

Fullerenes: three dimensional electron acceptor materials

Dirk M. Guldi

University of Notre Dame, Radiation Laboratory, Notre Dame, IN 46556, USA. E-mail: guldi.1@nd.edu

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This feature article highlights the advantages of employing [60]fullerene as a viable electron accepting building block in novel donor acceptor systems. Different strategies that aim towards improving charge separation in fullerene containing systems are presented. This is accomplished, for example, *via* utilisation of additional stabilisation forces of the radical pair or, alternatively, diffusional splitting of the last mentioned. Fine-tuning the topology of the electron donor moiety has been shown to be a powerful means of influencing the relative energies of the two states involved (*e.g.* the charge-separated state *vs.* the singlet ground state). Remarkable effects concerning the lifetime of the charge-separated radical pair were observed, in particular, in systems that upon charge separation led to a gain of aromaticity and planarity of the oxidised fragment.

Introduction

In the photosynthetic reaction centre (PRC), a variety of short-range electron transfer (ET) and energy transfer (ENT) events occur between well-arranged organic pigments and other cofactors. Thereby, charges are separated with remarkable efficiency to yield a spatially and electronically well-isolated radical pair and thus eliminate the energy-wasting back electron transfer (BET). The arrangement of the donor–acceptor couples in the PRC is accomplished *via* non-covalent incorporation into a well-defined protein matrix.¹

Owing to the importance and complexity of natural photosynthesis, the study thereof necessitates suitable simpler models. The ultimate goal is to design and assemble synthetic systems which can efficiently convert solar energy into useful chemical energy. An important approach to PRC modelling has

been the covalent linking of a photoexcitable chromophore with an electron acceptor or an electron donor. It is important to note that in these artificial systems the organising property is the covalent linkage between the redox active moieties.²

A number of factors have been systematically altered over the past decades to overcome the difficulties encountered in the early artificial, covalently linked donor-acceptor dyads:² the energies of the donor and acceptor molecules have been adjusted to increase the rates of the forward ET and to slow down the BET. Also, the electronic coupling between donor and acceptor moieties has been tuned to alter ET rate constants in favourable directions. The most important strategy, however, focuses on the incorporation of secondary electron donor or acceptor moieties into multicomponent arrays (triads, tetrads, pentads *etc.*).

In the following contribution some noteworthy features are summarised concerning [60]fullerene as a new, three-dimensional electron acceptor unit in artificial reaction centres. Additionally, different strategies are presented which aim towards improving charge separation in fullerene containing supermolecular (*e.g.* covalently linked) and supramolecular (*e.g.* non-covalently linked) systems. It should be pointed out that the highlighted systems are restricted to composites that bear a single electron acceptor and a single electron donor block. The key feature in these dyads relies on additional stabilisation of the radical pair such as (i) a gain in aromaticity and planarity of the electron donor, or (ii) a dissociation of the charge-separated state. These effects are expected to result in diminishing of the BET.

Small reorganisation energies of fullerenes

One of the most fascinating phenomena in the field of fullerene chemistry is the small reorganisation energy associated with almost all their reactions, especially in photoinduced electron transfer (PET).³ This is an important requisite for the directional control and also the efficiency of ET reactions, as illustrated by the well-organised special pair (*e.g.* bacterial chlorophyll and ubiquinone) in the photosynthetic reaction centre. The total reorganisation energy (λ) is the sum of a solvent-independent term λ_i and the solvent reorganisation energy λ_s .⁴ The λ_i contribution stems from the nuclear configurations, associated with the transformation of the molecule, for instance, in a photochemical reaction from an initial to a final state. It is notable that the rigid structure of the fullerene core leads to small Raman shifts under reductive conditions, and small Stokes shifts in excitation experiments.⁵ A reasonable interpretation for these observations is the structural similarity between [60]fullerene in the ground, reduced and also excited states. It is also believed that the solvent-dependent term (λ_s) is small, thus requiring little energy for the adjustment of a generated state (*e.g.* excited or reduced states) to the new solvent environment.

These effects have fundamental consequences upon the classical Marcus treatment of ET theory.⁴ The latter predicts an increase in rate with increasing thermodynamic driving force in

Dirk M. Guldi graduated from the University of Cologne (Germany) in 1988, from where he received his PhD in 1990 (under the supervision of Professor Fritz Wasgestian). In 1992, after a postdoctoral appointment at the National Institute of Standards and Technology (with Dr Pedatsur Neta), he took a research position at the Hahn-Meitner-Institute Berlin in the group of Professor Klaus-Dieter Asmus. After a brief stay as a Feodor-Lynen Stipend at Syracuse University (within the framework of the Alexander von Humboldt Foundation) he joined in 1995 the faculty of the Notre Dame Radiation Laboratory where he was promoted to Associate Scientist in 1996. In 1999 he completed his Habilitation at the University of Leipzig (Germany). His primary research interests are in the areas of charge separation in super- and supramolecular systems with three-dimensional electron acceptors and mechanistic aspects of radiation and photosensitization. He is particularly interested in molecular recognition as a means to control the dynamics in intra- and intermolecular electron transfer events and the efficiency of charge separation in donor–acceptor assemblies.

the 'normal' region up to a maximum value, where $-\Delta G^\circ$ equals the reorganisation energy λ . As the standard free energy becomes more negative ($-\Delta G^\circ > \lambda$) the ET rate decreases in the 'inverted' region. Based on the small λ value for fullerenes, the maximum of the Marcus curve should be reached at smaller $-\Delta G^\circ$, relative to two-dimensional electron acceptors, which in general have less rigid structures and higher reorganisation energies than three-dimensional fullerenes. This shifts the more exothermic BET clearly into the Marcus 'inverted' region, far from the thermodynamic maximum ($-\Delta G^\circ = \lambda$) and inhibits the undesired BET event. At the same time, the 'normal' region is steeper, which leads to a notable acceleration of ET.

