge permits transformation of the presumably linear conformer into a bent conformer. Thus, an excited-state quenching, if it takes place, necessitates a conformational rearrangement to form the ET-mediating intramolecular exciplex. The

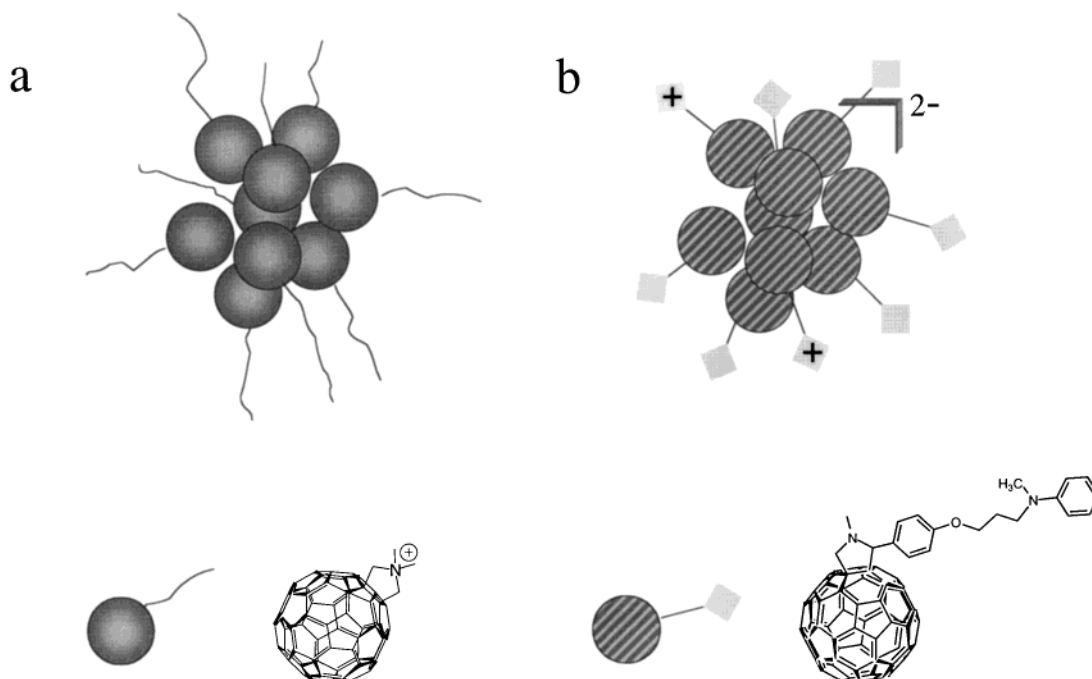
Scheme 3. C₆₀–Donor Dyads, Bearing Ferrocene (Fc) or Tetrathiafulvalene (TTF) as the Electron Donor, in Which Excitation of the Fullerene Moiety (Sen) Is Followed by a Rapid Intramolecular Electron Transfer from the Donor (D)



quenching data, derived from picosecond-resolved transient absorption measurements and steady-state fluorescence, speak for rather high rate constants in all dyads, regardless of the spacer nature. While a through-bond mechanism can be reasonably postulated for the rigid dyads, on the basis of the free energy considerations, the same mechanism can plausibly be ruled out for the flexible dyads. In the latter systems, the rapid deactivation of the fullerene excited state can only be rationalized via the formation of a rate-determining transient intramolecular exciplex.^{25,43}

As a general conclusion, these photophysical studies indicate that, when structurally possible, C₆₀-based dyads adopt conformations in which the fullerene and the donor moieties are in close proximity, thus facilitating through-space interactions. More recently, the observation of a solvent-independent excited-state emission quenching in, for example, C₆₀–[Ru(bpy)₃]²⁺^{45,46} provided further corroboration for the tendency of fullerenes to form complexes with electron donors. The anisotropy of the fullerene surface, as it prevails in the well-ordered but alternating assembly of electron-rich hexagons with electron-deficient pentagons,²⁸ facilitates the electronic interaction.

