

Functionalized Fullerenes as Photosynthetic Mimics

by K. George Thomas

Photoinduced electron transfer is an important primary event in many chemical and biological systems. In bacterial photosynthesis, the early events involve the trapping of sunlight by antenna complexes, a protein structure containing several bacteriochlorophylls.¹⁻³ The singlet excitation energy is then transferred to another membrane-bound protein pigment complex called the reaction center. In the reaction center, the excitation energy is converted to electrochemical energy (as transmembrane charge separation) through a series of electron transfer processes between the donor and acceptor molecules.¹⁻³ The transferred electron, in principle, can be reverted back to the donor molecule via back electron transfer. In bacterial photosynthesis, the electron transfer occurs along cascades of donor and acceptor systems, which increases the distance of separation of the radical ion pairs and prevents the back electron transfer.¹⁻³ Photosynthetic systems are complex in nature and attempts have been made by several research groups to design model molecular systems, which can mimic the various primary processes in natural photosynthesis.

The simplest form of a model system is a dyad molecule (Fig. 1), in which a donor (D) group is covalently linked to an acceptor (A) group through a rigid or flexible bridging unit (B). Photoexcitation of either donor or acceptor group of the dyad (e.g., in Step 1 of Figure 2, the acceptor group is excited) leads to an electron transfer, to form a radical cation of the donor and radical anion of the acceptor group. The stabilization of the charge-separated state, by avoiding the energy wasting back electron transfer process (Step 4), is very important for the successful use of these molecular systems for energy conversion devices. Efforts have been made to study the rate of electron transfer processes in these systems

by tuning the energetics of the donor-acceptor pair, and optimizing the distance and orientation between the donor and acceptor molecules (see Fig. 2). Another strategy employed to enhance the charge-separation yield is by involving D-B-A systems in heterogeneous and microheterogeneous media.⁴ Covalently linked porphyrin-quinone dyads are amongst the most widely studied D-B-A systems and one of the major limitations of these systems is the short lifetimes (picosecond) of the charge-separated pair.⁵ Attempts have been made to slow down the charge recombination process by designing triad systems (dyad linked with a second donor or acceptor), which employ a multistep electron transfer. Photophysical and electron accepting properties as well as the stability of C₆₀ make it an ideal candidate for the design of artificial photosynthetic systems.⁶⁻⁹ A few of the important properties are listed below:

- C₆₀ absorbs light throughout the visible region.
- The relatively low energy gap between the excited singlet and triplet states of C₆₀ (5.5 kcal/mol) facilitates efficient intersystem crossing and hence the triplet state is formed in high yield (>95%).

- C₆₀ is an excellent photosensitizer for the generation of singlet oxygen.
- C₆₀ is found to be a good acceptor of electrons, with the ability to accommodate up to six electrons reversibly.
- C₆₀ possesses exceptionally low reorganization energy in electron transfer, which is associated with the high degree of charge delocalization and rigidity.
- The rigid spherical carbon framework of C₆₀ is highly stable.

C₆₀ Based Dyads

A major focus of recent fullerene research has been the investigation of redox and excited state properties of fullerenes and functionalized fullerenes. Several synthetic methodologies have been developed which allow covalent linkages of C₆₀ with other photo- and electroactive molecules. Covalent linkages of C₆₀ with specific electron donors have facilitated the tailoring of this class of molecules for solar energy harvesting devices. Several fullerene based donor-acceptor systems, containing porphyrins, phthalocyanines, ruthenium complexes, ferrocenes, and anilines, as donor groups, have been synthe-

Fig. 1. Block diagram illustrating the basic components of a dyad.

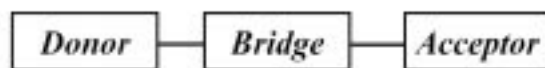
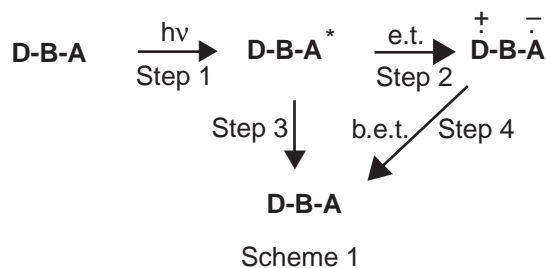
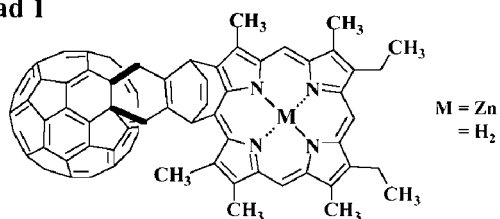


Fig. 2. Some of the photophysical events in a donor-bridge-acceptor system.