In conclusion, the ability of these three-dimensional carbon allotropes to inhibit BET and still combine it with a fast forward ET renders them as unique probes for *inter*- and *intramolecular* ET studies. In addition, the low reduction potential of [60]fullerene ($E_{1/2} = -0.44$ V vs. SCE) appears profitable for their utilisation as novel electron acceptors or relays in multicomponent donor acceptor systems.⁶

To illustrate the benefits of incorporating a fullerene rather than a quinone acceptor, which has a similar reduction potential but higher reorganisation energy, a fullerene-based porphyrin dyad with a rigid spacer guaranteeing a fixed separation between the two redoxactive moieties was compared with a quinone-based porphyrin dyad. Remarkably, the fullerene-based dyad gives rise to an accelerated ET (~ 6 times) and decelerated BET process (~ 25 times) relative to the kinetics of the corresponding quinone dyad.^{3a}

Fullerene containing donor–bridge–acceptor dyads

The covalent linkage of fullerenes to a number of interesting electro- or photoactive species offers new opportunities in the preparation of materials that may produce long-lived charge-separated states in high quantum yields. Most importantly, the covalent linkage eliminates diffusion as the rate determining ET step and helps to enhance the transfer dynamics in donor acceptor dyads. Consequently, the PET event is converted to a truly *intramolecular* reaction controlled only by the activation energy of the reaction. A fixed and short distance between the two electroactive components prevents the undesired loss of excitation energy *via* alternative radiation and radiationless decay channels.

In this context various fullerene-based donor acceptor dyads, encompassing the linkage of the fullerene core to different donor moieties, ranging from ferrocene and aniline derivatives to phenothiazine, have been reported in recent years.⁷ In these systems the fullerene moiety operates as the photosensitizer, absorbing the visible light to generate an excited species. The electron donor is not initially affected and remains in its singlet ground state (see Fig. 1). In a follow-up step the sacrificial electron donor is oxidised *via* quenching of the photoexcited sensitizer.

The singlet excited state energies of monofunctionalized fullerene building blocks, such as methanofullerenes^{8a} (1.796 eV) or pyrrolidinofullerenes^{8b} (1.762 eV) are sufficiently high to activate an *intramolecular* ET from the appended donor moiety.^{5b} This principally yields the $C_{60}^{\bullet-}-D^{\bullet+}$ charge-separated state, in which $D^{\bullet+}$ denotes the oxidised donor moiety. A diagnostic probe for the identification of the π -radical anion of the fullerene moiety (*e.g.* $C_{60}^{\bullet-}$) is the sharp band in the NIR around 1000 nm.⁹ The spectral signature allows a precise analysis of *inter*- and *intramolecular* ET and BET dynamics in [60]fullerene containing donor acceptor systems.

The Coulombic term, which results from the destabilisation when charges are separated, governs the fate of the $C_{60}^{\bullet-}-D^{\bullet+}$ pair. Accordingly, BET is, in general, very fast and produces the singlet ground state. Increasing the distance between the donor and acceptor, by means of increasing the size of the spacer units,

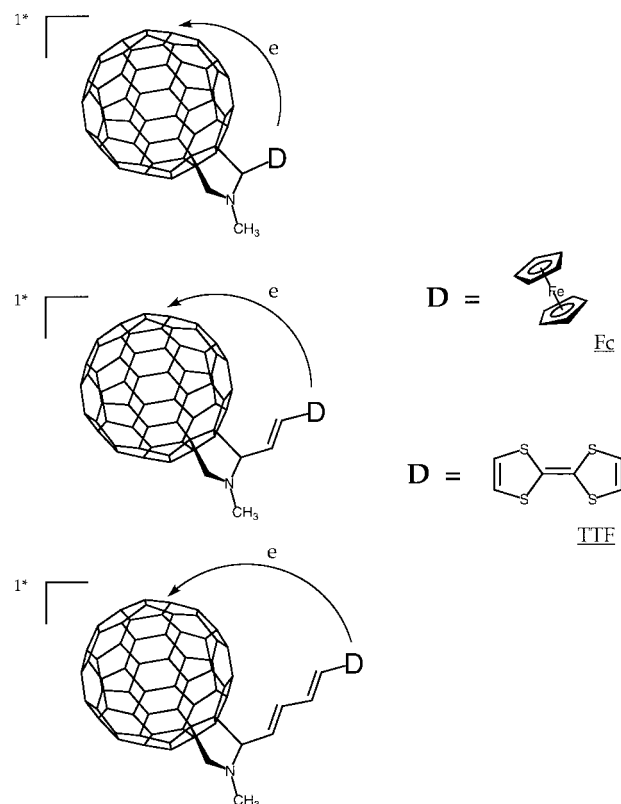


Fig. 1 Schematic illustration of photoinduced electron transfer processes from an electron donor [A = ferrocene (Fc) and tetrathiofulvalene (TTF)] to the singlet excited state of a fullerene moiety.

is one approach to reduce the Coulombic term and to slow down the BET kinetics. For example, substitution of a simple C–C linkage of the donor and acceptor moieties by various vinyl units or a norbornylogous bridge led to enhanced lifetimes of the charge-separated state.¹⁰ At the same time, the spatial separation impacts the thermodynamic driving force ($-\Delta G^\circ$) for an *intramolecular* ET event. Specifically, increasing the donor–acceptor separation lowers the free energy change. Thus, an ET that is exothermic in a closely spaced dyad may become endothermic or only weakly exothermic in a widely spaced dyad, and therefore cannot compete with other deactivation processes (*e.g.* radiation and radiationless decay channels).