The concept of coupling an organic donor such as tetrathiafulvalene (TTF) in conjunction with a photoexcitable fullerene acceptor has a fundamental benefit for

Scheme 4. Possible Structures of (a) Fullero-pyrroli-dinium and (b) C₆₀-Aniline Clusters in Aqueous Solutions and Polar Media^a

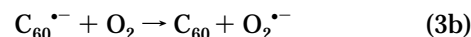
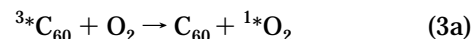
^a In the C₆₀-aniline cluster the charge delocalization is illustrated by placing two positive charges randomly on different aniline moieties, while the two negative charges are delocalized within all the hydrophobic fullerene cores.

the design of donor-acceptor arrays.⁴⁰⁻⁴² Besides its leading role as an efficient π -electron donor with moderate oxidation potentials in the field of organic molecular materials, TTF is not an aromatic substrate in its singlet ground-state configuration. However, once oxidized, TTF converts into the thermodynamically stable six- π -electron heteroaromatic 1,3-dithiolium cation. Not surprisingly, the fullerene singlet excited state in a series of C₆₀-TTF dyads is subject to rapid intramolecular ET. The gain in aromaticity as a result of the formation of the TTF radical cation increases the lifetime of the charge-separated state C₆₀^{•-}-TTF^{•+} by a factor of about 4 relative to comparable systems that do not contain TTF, such as ferrocene, aniline, etc.

Photoexcited States of Water-Soluble Fullerenes

The easy excitation of fullerenes by visible light provides strong promise for the application of these compounds in medicinal chemistry. The affinity of the hydrophobic spheroid for biomembranes might cause photodamage followed by membrane disordering.⁴⁷ In addition, prospective uses of fullerenes in photoinactivation of viruses⁴⁸ or artificial photonucleases⁴⁹ are emerging topics in biology. There are two main ways of producing photoinduced biological activity with fullerenes: (i) energy transfer to molecular oxygen^{2,50} or/and (ii) direct electron transfer to the fullerene and subsequent reaction with oxygen.^{51,52} Both processes, which in principle also pertain to water-soluble derivatives, will lead to the formation of cytotoxic species, namely, singlet oxygen and superoxide radical anions, respectively, which are precursor states to the

physiologically important oxidative damage (eq 3a,b).

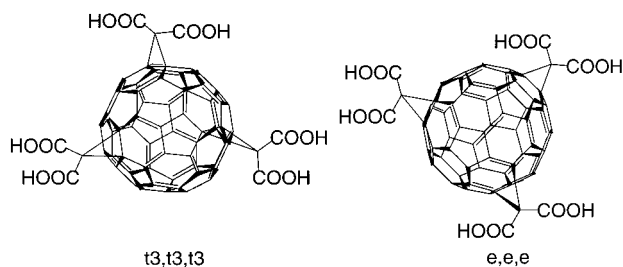


DNA damage has also been observed as one of the consequences and attributed to single electron transfer followed by hydrolytic degradation of the affected guanines.¹⁶

Unmodified fullerenes are practically insoluble in aqueous and most polar media. Functionalization with solubilizing appendages is thus necessary for any studies in these solvents. Although this can be achieved in a relatively easy way, owing to the high degree of sophistication reached in organic synthesis, new problems such as aggregation and clustering may arise upon solubility-enhancing functionalization. In polar solvents, the strong hydrophobicity of the fullerenes causes these spheres to stick together, leaving the hydrophilic headgroups on the outside. The results are clusters of undefined sizes (Scheme 4a).⁵³⁻⁵⁵

Evidence for clustering can be obtained by UV-visible spectrophotometry. The typical fullerene bands at 215, 260, and 330 nm become broader than in organic solvents, and their intensities decrease. In addition, the fine structures are lost due to significant light scattering by the particles formed, which reach sizes as large as hundreds of nanometers in diameter. This crude size estimation was obtained by means of gel-exclusion chromatography and independent measurements with dynamic light scattering.

