

FULLERENES AS COMPONENTS OF ARTIFICIAL PHOTOSYNTHETIC CONSTRUCTS

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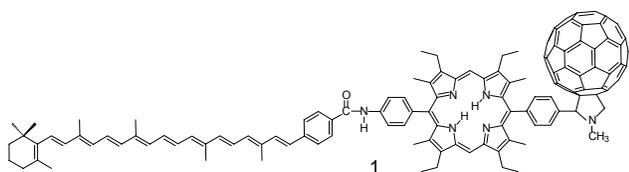
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Recent investigations by numerous laboratories have revealed that fullerenes are extremely useful components of molecular constructs that mimic various aspects of photosynthetic energy conversion. Fullerene moieties have been found to be:

- Reversible (multiple) electron acceptors,
- Chromophores that absorb throughout the visible,
- Singlet and triplet energy donors and acceptors that can function as parts of antenna or photoprotection systems,
- Soluble in biological membranes,
- Relatively insensitive to solvent stabilization of the radical anion,
- Characterized by low internal and solvent reorganization energies for electron transfer.

By using theoretical descriptions of energy and electron transfer as guides, fullerene-containing artificial photosynthetic systems can be engineered in order to maximize desirable properties. Various examples illustrate this point.

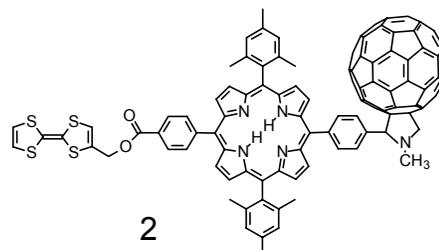
Carotene (C) porphyrin (P) fullerene (C₆₀) triad **1**, for instance, undergoes rapid, multistep photoinduced electron transfer from the porphyrin first excited singlet state C⁻¹P-C₆₀ to give first the C-P^{•+}-C₆₀^{•-} charge-separated state and finally the C^{•+}-P-C₆₀^{•-} state.¹



The final state has a lifetime of 170 ns in 2-methyltetrahydrofuran solution, and preserves 1.20 eV of the ~1.9 eV inherent in the porphyrin first excited singlet state as electrochemical potential energy. However, it is formed with a yield of only 0.14. By fine-tuning the energetics and electronic coupling in this molecular system through minor structural changes, new triads with quantum yields of 0.88 and ≥0.96 have been prepared.

Charge recombination of C^{•+}-P-C₆₀^{•-} in **1** yields the carotenoid triplet state, rather than the ground state. This can be useful in some circumstances, and indeed forms the basis for a molecular AND gate function.² However, this charge recombination limits the lifetime of the charge separation. Recombination to yield a triplet state may be eliminated by employing an electron donor that lacks a low-lying triplet state, so that recombination to form the triplet is endergonic. For example, the carotenoid moiety can be replaced with a tetrathiafulvalene (TTF), which lacks a low-energy triplet. In addition, suitable TTF derivatives can in principle serve as two-electron donors, as the first and second oxidation potentials can be nearly equal.

Triad **2** exemplifies the use of a TTF donor. Excitation of the porphyrin moiety of **2** yields the porphyrin first excited singlet state TTF⁻¹P-C₆₀, which undergoes photoinduced electron transfer with a time constant of 25 ps to give TTF-P^{•+}-C₆₀^{•-}. This intermediate charge-separated state has a lifetime of 280 ps, decaying mainly by a charge-shift reaction to yield a final state, TTF^{•+}-P-C₆₀^{•-}. The final state has a lifetime of 660 ns, is formed with an overall yield of 0.92, and preserves ~1.0 eV of the 1.9 eV inherent in the porphyrin excited state.



In photosynthesis, the photoinduced electron transfer that lies at the heart of reaction center function is combined with singlet-singlet energy transfer in an antenna system to produce a composite that harvests light energy more efficiently. We have previously reported the embodiment of this idea in a molecular hexad consisting of an antenna of four covalently-linked zinc porphyrins joined to a porphyrin-fullerene artificial reaction center.³ Although this molecule exemplified the principles involved, it suffers from a quantum yield of only ~0.70 and a charge-separation lifetime of only 1.3 ns.

By suitable molecular engineering, a hexad with improved properties has been prepared. As revealed by time-resolved absorption and emission studies in 2-methyltetrahydrofuran solution, excitation of a peripheral zinc porphyrin moiety (P_{ZP}) of the (P_{ZP})₃-P_{ZC}-P-C₆₀ hexad is followed by singlet-singlet energy transfer to the central zinc porphyrin to give (P_{ZP})₃-¹P_{ZC}-P-C₆₀ with a time constant of 50 ps. The excitation is passed on to the free base porphyrin in 32 ps to produce (P_{ZP})₃-P_{ZC}-¹P-C₆₀, which decays by electron transfer to the fullerene with a time constant of 25 ps. The resulting (P_{ZP})₃-P_{ZC}-P^{•+}-C₆₀^{•-} charge-separated state is generated with a quantum yield of 0.98 based on light absorbed by the porphyrin antenna. Direct excitation of the free-base porphyrin moiety or the fullerene also generates this state with a yield near unity. Thermodynamically favorable migration of positive charge into the zinc porphyrin array transforms the initial state into a long-lived ((P_{ZP})₃-P_{ZC})^{•+}-P-C₆₀^{•-} charge-separated state with a time constant of 380 ps. The final charge-separated state, formed in high yield (~0.90), decays to the ground state with a lifetime of 240 ns. In benzonitrile, the lifetime is 25 μs.

References

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