One possible way to alter the free energy gap is to increase the chemical potential of the donor and/or acceptor moiety.^{2,10} Alternatively, solvents with high relative permittivities may be used. Polar solvents impose two major effects on the ET dynamics: first, it assists in reactivating the ET even in widely separated dyads, and secondly, it helps stabilise the charge-separated radical pair by lowering the Coulombic term.

Employing the dielectric continuum model these terms and separation effects can be quantified. This model handles the charge-separated radical pair as two spherical ions separated by a distance (R), submerged into a solvent of a static relative permittivity (ϵ).¹¹

Gain of aromaticity

In addition to the Coulombic term, energetic considerations associated with the topology of the donor molecule also control the energies of the ground and oxidised states. Donor moieties, such as aniline and ferrocene, reveal aromatic structures in their ground states.^{10,12} The delocalization that the aromatic core helps to stabilise the generated radical cation. For molecules whose ground state is aromatic, one-electron oxidation will result, however, in a partial loss of their aromatic resonance stabilisation (see case I in Fig. 2). This loss of aromaticity, consequently, yields a state of higher energy.

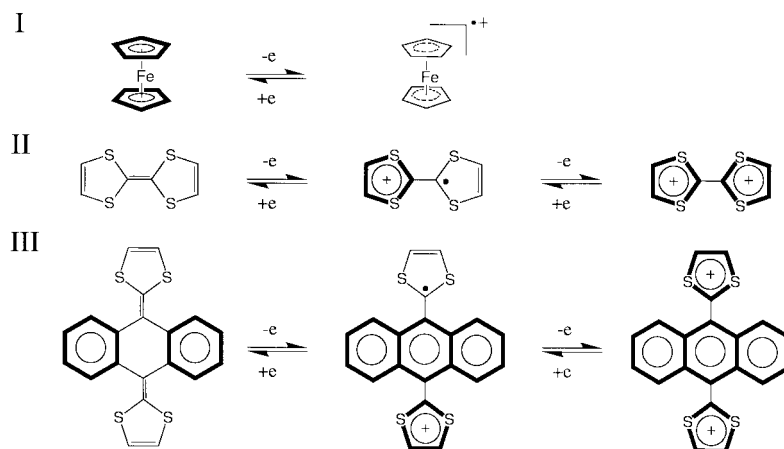


Fig. 2 Concept of gain of aromaticity and planarity. (I) Loss of aromaticity in one-electron oxidised ferrocene. (II) Gain of aromaticity in one- and two-electron oxidised TTF. (III) Gain of aromaticity and planarity in one- and two-electron oxidised (extended)TTF.

The gain in aromaticity associated with the reverse reaction (*e.g.* the BET reaction), on the other hand, provides a driving force for destabilisation of the oxidised species and acceleration of the BET in $C_{60}^{\bullet+}$ - D^{+} pairs. To circumvent this problem a strategy has been proposed for special donor-acceptor composites in which a series of novel organic donors were linked to the fullerene core that gain rather than lose aromaticity on charge separation (CS). This is an important difference to alternative approaches that imply stabilisation of the charge-separated state energy at the expense of subsequent, irreversible chemistry or decomposition of the oxidised donor. It is expected that the gain of aromaticity leads to noticeable effects by enhancing the lifetime of the charge-separated radical pair. This strategy was pursued using molecules, such as tetrathiafulvalenes (TTF), which contain donors whose electronic structure dictates that aromaticity is gained on CS. TTF molecules fulfil this important requisite by means of forming the 1,3-dithiolium cation, which, in contrast to the ground state, displays an aromatic character (see case II in Fig. 2).¹³

Steady-state and time-resolved photolysis studies reveal that the fullerene singlet excited states in C_{60} -TTF dyads¹⁴ undergo rapid *intramolecular* ET events, yielding a charge-separated radical pair, namely, $(C_{60}^{\bullet-})(TTF^{\bullet+})$. *Intramolecular* ET rate constants range between $1.2 \times 10^{10} \text{ s}^{-1}$ for closely spaced dyads (donor-acceptor separation of 4.8 Å) in benzonitrile and $1.5 \times 10^9 \text{ s}^{-1}$ for widely spaced analogues (donor-acceptor separation of 10.5 Å) in toluene. The ET rate constants of these processes increase with increasing solvent polarity (*i.e.* larger $-\Delta G^\circ$), which is consistent with the processes occurring in the 'normal' Marcus region. A radical pair lifetime of *ca.* 2 ns was observed for the closely spaced C_{60} -TTF dyads.¹⁵ In comparison, lifetimes of 0.526, 0.05 and 0.294 ns are reported for similarly spaced carotene- C_{60} , ZnTPP- C_{60} and H_2 TPP- C_{60} dyads, respectively.¹⁶ This improvement is clearly an experimental demonstration of the 'gain of aromaticity' concept.