The degree of aggregation, however, cannot be deduced from a simple absorption spectrum. A better understand-

Scheme 5. Structures of Tris-dicarboxylate Derivatives ($C_{60}[C(COOH)_2]_3$): Isomers *trans-3,trans-3,trans-3* and *e,e,e*

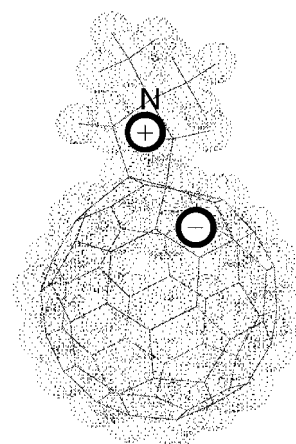
ing of aggregation phenomena can be obtained through the study of the excited fullerenes. The lifetime of the triplet excited state is very sensitive to the environment and in clusters becomes subject to an efficient triplet–triplet annihilation. In a fullerene cluster, triplet lifetimes are typically reduced to $<0.1 \mu\text{s}$. In contrast, the monomeric analogue, either surfactant-capped or dissolved in an organic solvent, gives rise to lifetimes of several tens to a hundred of microseconds.⁵⁶ Needless to say, the reduced triplet lifetimes of the fullerene clusters preclude most biological applications in physiological media.

The controlled formation of fullerene clusters in polar media, however, can be used as a useful approach to improve the performance of fullerene-containing dyads in terms of their charge separation.⁵⁷ In particular, it is assumed that electron delocalization within a fullerene cluster occurs over all the fullerene molecules contained in this aggregate. This, in turn, proved to be beneficial for the stabilization of charge-separated radical pairs. For example, in C_{60} –aniline dyads in an aggregate (Scheme 4b), radical pairs have a lifetime of $60 \mu\text{s}$, while no detectable charge-transfer intermediates were noted for the isolated dyad. A logical further development of these considerations can be envisioned in the synthesis of water-soluble donor–acceptor dyads, including fullerene–porphyrin conjugates.

The solubility of fullerene derivatives can be improved and the formation of clusters can be reduced when using higher adducts of C_{60} . For instance, the tris-dicarboxylate derivatives ($C_{60}[C(COOH)_2]_3$), isomers *e,e,e* and *trans-3,trans-3,trans-3*, are highly soluble in water while not losing their radical scavenger capacity (Scheme 5).⁵⁸ These trisadducts have been shown to possess both neuroprotective and antiapoptotic properties.⁵⁸ It is important to note that these compounds, which have three malonate units regularly spaced on the fullerene surface, do not aggregate at all.²⁴

The electrochemical and photophysical properties of the functionalized fullerenes are strongly affected by the number of addends linked to the fullerene core.^{59,60} In fact, monoadducts are more difficult to reduce than C_{60} itself, and the reduction processes become progressively more difficult as the number of addends increase on the fullerene spheroids.^{59,60} For instance, if we consider the electrochemical behavior of a monoadduct and a bisadduct, as compared to C_{60} , we see that, by and large, the first reduction potential for each species becomes more negative by about 100–150 mV for any saturated double

Scheme 6. Zwitterionic Structure of the One-Electron-Reduced Fulleropyrrolidinium Salt



bond of C_{60} . More precisely, the reduction potentials of the bisadducts depend on the pattern of the bisaddition.⁶¹

