Electron-transfer dyads suitable for novel self-assembled light-harvesting antenna/ electron-transfer devices*

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Abstract: The synthesis and photophysical and photochemical characterization of four novel bacterio-chlorin-fullerene dyads with fullerene C_{60} coupled at various positions and by various bridges to the chlorin ring are described. All dyads undergo rapid charge separation in the sub-picosecond to picosecond time range as characterized by time-resolved fluorescence and transient absorption spectroscopy.

INTRODUCTION

The early steps in natural photosynthesis involve absorption of light by antenna systems followed by rapid excitation energy transfer to reaction centers which perform photochemical charge separation across a membrane. The efficiency of these steps is realized by an optimal organization of an antenna pigment network and a well arranged chain of electron donors and acceptors in the reaction center unit embedded in the transmembrane proteins [1,2]. Mimicking these processes in order to perform artificial photosynthesis has been the aim of many research groups in recent years. While artificial reaction center models have been quite successful, little progress has been made so far to achieve artificial antenna functions, notably in supramolecular self-assembled systems.

Green photosynthetic bacteria possess a unique light-harvesting system, the so-called chlorosomes, where a large number of bacterio-chlorophyll (BChl) molecules form the supramolecular antenna array in a self-assembly process [3]. In contrast to other more conventional light-harvesting antennae, the BChls in chlorosomes are not organized by proteins. This provides an elegant and straightforward principle allowing to mimic the photosynthetic antenna of natural systems based on the bacterio-chlorophyll self-aggregation process. Recently, we have demonstrated that self-aggregates of modified Zinc chlorin in either lipid monolayers or organic solvents show a close spectral similarity to native chlorosomes [4,5]. More importantly, the addition of a small amount of BChl *a* molecules to the aggregates can serve as an ideal energy acceptor to efficiently trap the singlet excitation energy absorbed by the aggregated Zinc chlorins. This is the first biomimetic example of an artificial light-harvesting antenna based on the self-assembly principle. The results of these antenna studies motivated our ongoing project aimed at building an artificial photosynthetic unit by combining an artificial light-harvesting antenna and a charge-transfer unit all based on the self-assembly principle.

Artificial photosynthetic reaction centers have been the subject of intensive studies [6]. A large variety of electron-transfer assemblies have been synthesized and spectroscopically and electrochemically characterized. These assemblies generally consist of a covalently linked electron donor (D) and an acceptor (A), the so-called dyads [7]. A variety of molecular bridges (B) were built into these dyads in

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order to maintain a long-lived charge-separated (CS) state for potential use in subsequent charge stabilization processes [8]. The most widely employed electron donors were free-base and metallated porphyrin derivatives due to their favorable electron-donating properties and their synthetic accessibility. As electron acceptors, quinones and the recently discovered fullerenes, in particular C_{60}, with its remarkable photophysical properties and the development of powerful synthetic methods for functionalizing the fullerene surface, have been widely used [9,10]. C_{60} is for several reasons an ideal electron acceptor unit in D-A assemblies, due to (i) its favorable electron-accepting properties, which are comparable to those of benzo- and naphthoquinones [11,12]; and (ii) its rigid framework in ground and excited state and high stability under a variety of conditions. Moreover, it has been reported that fullerenes can act as electron carriers in lipid layers which make this electron acceptor attractive to design supramolecular devices that mimic photosynthetic processes [13].

Our aim of combining in a supramolecular self-assembly process an artificial antenna with an electron-transfer dyad whose electron donor at the same time acts as an energy acceptor puts special requirements on the electron donor unit in the dyads. Metal-free chlorins or bacterio-chlorins with special side groups suitable for self-aggregation would seem to be ideal, based on our previous results [3,4,14]. As electron acceptors, fullerenes seem to provide a lot of the desired properties. However, only few such dyads have been synthesized [15–17]. In the present work we report on the synthesis and photochemical properties of several novel chlorin dyad units that appear to be suitable in that context.

NOVEL CHLORIN-FULLERENE DYADS AS REACTION CENTER MODELS

Synthesis of dyads with these natural chromophores (Chls and BChls) demands powerful methods to functionalize these sensitive compounds for our purposes and at the same time to avoid undesirable side reactions due to the additional substituents. We make use of these substituents to attach fullerenes in different positions and at the same time trying to keep the good aggregation characteristics of the chromophores. The latter is of central importance with regard to the self-assembly process with the artificial antenna. It has been shown that for the aggregation process of these bacterio-chlorins the 3^1 and 13^1 positions are essential for an optimal interaction.

For coupling these chlorins to C_{60} fullerene Prato's method was chosen. For this reaction, an aldehyde group on the donor unit is required which in refluxing toluene forms with *N*-methylglycine an azomethine ylide that undergoes a cycloaddition with the dipolarophile C_{60} at a 6,6 junction with yields of 35–42% as shown in Fig. 1.