Gain of aromaticity and planarity

A further development with respect to increasing the degree of stabilisation is to add heteroaromatic rings to the aromatic arenes that possess larger aromatic stabilisation energies. This approach was successfully carried out by using conjugated TTF analogues with a *p*-quinodimethane structure (see case III in Fig. 2).¹⁷ In addition to the aromatic 1,3-dithiolium cations, the π -conjugation in the oxidised form of the two isolated benzene rings is extended to the entire anthracene backbone. As a net result, the dicationic species is fully aromatic.

The geometrical features of *p*-quinodimethane analogues of tetrathiafulvalene further widens the scope of the stabilisation concept, from simply a gain of aromaticity to both a gain of aromaticity and of planarity.¹⁸ In particular, the molecular

geometries in π -extended tetrathiafulvalene derivatives with *p*-quinonoid structures reveal highly distorted orientations. They adopt a butterfly-shaped structure in the ground state to avoid the short contacts between the sulfur atoms and the hydrogen atoms. In contrast, optimisation of the two-electron oxidised state, *i.e.* the dication, with the aromatic anthracene as a basic constituent reveals a planar structure. The two aromatic 1,3-dithiolium cations align orthogonally with respect to the anthracene plane. It should be added that the oxidation process is fully reversible but necessitates, due to the loss of planarity and aromaticity, higher activation energies for the return process to occur.¹⁸

Pico- and nanosecond time-resolved transient absorption measurements with C_{60} -(extended)TTF dyads reveal that the initially formed singlet excited fullerene states transform rapidly into the charge-separated radical pairs. Generally, the *intramolecular* ET rates depend on (i) the spatial separation, (ii) the oxidation potential of the π -extended tetrathiafulvalene derivative, (iii) the reduction potential of the fullerene derivative, and (iv) the solvent polarity. They vary between $1.9 \times 10^{10} \text{ s}^{-1}$ (donor-acceptor separation of 4.4 Å) in benzonitrile and $1.3 \times 10^9 \text{ s}^{-1}$ (donor-acceptor separation of 10.35 Å) in toluene. In all cases, the lifetimes of the charge-separated radical pair (*ca.* 100 ns) are promisingly increased relative to donor molecules which lack the gain in planarity or aromaticity upon oxidation (far less than 1 ns, see above).¹⁹

The above-summarised observations illustrate the key to controlling the structure *via* a combination of donor-acceptor potential and topology to fine-tune the relative energies of the two forms, namely, the singlet ground state and the charge-separated state.

Donor-acceptor complex association and dissociation

A major drawback, associated with *intramolecular* ET events, concerns the rapid BET, driven by the covalent linkage of the donor and acceptor moieties. The rate of BET determines the efficiency of a multicomponent system for practical applications.

In the following a supramolecular approach is summarised, which aims to retard the fast BET, commonly observed in supermolecular systems.²⁰ It entails the biomimetic assembly of two or more individual molecules, linked by weak *intermolecular* interactions such as van der Waals' forces, hydrogen bonding, salt bridges or ligand complexation. The reversible coordination of the acceptor moiety (ligand or substrate) to the donor (coordination centre or receptor) rather than their covalent linkage enables the diffusional splitting of the charge-separated radical pair after the initial ET takes place. Thus, complexation of the donor-acceptor couple appears a viable

alternative to supermolecular polyads (*e.g.* triads, tetrads, *etc.*) involving covalent links between the components. In the latter, a multistep electron relay along a vectorial redox gradient governs the lifetime of the radical pair: as the number of sequential steps involved in the electron relay increases, the lifetime lengthens. However, with each step the overall efficiency for transport of the charge from one end to the other decreases.

Ideally, light-induced intramolecular ET from the porphyrin chromophore to C_{60} proceeds very fast. Then, in a weakly coordinating solvent, complex dissociation should follow the ET event, which leads to diffusional separation of the charge-separated radical pair. As a consequence the BET is limited to a simple *intermolecular* process. In the case of the depicted fullerene complexes BET within the associated complex will compete with complex dissociation and, therefore, govern the quantum efficiencies of CS. Since the rate of complex dissociation depends on the strength of the coordination bond, optimisation of the CS is possible by using different coordination metals. For example, the strong π -back bonding in CO–RuTPP complexes *vs.* the weaker σ -bonding in ZnTPP composites leads to drastically different complexation strengths (see Fig. 3) with, for example, pyridine.²¹ While the former complex is quite stable in solution, the latter exhibits a complexation equilibrium constant (*K*) of nearly $5900 \text{ dm}^3 \text{ mol}^{-1}$ (in toluene) and thus is only shifted towards the complexed form.

The assembly of a rigid but non-covalently connected dyad was obtained by coordinating a fullerene ligand to a zinc tetraphenylporphyrin (ZnTPP) *via* axial pyridine coordination to the metal. This ensemble gives rise to an edge-to-edge distance of 4.5 \AA between the entities or a centre-to-centre distance of 9.5 \AA . The complex association is conveniently followed by absorption spectroscopy (*e.g.* shift of the Q-band transitions) and also by steady state emission spectroscopy (*e.g.*

fluorescence quenching). In particular, a concentration-dependent fluorescence quenching of the $(^1\pi\text{-}\pi)\text{ZnTPP}$ correlates with a very efficient CS upon irradiation.