Dyad 1



Dyad 2

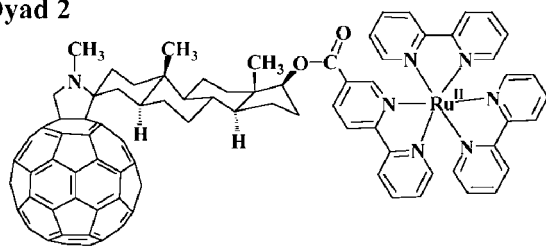
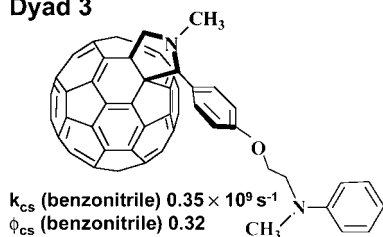


Fig. 3. Examples of two fullerene-based dyads.

Dyad 3



Dyad 4

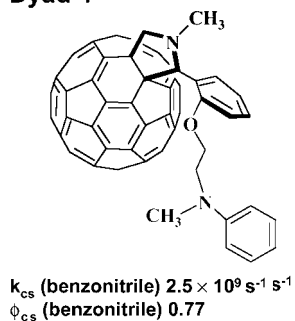


Fig. 4. Forward electron transfer processes in *ortho*- and *para*-substituted fullerene-aniline dyads.

sized.^{6,7,10-12} Two representative examples of fullerene-based donor-acceptor dyads are presented in Fig. 3. Gust and coworkers^{6, 11} designed a photosynthetic pigment by covalently linking a porphyrin moiety to C₆₀ through a bicyclic bridge (dyad 1 in Fig. 3) for demonstrating the use of such molecular systems for mimicking photosynthesis. Photoinduced electron transfer between C₆₀ and porphyrin moieties was confirmed using laser flash photolysis experiments. The formation of C₆₀ radical anion and porphyrin radical cation served as a fingerprint to establish the charge separation in this molecular dyad. Researchers were able to extend the life of charge-separated state (770 ns in benzonitrile) in a porphyrin-C₆₀ system, by linking a carotenoid polyene, which acts as a secondary electron donor group.^{6, 11} Thus, long lived charge separation was demonstrated in a carotene-porphyrin-C₆₀ triad system through a multistep electron transfer sequence.^{6, 11}

The rate and efficiency of photoinduced electron transfer processes in fullerene based donor-bridge-acceptor systems were tuned by varying the distance and orientation of the donor-acceptor pair.¹³ This was achieved by attaching an aniline donor to the *ortho*- as well as *para*-positions of the phenyl groups of 1-methyl-2-phenyl pyrrolidinofullerene, using alkyl chains as bridging units (for example, dyad 3 and 4 in Fig. 4). A marked increase in the rate constants and quantum yields of charge separation (k_{cs} and ϕ_f respectively) were observed for *ortho*-substituted dyads in polar solvents. The folding of the aniline group in close proximity to the π -cloud of C₆₀, enhances the probability of forward electron transfer for the *ortho*-substituted fullerene-aniline dyads. However, the quick recombination of photogenerated charge transfer products was a limiting factor in achieving charge stabilization in these systems.

A novel approach for charge stabilization was demonstrated by taking advantage of the clustering behavior of C₆₀.^{8,14} Fullerene-aniline dyad 3 forms stable, optically transparent clusters (mean diameter of ~175 nm) in mixtures (3:1) of acetonitrile and toluene.¹⁴ Laser excitation of clustered dyads yielded remarkably stable charge transfer products, with lifetimes of several hundred microseconds. The self-induced aggregation of dyads in the mixed solvents provides a microheterogeneous environment favorable for charge stabilization. The close network of fullerene moieties in the cluster facilitates the hopping of electrons from the parent fullerene to the adjacent molecule, thus increasing the spatial distance between the charge-separated pair (see Fig. 5).¹⁴

Elegant studies carried out by several research groups on the photophysical and photosensitizing properties of C₆₀ based dyad systems have provided basic information about the electron transfer mechanism in homogeneous solutions (see, for example, References 6 and 7). For device applications, it is desirable to have a detailed mechanistic understanding of their photophysical and electron transfer properties in the solid state. It is difficult to investigate the electron transfer processes in solids. Studies using optically transparent clusters can provide intermediary information about their properties between the solution and the solid state.

