Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron 62 (2006) 1928–1936

Tetrahedron

Synthesis and photophysics of porphyrin–fullerene donor–acceptor dyads with conformationally flexible linkers

David I. Schuster,[a,*] Shaun MacMahon,[a] Dirk M. Guldi,[b] Luis Echegoyen[c] and Silvia E. Braslavsky[d]

[a] *Department of Chemistry, New York University, New York, NY 10003, USA*
[b] *Institute for Physical and Theoretical Chemistry, University of Erlangen, 91058 Erlangen, Germany*
[c] *Department of Chemistry, Clemson University, Clemson, SC 29634, USA*
[d] *Max Planck Institute for Bioinorganic Chemistry (formerly Strahlenchemie), D 45413 Mülheim, Germany*

Received 7 June 2005; revised 26 July 2005; accepted 30 July 2005

Abstract—The synthesis and photophysics of a series of porphyrin–fullerene (P–C_{60}) dyads in which the two chromophores are linked by conformationally flexible polyether chains is reported. Molecular modeling indicates the two moieties adopt a stacked conformation in which the two chromophores are in close proximity. Photoexcitation of the free base dyads in polar solvents such as tetrahydrofuran and benzonitrile, causes electron transfer (ET) to generate charge-separated radical pair (CSRP) states, which were directly detected using transient absorption (TA) techniques. In nonpolar solvents such as toluene, where CSRP states were not directly detected, fullerene triplet state states were formed, according to TA studies as well as singlet oxygen sensitization measurements. The low value of the quantum efficiency for sensitized formation of singlet molecular oxygen $[O_2(^1\Delta_g)]$ in toluene and chloroform indicates that singlet energy transduction to give $H_2P–^1C_{60}^*$, followed by intersystem crossing to $H_2P–^3C_{60}^*$ and energy transfer to $^3O_2$, is not the operative mechanism. Rather, a mechanism is proposed involving ET to give CSRP states followed by exergonic charge recombination to eventually generate fullerene triplets. Such a mechanism has been demonstrated experimentally for structurally related P–C_{60} dyads. For the corresponding ZnP–C_{60} dyads with flexible linkers, only photoinduced ET to generate long-lived CSRP states is observed. Photoinduced charge separation in these dyad systems is extremely rapid, consistent with a through space rather than through-bond mechanism. Charge recombination is up to three orders of magnitude slower, indicating this process occurs in the inverted region of the Marcus curve that relates ET rates to the thermodynamic driving force. These observations once again demonstrate the advantages of incorporating fullerenes as electron acceptor components in photosynthetic model systems.

---

1. Introduction

Fullerenes, C_{60} in particular, have been found to make ideal acceptors in model photosynthetic systems, due to their unique photophysical, electrochemical, and chemical properties.[1] C_{60} has been shown to reversibly accept up to six electrons in solution due to its three low lying degenerate lowest unoccupied molecular orbitals (LUMOs), with a first electrode potential resembling that of the quinone-derived electron acceptor in the photosynthetic reaction center.[2] Fullerenes accelerate charge separation and slow down charge recombination versus donor–acceptor (DA) dyads containing traditional two-dimensional electron acceptors such as quinones and imides. This phenomenon, which is general, has been rationalized by the small Marcus reorganization energy (λ) accompanying electron transfer in fullerenes. Since the negative charge on the fullerene produced after photoexcitation of the donor moiety is delocalized over the entire π-system, the charge density is much lower than it would be on acceptors such as quinones, where the charge is concentrated mainly on the oxygens. The structural inflexibility of fullerene-based systems results in small internal reorganization energies (λ_v), while the charge dispersion minimizes the solvent reorganization energy (λ_s).[3]

For electron DA systems, Marcus theory predicts that as the free energy change (ΔG^0) for electron transfer (ET) becomes more negative, that is, increasingly exergonic, the ET rates increase, reaching a maximum when $-\Delta G_{ET} = \lambda$, the reorganization energy. As $-\Delta G^0_{ET}$ becomes more negative than the absolute value of λ, the ET rate decreases. For C_{60} dyads, the maximum in the Marcus curve is reached at smaller values of $-\Delta G^0_{ET}$ compared to two-dimensional acceptors.

Keywords: Fullerenes; Porphyrins; Dyads.

* Corresponding author. Tel.: +1 212 998 8447; fax: +1 212 260 7905; e-mail: david.schuster@nyu.edu

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.07.127

Thus, charge separation (CS) rates for most fullerene-based DA dyads are located along the upward slope of the Marcus curve, near the maximum, leading to enhanced CS rates, whereas the large thermodynamic driving force for charge recombination (CR) places this process on the downward side of the Marcus parabola in the inverted region. This phenomenon causes a noticeable enhancement in the lifetime of charge-separated radical pair (CSRP) states in C_{60}-based DA systems versus analogous two-dimensional DA systems.[4]

Porphyrins are frequently used as donors in artificial photosynthetic systems. Porphyrins are synthetically accessible in a laboratory, (although their synthesis can be a rather arduous task),[5] and they absorb light much more effectively than fullerenes in the visible region between 400 and 600 nm. Favorable van der Waals interactions between the curved π surface of the fullerene and the planar π surface of the porphyrin assist in the formation of supramolecular structures, overcoming the necessity to match a concave-shaped host to a convex-shaped guest.[6] This unique intermolecular electronic interaction is observed in condensed media as well as in the solid state.