We have synthesized several dyads that appeared suitable in our context using a chlorin donor and a fullerene acceptor (cf. Fig. 2). In dyad (**1**) the C_{60} moiety is covalently bound in the 3^1 position without any large bridge. In order to slow down the back electron transfer and to avoid possible atropiso-
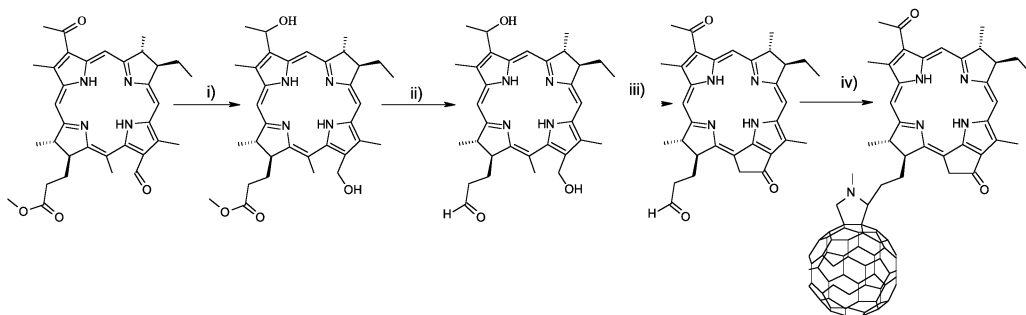

Fig. 1 Synthetic scheme leading to bacterio-chlorin-fullerene dyad; i) $NaBH_4$; MeOH (72%); ii) DIBAH, Toluene, –78 °C (68%); iii) TPAP, NMO, CH_2Cl_2 (75%); iv) C_{60}, Sarcosine, Toluene, reflux (30–40%).
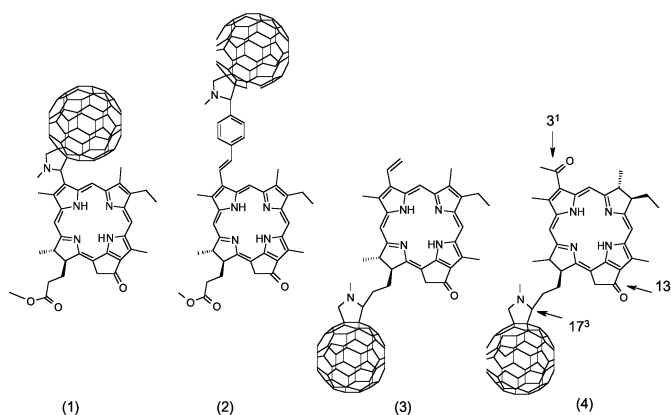
Fig. 2 Bacterio-chlorin-fullerene dyads as reaction center models.

mers like the ones occurring in dyad (**1**), we also synthesized dyad (**2**) where the acceptor is attached at the same position but now via a rigid styryl bridge. For obtaining this dyad a short and effective synthesis of a chlorin building block via a Heck-type reaction without further side-chain modification of the chlorin macrocycle has been developed. In dyad (**3**) we have chosen the 17^3 position of the chlorin to attach the fullerene acceptor in a simple synthetic pathway. In this case, using the natural ester side chain as a bridge consisting of sp3 carbon atoms the connection is more flexible. This unit has the advantage, however, that positions possibly important for the aggregation process are not blocked by the electron acceptor as in dyads (**1**) and (**2**).

The vinyl group in 3^1 position can be easily turned into a hydroxyl-group, thus fulfilling several requirements for co-aggregation with the artificial antenna. Finally, dyad (**4**) is similar to dyad (**3**), but carries a bacterio-chlorin moiety, which has a lower-lying excited state than the chlorins, thus enabling a better energy-accepting function in a supramolecular antenna/electron-transfer unit.

Energy and electron transfer in dyads (**1–4**) has been studied by steady-state absorption and fluorescence, picosecond (ps) time-resolved fluorescence as well as femtosecond (fs) to nanosecond (ns) transient absorption techniques in benzene and other solvents. Some important results will be discussed briefly in the following.

PHOTOPHYSICS OF CHLORIN-FULLERENE DYADS

The photophysics of fullerene dyads is more complex than that of their quinone acceptor analogs since fullerenes have low-lying excited states that can act both as energy acceptors and as electron acceptors. Thus, a variety of competing pathways is possible in principle for the deactivation of the excited state and the radical pair formation. Sub-picosecond energy transfer from the chlorin moiety to the fullerene is most pronounced for these compounds which absorb at about 670 nm which is indicated by time-resolved fluorescence studies. A small negative amplitude in the spectral region between 750 and 800

Table 1 Fluorescence decay lifetimes (τ_i), amplitudes a_i (in parentheses), and quantum yields Φ of bacterio-chlorin moieties in dyads **1–4** in benzene.

