PORPHYRIN-FULLERENE LINKED SYSTEMS AS ARTIFICIAL PHOTOSYNTHETIC MODEL

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The primary challenge in artificial photosynthesis lies in the design of photoinduced electron transfer (ET) systems, which, upon photoexcitation, give rise to a long-lived charge-separated state in high quantum yields. An important design consideration merging from the natural process is that photosynthesis utilizes relays of multistep ETs, which facilitate separating radical ion pairs over long distances and, thereby, successfully retarding energy-wasting charge recombination (CR). Along this line considerable efforts have been directed towards the preparation of novel donor-acceptor systems with the purpose being to prolong the lifetime of the charge-separated state, while, simultaneously, optimizing the efficiency of charge separation (CS). Despite the extreme difficulties, connected with the design and synthesis of rigidly spaced ensembles, a long-distance CS can only be attained in multistep ET systems. In particular, in triad, tetrad and pentad structures distantly- separated donor-acceptor radical ion pairs are generated as a result of an initial CS followed, in succession, by several charge shift (CSH) reactions along well-tuned redox gradients. With the advent of fullerenes, a new three-dimensional electron acceptor became available, exhibiting attractive characteristics. In particular, fullerenes have remarkable small reorganization energies of ET, which result from the p electron systems delocalized over the three-dimensional surface together with the rigid, confined structure of the aromatic p sphere. In this regard, it has been observed frequently that photoinduced CS is accelerated and CR is decelerated in donor-linked fullerenes, as compared to those with conventional acceptors such as quinones and imides. The primary ET processes of the photosynthesis, on the other hand, are also characterized by an extremely small reorganization energy (l = 0.2 eV). This is essential to achieve the ultrafast forward ET and to retard the energy-wasting back ET, which is highly exergonic (DG0ET = 1.1 eV) and thereby deeply in the Marcus inverted region. Taking these facts into concert, a significant impact, concerning the lifetime of CS, is expected without, however, lowering the overall efficiency of CS in fullerene-containing multicomponent systems. Along this line we and others have prepared a variety of donor-fullerene linked dyads and triads, some of which have successfully mimicked photosynthetic ET on electrodes as well as in solutions. We report herein the photodynamical properties of a series of porphyrin- fullerene linked systems studied by means of time-resolved transient absorption spectroscopy and fluorescence lifetime measurements. The investigated compounds comprise a homologous series of rigidly linked, linear donor-acceptor arrays with different donor-acceptor separations and diversified donor strength: freebase porphyrin-C60 dyad (H2P-C60), zincporphyrin-C60 dyad (ZnP-C60), ferrocene-zincporphyrin-C60 triad (Fc- ZnP-C60), ferrocene-freebase porphyrin-C60 triad (Fc-H2P-C60), zincporphyrin-freebase porphyrin-C60 triad (ZnP-H2P-C60), and ferrocene- zincporphyrin-freebase porphyrin-C60 tetrad (Fc-ZnP-H2P-C60). Most importantly, the lowest-lying charge-separated state of all the investigated systems, namely, that of ferrocenium ion (Fc+) and C60 radical anion (C60) pair in the Fc-ZnP-C60 triad has been generated with the highest quantum yields (close to unity) and reveals a lifetime as long as 16 ms. Determination of CS and CR rate constants, together with the one-electron redox potentials of the donor and acceptor moieties in different solvents, has allowed us to examine the driving force dependence (DG0ET) of the electron transfer rate constants (kET). Hereby, the semi- logarithmic plots (i.e., log kET versus DG0ET) lead to the evaluation of the reorganization energy (l) and the electronic coupling matrix element (V) in light of the Marcus theory of electron transfer reactions: l = 0.66 eV and V = 3.9 cm-1 for ZnP-C60 dyad, l = 1.09 eV and V = 0.019 cm-1 for Fc-ZnP-C60, Fc-H2P-C60, and ZnP-H2P-C60 triads, and l = 1.32 eV and V = 0.00017 cm-1 for Fc-ZnP-H2P-C60 tetrad. Interestingly, the Marcus plot in Fc-ZnP-C60, Fc-H2P-C60, and ZnP-H2P-C60 has provided the first evidence for intramolecular CR located in both the normal and inverted regions of the Marcus parabola. The coefficient for the distance dependence of V (damping factor: bCR = 0.60 -1) is deduced that depends primarily on the nature of the bridging molecule. Most importantly, the lifetime of the resulting charge-separated state of Fc-ZnP-H2P-C60 (i.e., ferricenium ion- C60 radical anion pair) in a frozen benzonitrile is determined as 0.38 s, which is more than one-order of magnitude longer than any other intramolecular charge recombination processes of synthetic systems, and is comparable to that observed for the bacterial photosynthetic reaction center.

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