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Purpurinimide–Fullerene Dyads: Introduction of Fullerene Moiety at Various Peripheral Positions of the Purpurinimide System

Guolin Li,[†] Mahabeer P. Dobhal,[†] Masayuki Shibata,[§] and Ravindra K. Pandey*,[†,‡]

Photodynamic Therapy Center and the Department of Nuclear Medicine and
Radiology, Roswell Park Cancer Institute, Elm & Carlton Streets,
Buffalo, New York 14263, and Department of Health Informatics,
UMDNJ-SHRP, 65 Bergen Street, Newark, New Jersey 07107

ravindra.pandey@roswellpark.org

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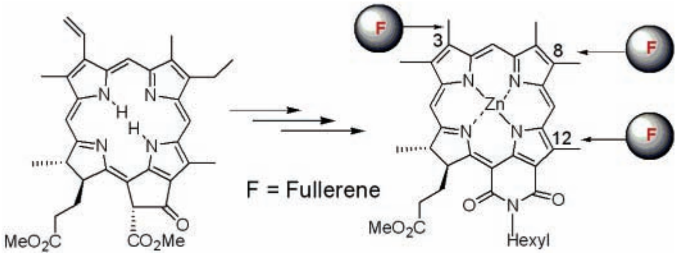
ABSTRACT



Fullerene was regioselectively introduced at various peripheral positions of *N*-hexyl-purpurinimide for photoinduced electron transfer studies. Remarkably different effects of the position of the fullerene moiety in the formation of atropisomers were observed.

Investigation of photoinduced electron transfer (ET) in a natural photosynthetic reaction center (RC) by developing a donor−acceptor (DA) system has brought tremendous interest in recent decades.[1] A large number of donor−acceptor dyads, tryads, or more complex systems have been synthesized, and their electron-transfer properties have been studied.[1] Compared to other electron acceptors such as quinone and its analogues, fullerene has many merits including highly delocalized π electron systems over a rigid three-dimensional surface and a remarkably small reorganization energy of charge separation.[2] As for electron donors, porphyrin has dominated literature for quite some time, and one apparent reason to choose porphyrin is that it has 22 highly delocalized π electrons, which upon receipt or release of an electron results in minimal structural and solvation changes during electron transfer.[3] However, instead of porphyrin, the natural RC utilizes chlorin (a type of reduced porphyrin with 20 delocalized π electrons) or bacteriochlorin (a type of reduced porphyrin with 18 delocalized π electrons) as pigments. A literature research revealed that some chlorin−fullerene systems have been prepared,[2c,4] but only a few of these systems have fixed geometry, which could

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[†] Photodynamic Therapy Center.

[‡] Department of Nuclear Medicine and Radiology.

[§] UMDNJ-SHRP.

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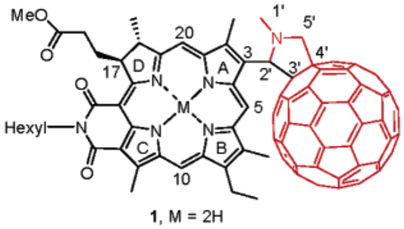
be an extremely important factor for affecting electrochemical and photochemical properties.[4a,e,g,j]

Recently, we investigated the photophysical characteristics of a series of bacteriochlorin− and chlorin−fullerene dyads.[2c,4c,4f,5] Among these compounds, the Zn(II) purpurinimide−fullerene dyad in which the fullerene moiety was introduced at position 3 of the macrocycle produced an unexpected ultralong charge separation (CS) state, up to 120 s, at −150 °C without any loss of energy, which is inevitable for the charge separation via multistep electron-transfer processes.[5] Encouraged and excited by this remarkable result, our objective was to regioselectively introduce a fullerene moiety at the various peripheral positions of the purpurinimide system and compare their photophysical properties with our lead compound.