It is pertinent to note that two different pathways for the ET processes exist (see Fig. 4). A fast *intramolecular* ET inside the associated fullerene-porphyrin complex follows the excitation of the porphyrin chromophore. Alternatively, the free porphyrin is excited and undergoes *intermolecular* ET as soon as the acceptor molecules approach closely enough during molecular diffusion. The former process, which occurs in all solvents, involves $(^1\pi\text{-}\pi)\text{ZnTPP}$, while the *intermolecular* process is likely to dominate the quenching of the energetically lower lying $(^3\pi\text{-}\pi)\text{ZnTPP}$. Complications arise from the fact that polar solvents, such as benzonitrile, interfere with the coordination of the zinc centre. It was shown that in coordinating media, the solvent displaces the fullerene ligand from the zinc, making the *intermolecular* route more effective.

Kinetic analysis of the fullerene π -radical anion transient absorption evolving from irradiation of the ZnTPP– C_{60} composite yields a remarkable lifetime of several hundred microseconds for the separated radical pair in deoxygenated benzonitrile. The quantum yield (Φ) for the truly separated radical pair, $C_{60}^{\bullet-}$ and $\text{ZnTPP}^{\bullet+}$ in deoxygenated dichloromethane is *ca.* 0.14.

The given example demonstrates the potential usefulness of these non-covalently linked systems in photovoltaic devices. But they also point to the fundamental challenge employment of a more polar environment, such as aqueous solutions, faces with respect to avoiding complexation of the zinc centre, while promoting the stabilisation of the radical pair. Future work will concentrate on water-soluble systems using additionally charged porphyrin macrocyclic ligands to slow down the BET step.

The coordination concept, namely, complexation of a fullerene-pyridine ligand by a macrocyclic π -system that bears

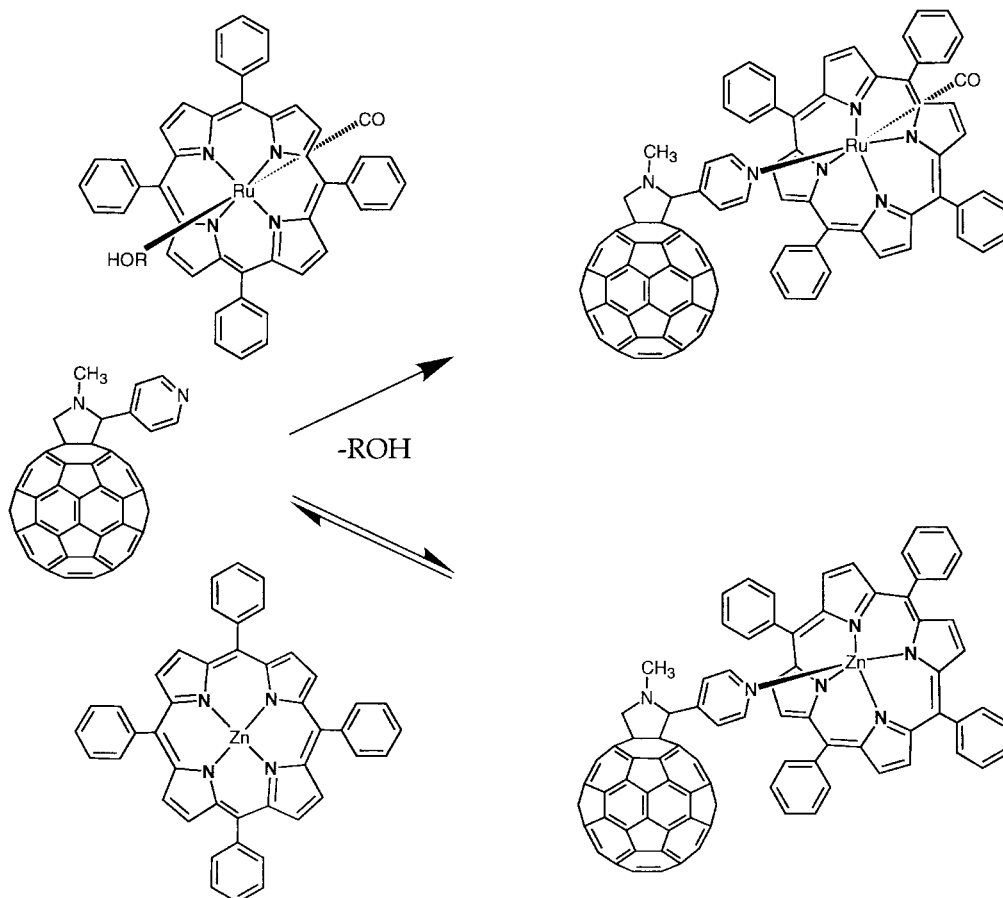


Fig. 3 Irreversible (upper case) and reversible complexation (lower case) of an electron acceptor (*e.g.* fullerene-pyridine derivative) to transition metal complexes (*e.g.* Zn^{II} and Ru^{II}) of tetraphenyl porphyrins.

