Novel chlorin–diene building block by enyne metathesis: synthesis of chlorin–fullerene dyads

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The first example demonstrating the utility of enyne metathesis in preparing a chlorin–diene system as a novel and versatile building block is discussed; Diels–Alder reaction [4 + 2] of the diene with fullerene (C$_{60}$) produced the chlorin–fullerene dyad, a new artificial photosynthetic model; compared to the non-fullerene analogs, the corresponding free base and Zn^{II} chlorin–C$_{60}$ dyads showed a remarkable decrease in their fluorescence intensity, indicating a rapid quenching of the chlorin excited singlet state by the fullerene moiety.

Fullerene C$_{60}$ is one of the most widely studied molecules of the decade.[1] It has been reported as a promising new building block acting as an acceptor in artificial photosynthetic models,[2] and several porphyrin–C$_{60}$ systems have been studied for this purpose.[3] It has been shown that C$_{60}$ acts as an effective primary electron acceptor in a carotene–porphyrin–fullerene triad system, generating long-lived charge separated states with reasonable quantum yields.[4] Recent work by Imahori *et al.* on a C$_{60}$-linked Zn^{II} porphyrin system demonstrate that photoinduced electron transfer rates depend on the nature of linkages between the two chromophores.[5]

Natural chlorin pigments stand in marked contrast to symmetric porphyrin pigments due to substantially stabilized S$_1$ energies, a strong Qy absorption band, and unique redox reactivities. As a result, work is underway in our and various other laboratories to construct chlorin and bacteriochlorin based dimers with variable geometry and distances between the chromophores.[6] In certain fullerene-based electron and energy transfer (ET) models it has been suggested that large and spherical acceptors like C$_{60}$ could show peculiar ET dynamics different from those shown by smaller counterparts such as benzoquinone and pyromellitic diimides, as well as by large π acceptors such as porphyrins and polycondensed aromatic compounds.[5] We believe that the synthesis of such chlorin–fullerene dyads with various spacers should provide valuable information for a deeper understanding of electron-transfer in photosynthetic reaction centers.

As a part of our research program to establish new methodologies for preparing such systems, the metathesis reaction caught our attention because of its unique ability to form C–C bonds. In recent years the applications of this approach have dramatically increased due to the availability of well-defined catalysts, in particular, Grubbs' catalyst Cl$_2$(PCy$_3$)$_2$Ru=CHPh (Cy = cyclohexyl).[7] However, olefin metathesis has rarely been used in porphyrin chemistry. The only applications reported are those in which ligand metathesis has been used for preparing metalloporphyrins.[8]

Recently, Mori and co-workers reported a novel 1,3-diene synthesis from alkynes and ethylene by ruthenium-catalyzed enyne metathesis.[9] We thought it worthwhile to extend this methodology to the preparation of chlorin–fullerene conjugates *via* a sequence of enyne metathesis and Diels–Alder reactions.

For our studies, purpurin-18 methyl ester **1** was used as a starting material.[10] As shown in Scheme 1, reaction of **1** with propargylamine in toluene at 80 °C for 6 h produced propargylimide derivative **2** in 80% yield, which was used as a