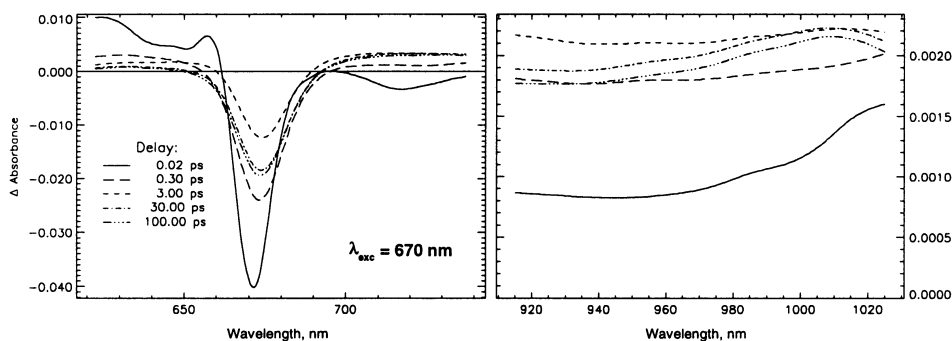| Dyad	λ_{em} (nm)	τ_1 (ps)/a_1	τ_2 (ps)/a_2	τ_3 (ps)/a_3	τ_4 (ns)/a_4	τ_5 (ns)/a_5	Φ
1	674	1 (0.929)	9 (0.05)	177 (0.001)	1.84 (0.01)	6.64 (0.012)	0.015
2	686	102 (0.92)			1.50 (0.07)	6.55 (0.013)	
3	677	20 (0.629)	88 (0.294)	993 (0.026)	2.56 (–0.004)	6.03 (0.056)	0.061
4	765	14 (0.448)	92 (0.328)	870 (0.136)	2.01 (0.086)		

Fig. 3 Femtosecond transient absorption spectra for dyad (**1**) in benzene.

nm which indicates excitation energy transfer from Chl* to C_{60} is observed in good agreement with the steady-state emission spectrum where a broad band at wavelengths > 800 nm was observed (not shown).

As summarized in Table 1, the fluorescence lifetimes of the fastest decay component of dyad (**3**) is longer than the corresponding lifetime of dyad (**1**) by at least one order of magnitude, and dyad (**2**) shows the longest excited-state lifetime.

Excitation of dyad (**1**) with a 60–70-fs laser pulse leads to the transient absorption spectra shown in Fig. 3. These data confirm the formation of the charge-separated state by the characteristic features of the fullerene radical anion (absorption in the 1000-nm region) and the chlorin radical cation (absorption in the 700–800 nm region). Excitation at 670 nm leads to the chlorin first excited singlet state, $Chl^*\text{-}C_{60}$, which undergoes rapid charge separation to $Chl^+\text{-}C_{60}^-$ and in parallel energy transfer to fullerene, forming $Chl\text{-}C_{60}^*$. From this state, the charge-separated state is also formed rapidly. Studies of the time evolution of the transient spectrum show that the charge-separated state is formed in times below ca. 1 ps with a quantum yield of > 0.6. The charge-separated state lives for 2–4 ns. The photophysical behavior of dyads (**2**) and (**3**) is in principle similar, except for their slower charge separation and their shorter lifetimes of the charge-separated states. A kinetic scheme for dyad (**1**) is shown in Fig. 4 and should be taken as an example of the competing pathways leading to the radical pair state in all dyads discussed here. The data from femtosecond transient absorption measurements on the dyads are summarized in Table 2.

Table 2 Dominant lifetimes from femtosecond transient absorption measurements on dyads **1–4** in benzene.

Dyad	Solvents	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	τ_5 (ns)
1	Benzene	90	0.7	13.5	–	2.3
3	Benzene	116	2.2	30.0	–	2.7
4	Benzene	70	–	–	–	0.3

The results for the dyads (**1–3**) show that they are in principle good reaction center models undergoing rapid charge separation with high yields. Nevertheless, these dyads have some disadvantages when judged from their ability to act as energy acceptors in a supramolecular antenna unit. The excited state of the chlorin energy acceptor is slightly too high and the important positions 3^1 and 13^1 for co-aggregation (Fig. 2) are partially blocked.
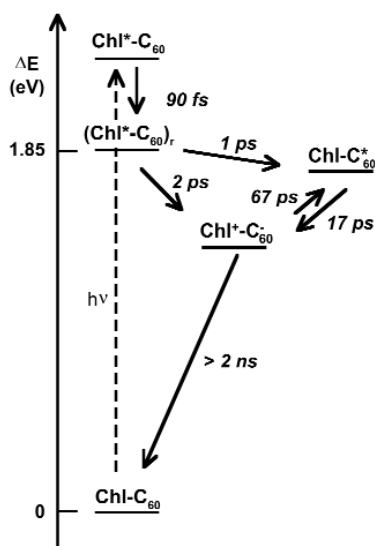
Fig. 4 Kinetic scheme for dyad (**1**) in benzene.

These properties have been optimized in dyad (**4**), which has the following features: i) free 3^1 and 13^1 position for the co-aggregation process; ii) long-wavelength absorbing (>750 nm) for good energy matching ($E_D = 1.63$ eV instead of chlorin $E_D= 1.85$ eV), and iii) flexible chain, which makes this dyad a promising reaction center unit. Preliminary data indicate that electron transfer from the bacterio-chlorin excited state occurs already in less than 100 fs to form a long-lived $BChl^+$-C^-_{60} radical pair. All these features render dyad (**4**) as an ideal candidate for incorporation into an artificial photosynthetic unit.

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