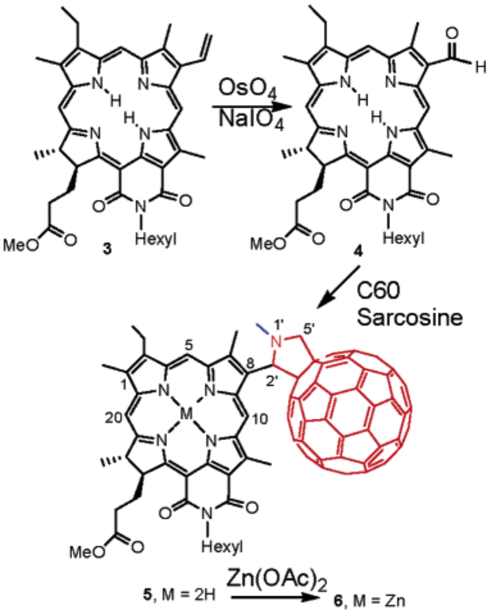


1, M = 2H
2, M = Zn

Figure 1. Structures of lead compounds **1** and **2**.

The ^{1}H NMR spectrum of our lead compound **1** showed four sets of signals in a ratio of 1:1:0.6:0.6, indicating the presence of four molecular species in the solution. These species apparently represent a pair of diastereomers and a pair of atropisomers of each diastereomer, differing in the orientation of the fullerene molecule with respect to the methyl propionate side-chain (ring D) of the purpurinimide system. The formation of two diastereomers is apparently a result of the newly formed chiral center at position 2′, while the atropisomerism arises from the short linkage between the fullerene and the chlorin ring, which restricts free rotation of the bulky ball. Such phenomena had previously been reported by Helaja et al.[4a] in phytochlorin−fullerene dyads.

Scheme 1



To compare the effect of the fullerene moiety at position 8 or 12 of the purpurinimide system with our lead compound **1** and the related Zn(II) complex **2**, 8-formyl- and 12-formyl purpurinimides **4** and **9**, respectively, were used as the substrates. For the preparation of 8-fullerene−purpurinimide dyad **5**, the purpurin-18-*N*-hexylimide methyl ester **12** was converted into the corresponding 8-vinyl derivative **3** by following the methodology developed in our laboratory.[6] Treatment of 8-vinyl-purpurinimide **3** with $OsO_4/NaIO_4$ with subsequent reaction with fullerene produced the desired purpurinimide−fullerene dyad **5** in 34% yield. The ^{1}H NMR spectrum of dyad **5** was quite similar to that of dyad **1** and also indicated the presence of four molecular species but with a different ratio of 1:1:0.3:0.3. However, we were able to separate the two possible atropisomers in dyad **5** by preparative silica TLC using 1% EtOAc−$CHCl_3$ as developing solvent, but a slow exchange between these two atropisomers was observed in solution at room temperature and was confirmed by TLC and NMR spectroscopy. For example, in the ^{1}H NMR spectra of the fast-moving isomers of dyad **5**, the ratio of the singlets at δ 6.57 and 6.52 ppm after leaving at room temperature (20 °C) for 0.5 h was 1:3.7 (the two singlets were assigned to 2′-H based on 2D NMR studies). Leaving the reaction for a longer period of time produced a significant difference in the ratio of the isomers. For example, it was 1:1.3 at 2 h, 1:0.6 at 5 h, and 1:0.3 at 17 h (see Supporting Information). No further exchange was observed

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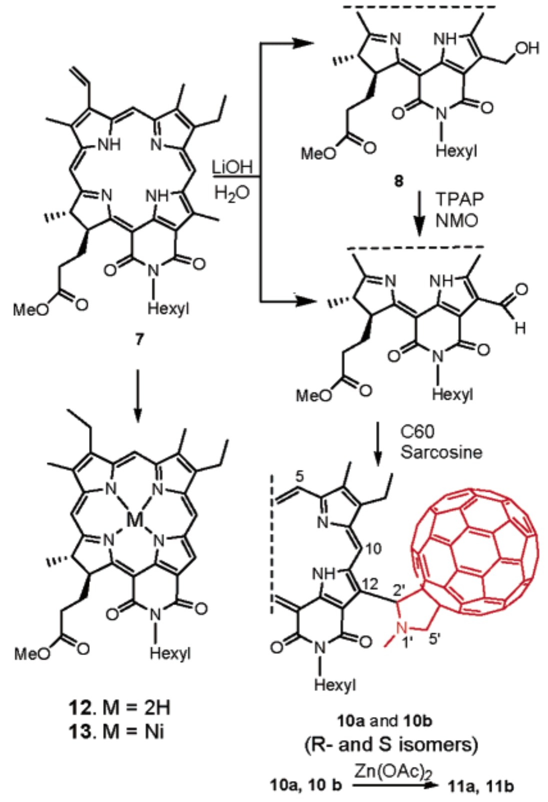
beyond this time. Similar results were obtained on performing the same study with the slow-moving isomers.