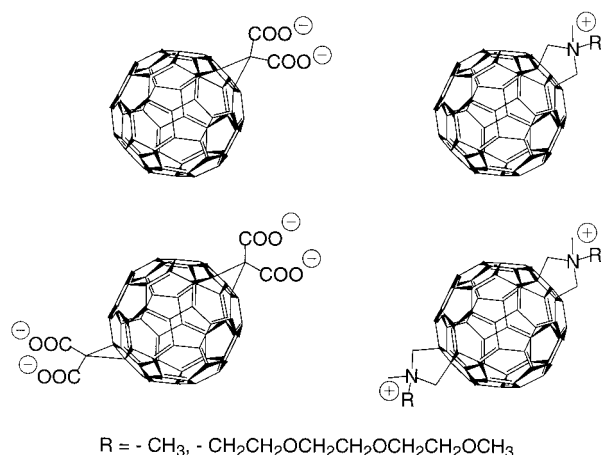
The photophysical properties are also heavily affected by the degree of addition. The blue shift observed for the excited states on going from a monoadduct to various bisadducts is similar to that observed on going from C_{60} to the monoadduct.²⁰ More importantly, the triplet quantum yield in bisadducts drastically decreases and, consequently, the amount of singlet oxygen generated by energy transfer is strongly diminished.⁶²

Fulleropyrrolidinium Ions

In the course of our investigations on the structure-induced modulation of electronic/electrochemical properties of functional fullerenes, we found that a new, general class of derivatives, the pyrrolidinium ions, are slightly easier to reduce than C_{60} and much easier than most monoadducts.^{54,63} Also, the stability of the singly reduced species seems to be greatly enhanced by the presence of an internal counterion (Scheme 6). This property renders these adducts particularly interesting for the elaboration of systems in which photoinduced intramolecular charge transfer is important. The use of these compounds as components in donor–acceptor dyads is, therefore, very appealing.

In addition, these salts are relatively soluble in water due to the presence of the positive charge and hydrophilic appendage (Scheme 7), and hence they are suitable for biological tests. Very interestingly, these compounds were found to be active against some resistant human strains of *Mycobacterium tuberculosis* and, specifically, much more active than neutral analogues.^{64,65} Also, similar cationic derivatives inhibited *Escherichia coli* growth by means of dioxygen consumption, whereas anionic salts (bis-malonate derivatives, Scheme 7) did not interfere.⁶⁶

As expected for monofunctionalized fullerene derivatives, fulleropyrrolidinium ions tend to aggregate in aqueous solutions, while bisadducts, containing two (or more) solubilizing groups, aggregate much less if at all. For example, bis-pyrrolidinium salts (Scheme 7) have triplet lifetimes of about $33 \mu\text{s}$, a value that indicates the presence of truly monomeric species.⁶⁷

Scheme 7. Structures of Mono- and Bisadducts of Dicarboxylate and Pyrrolidinium Derivatives of C₆₀

Independent confirmation for the electron-accepting properties, as measured by cyclic voltammetry in THF,⁶³ stems from a series of pulse radiolytic experiments, probing C₆₀, bis-pyrrolidinium, and bis-dicarboxylate ions with regard to their reactivity with hydrated electrons and (CH₃)₂•COH radicals. While C₆₀ and the bis-pyrrolidinium ions are reduced with nearly identical rate constants, the bis-dicarboxylates react much slower.^{67,68}

A similar trend was also observed in experiments that concentrated on the attack of free radicals on the fullerene core in aqueous media. For example, the addition of •OH radicals to a bis-pyrrolidinium salt of C₆₀ was much faster than the addition to C₆₀(OH)₁₈.⁶⁹ Polyfunctionalization is responsible for reducing the number of reactive sites on the fullerene surface due to increasing sp³ carbon hybridization. This leads eventually to fullerene derivatives that show little resemblance to the original C₆₀. In conclusion, utilization of the bis-pyrrolidinium salts appears to be a

promising compromise, keeping the balance between their solubility in aqueous media and their reactivity.