Attempts to suppress CR have led to the development of multi-chromophoric triads, tetrads and pentads, where ET can occur through a multi-step process, yielding CSRP with microsecond to second lifetimes.[1c,d,7] An inherent problem is the synthetic challenge involved in the synthesis of such complicated assemblies. These multicomponent materials are far less efficient in the storage of energy than dyad systems, since sequential ET dissipates more and more of the initial excitation energy, lowering the capacity for energy storage.

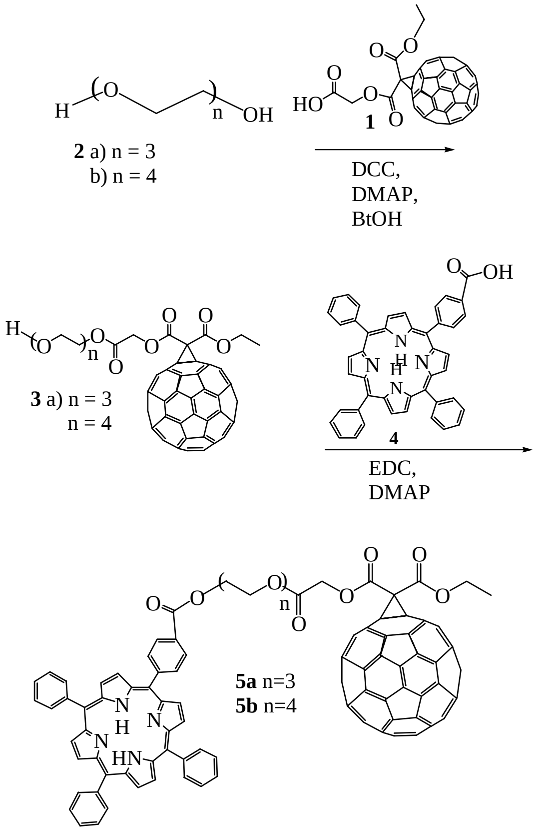
Herein, we report on simple porphyrin–C_{60} (P–C_{60}) dyads with flexible linkers, which are easily synthesized and which have many of the desirable properties of DA systems with respect to energy storage and CSRP state lifetimes.

2. Free base porphyrin–fullerene dyads (H_2P–C_{60})

2.1. Synthesis and structural characterization

Our initial foray into this area centered on the synthesis of porphyrin–fullerene (H_2P–C_{60}) dyads with flexible crown ether-like glycol linkers by a convergent route.[8] Steady-state fluorescence spectra demonstrated rapid and efficient quenching of the porphyrin S_1 state by the fullerene, but the CS and CR kinetics were not measured on these phase I dyads. Among the synthetic problems encountered were the extremely low yields (i.e., ~30%) when using simple methanofullerene carboxylic acid, due to the acid poor solubility properties. Coupling of tetraphenylporphyrin carboxylic acid to the polyether linker also proved difficult, making it extremely challenging to generate dyads on a milligram scale.

In order to circumvent these problems, fullerene carboxylic acid **1**, originally reported by Diederich and Nierengarten,[9] was used as the fullerene synthon. The strategy was to replace methanofullerene carboxylic acid by **1**, which would lead to flexibly linked H_2P–C_{60} dyads with much better solubility properties, as well as higher yields in the coupling reactions. Improved solubility would in turn allow more facile structural characterization. In the first series of reactions, summarized in Scheme 1, fullerene acid **1** was condensed with glycols **2a** and **2b** to give **3a** and **3b**, respectively, which were then condensed with 5,10,15,20-tetraphenylporphyrin carboxylic acid **4** to give dyads **5a** and **5b**, respectively. Details of these reactions are provided in an earlier paper dealing with the synthesis of a variety of P–C_{60} dyads.[10]



Scheme 1.

^1H NMR spectra of **5a** and **5b** showed characteristic porphyrin bands between 7.5 and 9 ppm, glycol bands at 3.5–4 ppm, and distinctive peaks from the C_{60} synthon **1**. Computer modeling using Insight II provided a prediction of the H_2P–C_{60} geometry in the ground state (see Fig. 1).[11] Because of favorable porphyrin–fullerene π–π interactions, the glycol linker curves around, placing the porphyrin and fullerene within van der Waals contact range.

UV–vis spectra of dyads **5a** and **5b** in chloroform demonstrated strong ground state interactions. The porphyrin Soret bands at 422 nm were red shifted by approximately 5–10 nm relative to methyl ester **8**, indicating that the fullerene was close enough to the porphyrin in the ground state to perturb its absorption spectrum. Similar spectral shifts were also visible in the porphyrin Q-band region in both dyads. The broadness of the absorption in both the Soret and Q-band regions was surprising, and could indicate the presence of more than one conformation of these dyads in solution.