substrate for enyne metathesis. Treatment of the CH$_2$Cl$_2$ solution of **2** with Grubbs' catalyst (10 mol%) under ethylene gas atmosphere for 48 h at room temperature afforded the desired chlorin–diene building block **3** in 40% yield (on the basis of the starting material recovered, the yield was 100%). The structures of the intermediate chlorins **2** and **3** were confirmed by ^{1}H NMR and FAB mass spectometry analyses [*m/z* 616.7 and 644.6 (M + 1) respectively, exact mass calculated for compound **3** (C$_{39}$H$_{41}$N$_5$O$_4$): 643.3158, found: 644.3150 (M + 1)]. On comparing the resonances observed for **2** and **3**, the *N*-CH$_2$ protons which appeared as a singlet in diene **3** (δ 5.31, 2H) were observed as a multiplet (δ 5.29, 2H) in propargylimide **2** due to long range coupling with the acetylene proton.
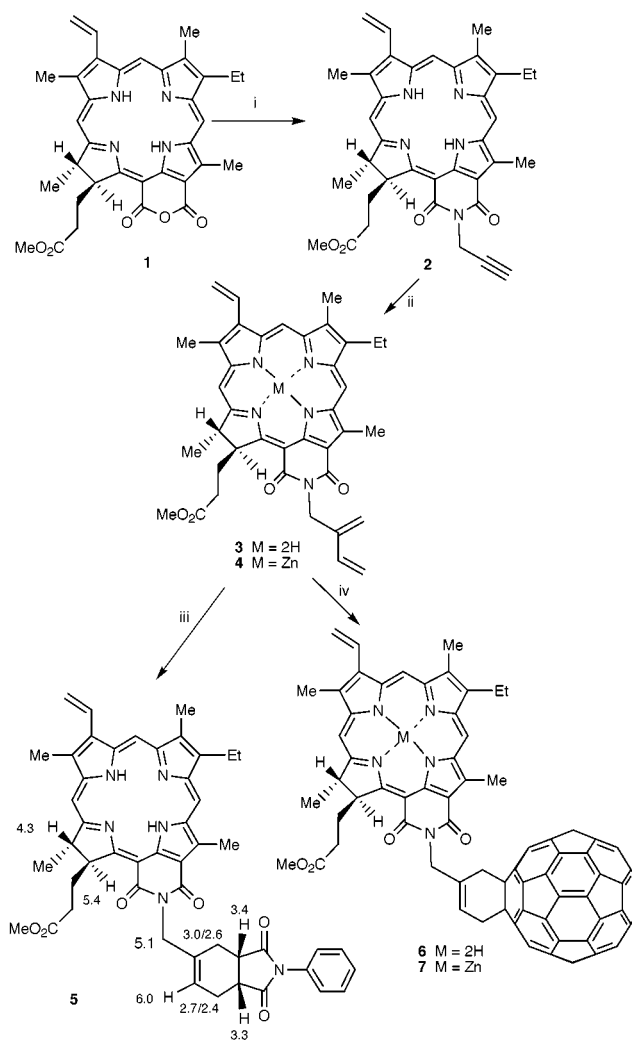
Scheme 1 *Reagents and conditions*: i, NH$_2$CH$_2$C≡CH, toluene, 80 °C, 6 h; ii, Grubbs's catalyst, CH$_2$=CH$_2$, CH$_2$Cl$_2$, 48 h; iii, *N*-phenylaleimide, toluene, reflux, 1 h; iv, C$_{60}$, toluene, reflux, 2 h.
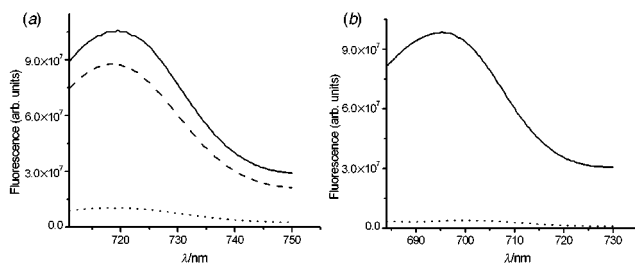
Fig. 1 (*a*) Fluorescence spectra of chlorin **3** (—), chlorin–maleimide **5** (- - -) and chlorin–C_{60} **6** (····) at 5 μmol l^{-1}. (*b*) Fluorescence spectra of Zn^{II} chlorin **4** (—) and Zn^{II} chlorin–C_{60} **7** (····) at 5 μmol l^{-1}.