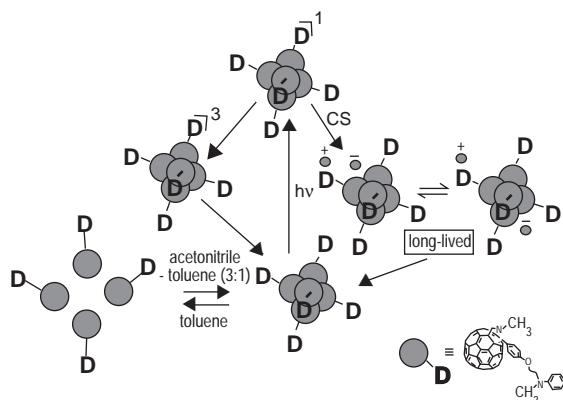


Fig. 5. Stabilization of the charge separated radical pair via clustering of dyads. (Reprinted with permission, J. Phys. Chem., **103**, 8864 (1999).

Optoelectronic Applications

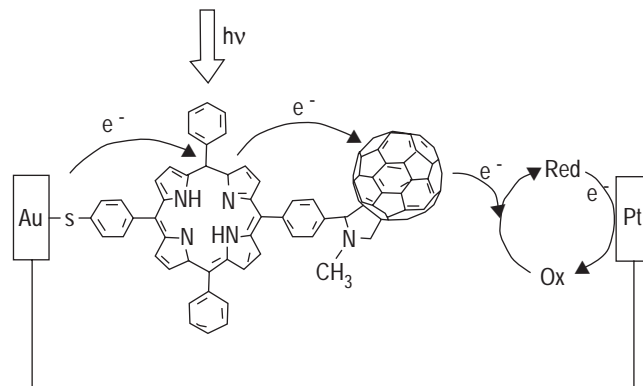
Although several technological applications were proposed for fullerene-based systems in the early 90s, only a few laboratory scale demonstrations have been successful. As discussed in the previous sections, the properties of fullerene compounds can be fine tuned by the addition of redox or photoactive moieties to C₆₀. Researchers are now focusing on the design and studies of functionalized fullerene derivatives. Applications of fullerene-based molecules, in optoelectronics⁶ and medicinal chemistry,¹⁵ have shown promising results. The ability of C₆₀ and functionalized C₆₀ to undergo photoinduced charge separation makes them suitable candidates for light energy conversion devices. Several research groups have investigated the photoelectrochemical and photovoltaic properties of these materials.^{6,7} A convenient approach is to design self-assembled monolayers of functionalized fullerenes on gold electrodes and a schematic representation of photocurrent generation using C₆₀-bridge-donor system is shown in Fig. 6 (adapted from Reference 6). Excitation of the porphyrin-fullerene dyad modified gold electrode results in charge separation and the electrons migrate from the collecting gold surface. The redox couple present in the electrolyte regenerates the C₆₀-bridge-donor system.

A fulleropyrrolidine derivative bearing an oligophenylenevinylene substituent has been recently proposed as a suitable candidate for the construction of solar energy conversion systems.¹⁶ Organic photovoltaic cells obtained by blending a semiconductor polymer (poly(2-methoxy-5-(2'-ethyl hexyloxy)-1,4-phenylene vinylene)) with C₆₀ as well as its functionalized derivatives have shown the promise of these materials for light energy conversion.¹⁷ Photoinduced electron transfer between the polymer and C₆₀ resulted in an efficient charge separation in this study.

Conclusion

The research on fullerene-based systems has now emerged as an exciting multidisciplinary field covering the areas from physical and materials sciences to molecular biology. Fullerene-based materials

Fig. 6. Photocurrent generation using a porphyrin-fullerene dyad. (Reprinted with permission, *Adv. Mater.*, **9**, 537 (1997).)



and their clusters, with broad absorption in the visible region, can act as sensitizers (or as electron relays) in light energy conversion devices. The D-B-A systems based on C₆₀ are an excellent class of dyads, for securing long-lived charge separation. A practical approach to mimic the photosynthetic assembly using these systems would be to build heterosupramolecular photovoltaic cells, with dyads as photosensitizers and semiconductor systems as electron relays. Transferring the charges to the adjacent electrode can, in principle, generate photocurrent. Future efforts are expected to focus on the design of new fullerene based systems which can stabilize the charge separated states, and on issues related to the optimization of photovoltaic or photoelectrochemical cells for achieving higher photoconversion efficiencies. ■

Acknowledgments

The author thanks the Office of Basic Energy Sciences of the U.S. Department of Energy and the Council of Scientific and Industrial Research, Government of India for their support. This is contribution No. RRLT-PRU 100 from RRL, Trivandrum and NDRL 4169 from Notre Dame Radiation Laboratory.

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K. George Thomas is a scientist in the Photochemistry Research Unit of the Regional Research Laboratory (CSIR), Trivandrum, India. He is currently (January-November 1999) working in the Notre Dame Radiation Laboratory as a Visiting Scientist. His research interests include the molecular design, synthesis and photophysical studies of sensitizing dyes, donor-acceptor systems, and switching devices.