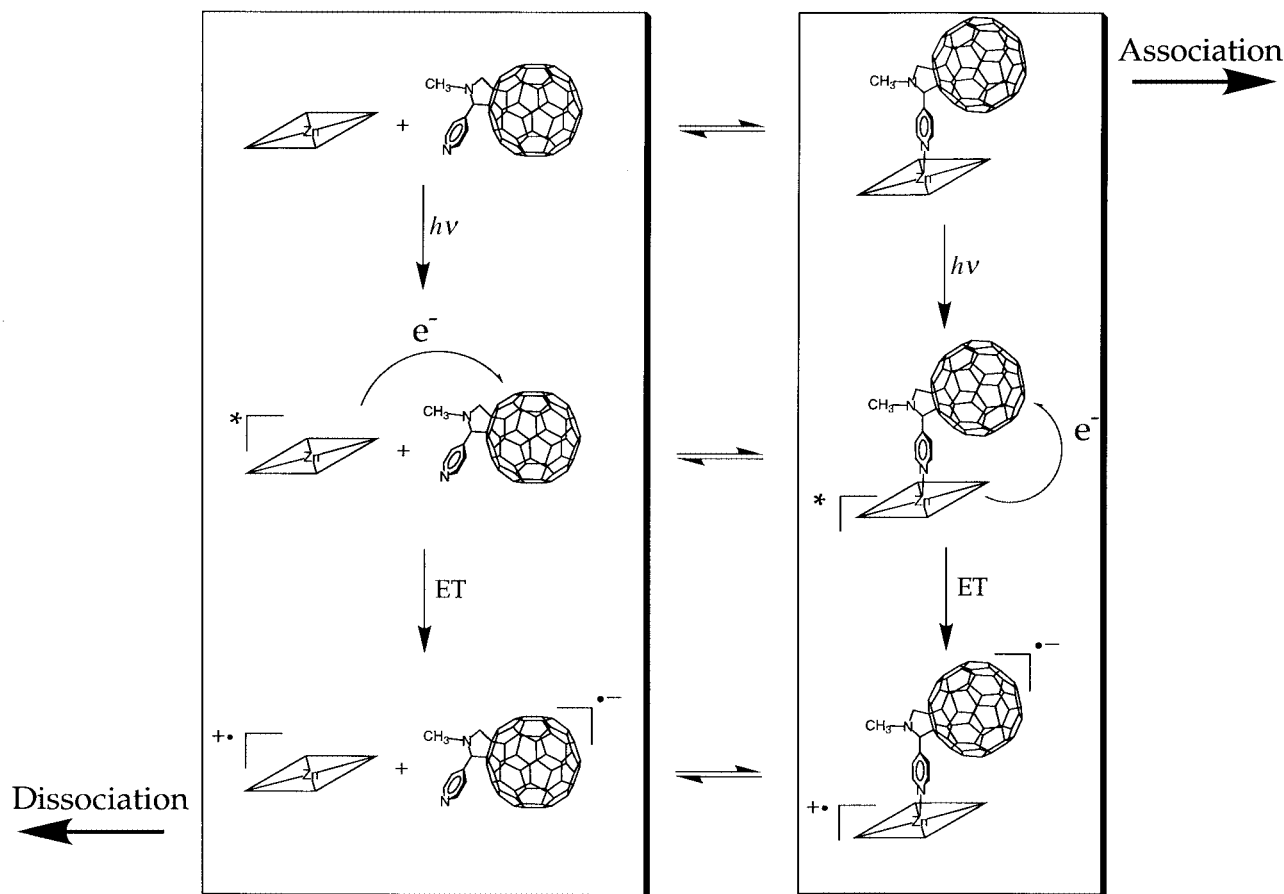


Fig. 4 Inter- and intramolecular electron transfer routes in an associated fullerene–porphyrin complex (right hand side) and in a free porphyrin fullerene mixture (left hand side), respectively.

a potential utilisation as a chromophore system, is very general and can be employed successfully for metallophthalocyanines and structural porphyrin isomers.²²

Peptides as molecular rulers

Molecular systems that respond precisely to environmental changes occurring at a microscopic level and signal the response at a macroscopic level are of great interest in the field of chemical sensing and molecular electronics. Peptide-based interchromophore bridges are attractive probes since cooperative transitions between the secondary structure, *e.g.* between ordered and disordered states, can be conveniently monitored.²³ Hydrogen bonding is one means that was expected to influence donor–acceptor interactions in a peptide based donor–acceptor dyad. Also, the key role of hydrogen bonding should be noted, especially with respect to mediating ET processes in biological and artificial systems.²⁴

Aib (α -aminoisobutyric acid) is a C $^{\alpha}$ -tetrasubstituted α -amino acid that strongly favours 3_{10} -helical structures more than any of the regular protein amino acids.²⁴ Tight helix–helix packing is a key feature of the α -helical bundle tertiary structures commonly found in biological proteins in which the photosynthetic reaction centre is embedded. In this context a hexapeptide (see Fig. 5) has been employed as a large molecular ruler to separate a pyrrolidinofullerene acceptor unit from a ruthenium(II) trisbipyridine (chromophore molecule) complex ([Ru(bpy)₃]²⁺).²⁵

The peptide-spaced ensemble, containing structurally constrained Aib, can be interrelated to rigid androstane- and flexible ethyleneglycol-spaced C₆₀–[Ru(bpy)₃]²⁺ assemblies previously reported (see Fig. 5).²⁶ The role played by the spacer is not just structural since its chemical nature governs the electronic communication between the terminal units (*e.g.*