To establish the reaction conditions needed to obtain chlorin–fullerene dyads, model studies were initially performed by using *N*-phenylmaleimide as dienophile, which is known to have similar reactivity to the fullerene C_{60} system.[11] As expected, reaction of free base chlorin **3** with *N*-phenyl-maleimide in toluene for 1 h at 120 °C produced the corresponding Diels–Alder adduct **5** as a diastereomeric mixture (1:1) in 60% yield. Structural identification of **5** was performed by NMR and mass spectrometry analyses. In the ¹H NMR spectrum, the equal splitting of the CO_2CH_3 protons (17-$CH_2CH_2CO_2CH_3$) clearly indicated the presence of a diastereomeric mixture. Extensive spin-decoupling experiments further enabled us to assign the resonances and the coupling constants attributed to the respective protons. The chemical shift assignments of selected protons for the chlorin–*N*-phenylmalemide conjugate are shown in Scheme 1.

The reaction conditions established for the preparation of the model chlorin conjugate were then followed for the construction of the desired chlorin–fullerene conjugate. The Diels–Alder reaction of diene **3** with fullerene in refluxing toluene for 2 h afforded the chlorin–fullerene dyad **6** in 30% yield. The structure of **6** was confirmed by NMR and mass spectrometry analyses [exact mass calculated for $C_{99}H_{41}N_5O_4$: 1363.3158, found 1364.3160 (M + 1)]. In the ¹H NMR spectrum, the resonances of the newly formed cyclohexene ring system were observed at δ 3.98 (d, *J* = 5.5 Hz, 2H), 4.33 (m, 1H) and 7.22 (t, *J* = 5.5 Hz, 1H). The signals for the cyclohexene CH_2 (δ 4.3, see Scheme 1) and *N*-CH_2 protons appeared as multiplets, each integrating for two protons.

In our attempts to determine the effects of metallochlorins on energy/electron transfer (ET), dyad **6** was converted into the related Zn^{II} complex **7** (λ_{max} 684 nm) in quantitative yield following the standard methodology. The fluorescence spectra of the dyads **5**–**7** were compared with the free base diene **3** and the related Zn^{II}–**4** in CH_2Cl_2 by exciting their corresponding long wavelength absorptions (Qy band).[12] As can be seen from Fig. 1, conversion of diene **3** into the related *N*-phenyl-maleimide adduct **5** had a limited effect on its fluorescence intensity. In contrast, dyads **6** and the Zn^{II} analog **7** containing the fullerene moieties showed a remarkable decrease in fluorescence, indicating a rapid quenching of the chlorin excited singlet state by C_{60}. The electronic absorption spectra of diene **3** and dyad **6** in CH_2Cl_2 and benzene indicate insignificant electronic interactions between the chromophores in the ground state. Detailed photophysical studies, such as fluorescence lifetime measurements, time-resolved transient absorption

spectroscopy and the estimation of energy levels of these newly synthesized compounds, are underway. In order to determine the linkage dependence of photoinduced charge separation (CS) and subsequent charge recombination (CR), the synthesis of a series of chlorin– and bacteriochlorin–fullerene dyads with various spacers of fixed distances and geometry is currently in progress.

In conclusion, we have developed a new approach for the preparation of a versatile chlorin–diene building block **3** *via* ruthenium-catalyzed enyne metathesis. The utility of this highly reactive diene has been demonstrated by preparing new chlorin–fullerene dyads by following the [4 + 2] cycloaddition approach. The novel chlorin–diene building block has great potential for preparing not only promising models for photosynthetic reaction centers, but also for constructing a wide variety of porphyrin-based compounds of other biological significance.

Notes and references

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12 Excitation wavelengths: chlorin **3**, 707 nm; Zn^{II} chlorin **4**, 680 nm; chlorin–maleimide **5**, 707 nm; chlorin–C_{60} **6**, 710 nm and Zn^{II} chlorin–C_{60} **7**, 683 nm. Compared to diene **3**, the fluorescence of dyad **6** in CH_2Cl_2 and benzene solution was quenched by 88 and 63%, respectively, indicating a significant interaction between the chlorin and fullerene moieties.

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