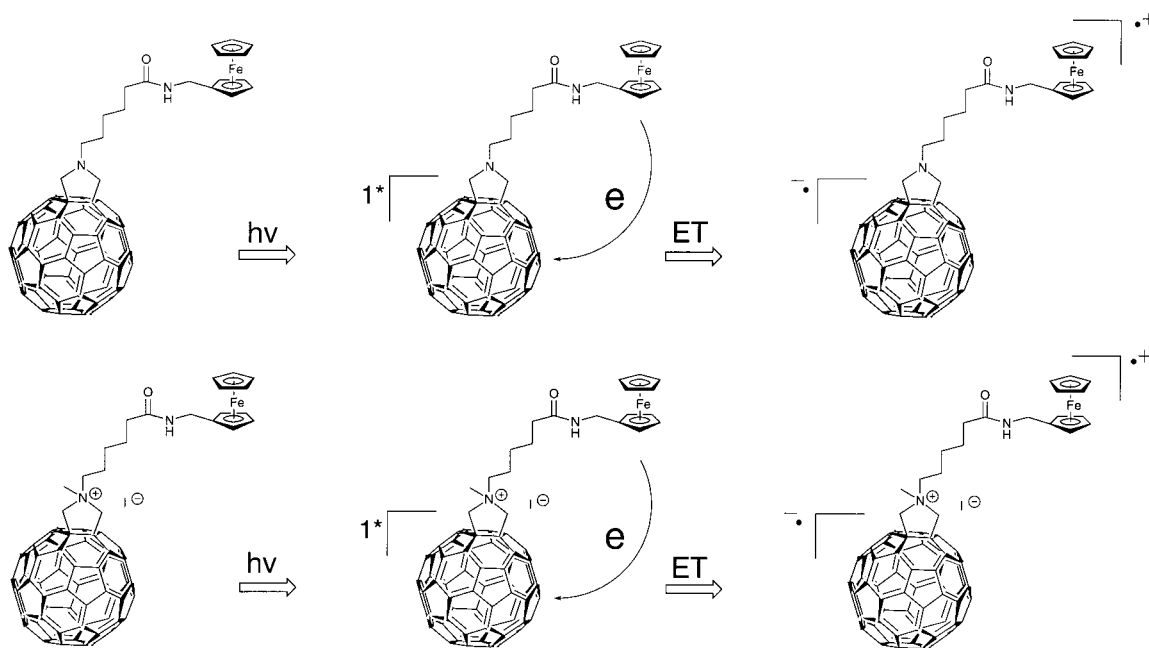
For the development of novel donor–acceptor arrays that display improved performance, the use of a fulleropyrrolidinium acceptor (i.e., a mono- or bis-pyrrolidinium salt) clearly has a distinct advantage over fulleropyrrolidine. For example, Scheme 8 compares the possible electron-transfer pathways induced by the singlet excited state in a fulleropyrrolidine–ferrocene and fulleropyrrolidinium–ferrocene dyad. Interestingly, the fulleropyrrolidinium-based dyads reveal faster charge separation dynamics, relative to the fulleropyrrolidine analogues, a trend that parallels their better acceptor properties. Regarding charge recombination, formation of the zwitterionic fullerene π-radical anion appears to be a key factor for stabilizing the charge-separated state, C₆₀^{•−}–Fc^{•+}.⁷⁰

Conclusions and Outlook

Excited states of fullerenes and fullerene derivatives are easily generated from their ground states, due to their wide absorption window ranging from the UV to the near-IR. These transient species play several key roles in diverse processes and applications. Importantly, the excited-state lifetimes are sensitive probes for environmental changes. The selected examples described in this Account illustrate that this parameter (lifetimes) can be used as a diagnostic tool to detect aggregation phenomena. This is a particularly relevant issue in the growing field of biological applications of fullerenes.

Fullerenes engage successfully not only as electron acceptors but also as competing energy acceptors, which constitutes another equally important and exciting feature. The outcome of this competition depends largely on the experimental conditions.

Scheme 8. Photoinduced Electron Transfer in a Fulleropyrrolidine–Ferrocene Dyad (Upper Part) and Fulleropyrrolidinium–Ferrocene Analogue (Lower Part)



Several groups reported, for example, on very fast photoinduced electron-transfer processes between π -conjugated polymers and C₆₀ in mixed composite films.⁷¹ This renders them promising materials for solar energy conversion, batteries and photovoltaics and rationalizes the continuing interest and potential of fullerenes as multi-functional electron storage moieties in well-ordered composites.

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