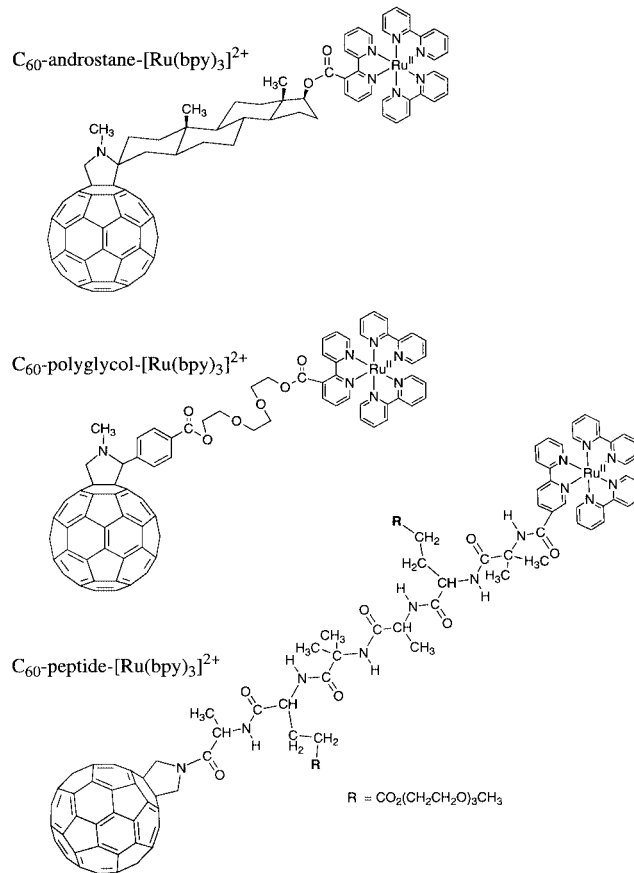


Fig. 5 Structures of C₆₀-androstane-[Ru(bpy)₃]²⁺, C₆₀-polyglycol-[Ru(bpy)₃]²⁺ and C₆₀-peptide-[Ru(bpy)₃]²⁺ donor–bridge–acceptor dyads.

fullerene and $[\text{Ru}(\text{bpy})_3]^{2+}$). Another important feature of the spacer is its modular composition, which allows alteration of the separation without affecting the electronic nature of the connection.

It may be pointed out that the geometry of the flexibly linked [*i.e.* $-(\text{CH}_2\text{CH}_2\text{O})_n-$ chain] system is not well-defined, and the rapid deactivation of the $^3\text{*(MLCT)}$ $[\text{Ru}(\text{bpy})_3]^{2+}$ state is ascribed to an 'intramolecular exciplex' mechanism (case II in Fig. 6). Owing to the rigid structure of steroids, such as

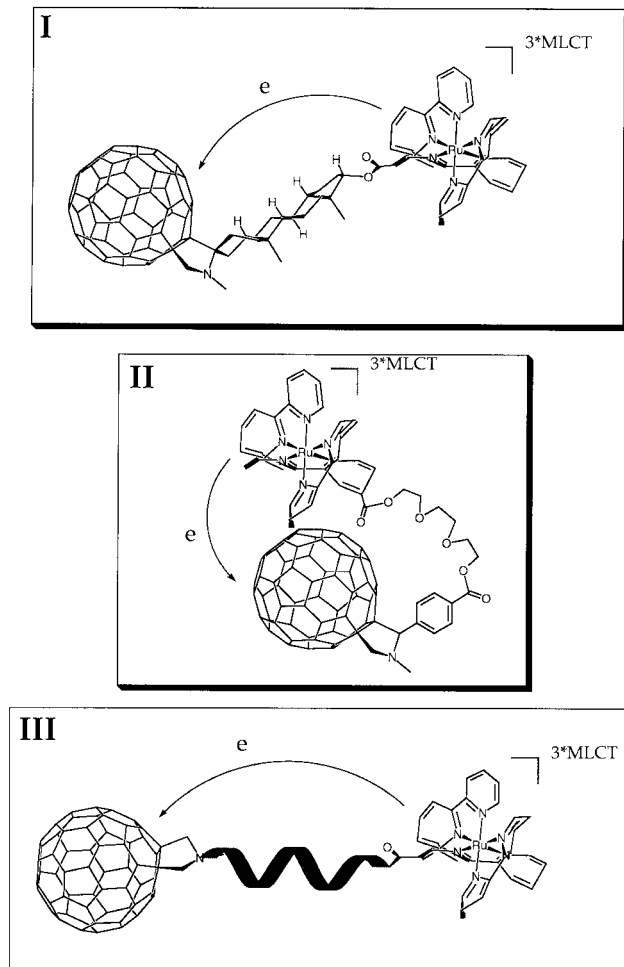


Fig. 6 Schematic illustration of photoinduced electron transfer processes from a $^3\text{*(MLCT)}$ state of a $[\text{Ru}(\text{bpy})_3]^{2+}$ complex to an electron accepting fullerene moiety in (I) C_{60} -androstane- $[\text{Ru}(\text{bpy})_3]^{2+}$, (II) C_{60} -polyglycol- $[\text{Ru}(\text{bpy})_3]^{2+}$ and (III) C_{60} -peptide- $[\text{Ru}(\text{bpy})_3]^{2+}$ dyads. Please note that the C_{60} -androstane- $[\text{Ru}(\text{bpy})_3]^{2+}$ dyad is represented by one of the two possible diastereoisomers.

androstane, a 'through-bond' mediated ET (case I in Fig. 6) prevails in the C_{60} -androstane- $[\text{Ru}(\text{bpy})_3]^{2+}$ dyad. The steroid acts as a wire allowing the electron to be passed from the donor to the acceptor through the intervening σ -bond framework. In both dyads (*e.g.* C_{60} -androstane- $[\text{Ru}(\text{bpy})_3]^{2+}$ and C_{60} -polyglycol- $[\text{Ru}(\text{bpy})_3]^{2+}$), quenching of the $^3\text{*(MLCT)}$ state of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex by ET to the fullerene generates the $\text{C}_{60}^{\bullet-}-[\text{Ru}(\text{bpy})_3]^{3+}$ radical pair. The different intramolecular ET mechanism in these dyads, leads, however, to quite different lifetimes for $\text{C}_{60}^{\bullet-}-[\text{Ru}(\text{bpy})_3]^{3+}$. For example, in dichloromethane solutions the rigidly spaced C_{60} -androstane- $[\text{Ru}(\text{bpy})_3]^{2+}$ dyad yields a lifetime of 304 ns, while no appreciable lifetime was noted for the flexibly spaced C_{60} -polyglycol- $[\text{Ru}(\text{bpy})_3]^{2+}$ analogue.²⁶

Structures, such as a 3_{10} -helix, are prone to conformational changes upon addition of protic solvents. In nonprotic solvents the helical secondary structure of the peptide spacer places the two redox active moieties into close proximity, which is favourable for their mutual electronic interaction. An edge-to-

edge distance of *ca.* 12 Å provides the means for a rapid intramolecular ET from the $^3\text{*(MLCT)}$ $[\text{Ru}(\text{bpy})_3]^{2+}$ state to the electron accepting fullerene (case III in Fig. 6). In fact, the initially formed $^3\text{*(MLCT)}$ $[\text{Ru}(\text{bpy})_3]^{2+}$ state transforms readily ($3.4 \times 10^8 \text{ s}^{-1}$) into a long-lived charge-separated state ($\tau = 608 \text{ ns}$). Protic solvents, on the other hand, interfere with the intramolecular hydrogen bonding of the peptide backbone. Unfolding of the relatively compressed secondary structure of the ordered peptide results in a statistically unordered conformation. Consequently, the spatial separation between the two components, donor ($[\text{Ru}(\text{bpy})_3]^{2+}$) and acceptor (C_{60}), located at the N- and C-termini of the peptide chain, respectively, tends to increase to a point that eventually disrupts their mutual electronic interactions. Despite the general flexibility of the peptide backbone, the experimental data fail to support either of the two possible ET mechanisms (*e.g.* a 'through bond' or an 'intramolecular exciplex' route), instead the $^3\text{*(MLCT)}$ $[\text{Ru}(\text{bpy})_3]^{2+}$ state decays with a lifetime of 535 ns (*e.g.* similar to a $[\text{Ru}(\text{bpy})_3]^{2+}$ reference complex). This leads to the conclusion that the peptide backbone is relatively stiff in comparison to true flexibility found in a hydrocarbon chain.

An intriguing feature of the intramolecular hydrogen bonding within the peptide backbone is that the more randomised configuration can be reversibly transferred into the starting conformation (*e.g.* the 3_{10} -helical character). After careful removal of the protic component from a binary solvent mixture (protic and nonprotic; 1 : 1 v/v) the luminescence intensity of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophore becomes comparable again to that for the original non-protic solution prior to the addition of the protic solvent. The reversible activation-deactivation of the ET mechanism was successfully repeated many times (*e.g.* 10 times) and, thus, serves as a sensitive probe for the secondary structure of peptides.

The strong electrostatic fields (10^9 V m^{-1}) in helices have been used in rationalising the observation that only one of the two branches of the bacterial PRC is active.²⁷ An oriented dipole, which spans from the N- to the C-terminus of the helix, is responsible for this field. In the system presented a charge-separated radical pair is created which resembles the helices' own electrostatic field and, therefore, destabilises the charge-separated radical pair. The observed $k_{\text{ET}}/k_{\text{BET}}$ ratio (209), as a meaningful measure of the usefulness of a PET system, is, nevertheless, promising. The $k_{\text{ET}}/k_{\text{BET}}$ ratio may be further improved by exchanging the two building blocks. In such a system the ET will operate with the dipole moment of the helix and, thus, be accelerated, while simultaneously the BET is rendered more difficult.

Concluding remarks and outlook

The selected examples described in this article illustrate the continuing interest and potential of fullerenes as multifunctional electron storage moieties in well-ordered multifunctional composites. Noteworthy in this context is the recent introduction of elegant and versatile protocols concerning the chemical functionalization of the fullerene core.^{8,28}

Remarkably, similar systems based on two-dimensional acceptors (*e.g.* quinone) failed to exhibit sufficient lifetimes of the charge-separated states formed because of the fast occurring BET. This is due, at least in part, to the slower ET and faster BET dynamics evolving from the larger reorganisation energies of two-dimensional electron acceptors. The unique delocalization, provided by the three-dimensional structure of the fullerene core, in combination with the small reorganisation energy, on the other hand, prevents a fast BET process in the contributed fullerene-containing systems.

The important idea presented by the current concepts (*e.g.* gain of aromaticity and planarity) is the stabilisation of the oxidised donor moiety and, in turn, of the resulting radical pair. In this line of thinking the diffusional splitting of the radical pair

in fullerene-metallocomplexes is the basis for the design of artificial photosynthetic systems with efficient and long-lived charge separation but fewer electron transfer steps and less energy loss.

In summary, the systematic investigation of fullerene chemistry has, already at a relatively early stage, played a significant role in the development of useful molecular composites. If the more technological problems can be solved, there is an almost unlimited field of application to be foreseen and eventually fullerenes may become important building blocks of future technologies, such as solar energy conversion, batteries and photovoltaics.

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Notes and references

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