For the preparation of the dyad in which the fullerene moiety was introduced at position 12, purpurinimide **7** was successively treated with $LiOH{\cdot}H_2O$ in the presence of oxygen (exposure of the reaction mixture to air) and CH_2N_2 to produce a mixture of the 12-hydroxymethyl derivative **8**[7] (33% yield) and 12-formyl derivative **9**[7] (26% yield). Oxidation of **8** with TPAP/NMO (TPAP = tetrapropylammoniumperruthenate; NMO = 4-methyl morpholine *N*-oxide)[8] gave **9** in 65% yield. Reaction of **9** with fullerene by following the procedure described for dyads **1** and **5** gave a mixture of purpurin−fullerene dyads **10a** and **10b** in 27% yield. By following the standard column or preparative chromatography techniques, these two isomers were extremely difficult to separate. However, on realizing a significant difference in solubility of these two isomers, **10a** and **10b** were easily separated into individual isomers (for details, see Experimental Section in Supporting Information). The ^1H NMR spectra of **10a** and **10b** showed a very close resemblance (solvent, $CS_2/CDCl_3 = 2/1$), and only one set of signals in their ^1H NMR spectra was observed. Unlike dyads **1** and **5**, which were obtained as a mixture of four isomers, dyads **10a** and **10b** were found to be distereomeric and no atropisomerism was observed. Comparing the downfield region of the ^1H NMR spectrum of **10a** or **10b** with that of dyad **5**, it clearly indicated that dyad **5** is a mixture of four isomers, whereas dyads **10a** and **10b** are single isomers. For example, in the ^1H NMR spectrum of **5**, 10-H appears at δ 11.58, 11.56, 9.94, and 9.89 ppm, which correspond to its four isomers. Comparing the chemical shift of 10-H ($\delta = 9.62$ ppm) in chlorin **12** (the corresponding chlorin without fullerene) with that of dyad **5**, a significant difference in downfield shifts ($\Delta\delta = 1.96$, 1.94, 0.32, and 0.27 ppm), caused by the deshielding effect of the fullerene moiety, indicates the differences in the degrees of proximity of this proton relevant to the bulky ball in four isomers. In the ^1H NMR spectrum of **10a** or **10b**, only one singlet at δ 11.62 ppm was observed for 10-H. Comparing chlorin **12** to the ^1H NMR spectral data of chlorin **7**, the large downfield shift of 10-H in these two isomers ($\Delta\delta = 2.03$ ppm) indicates the fullerene moiety positions close to the 10-H as shown in Scheme 2. The CD (circular dichroism) spectra of **10a** and **10b** are shown in Figure 2 and were similar to those expected from a pair of enantiomers (Figure 2). Efforts to confirm the stereochemistry of isomers **10a** and **10b** on the basis of extensive NMR analyses (COSY, ROESY studies) were not conclusive. Thus the following computational modeling study was performed to identify the 3D structure of isomers **10a** and **10b**.

Scheme 2



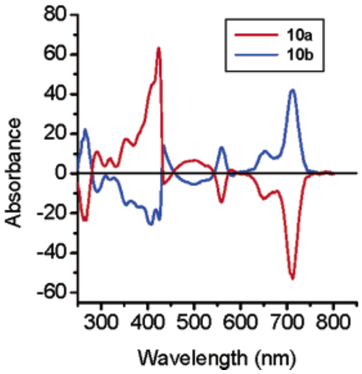


Figure 2. CD spectra of dyads **10a** and **10b** (26 μM in $CHCl_3$).

Preliminary computational results at the semiempirical level for compounds **1**, **5**, and **10** revealed that four isomers can exist for all of the compounds, similar to what was found for the phytochlorin−fullerene dyad by Helaja et al.[4a] It is interesting to note that overall structure and its characteristics are similar to those found for the crystal structure of pyrrolidine-linked tetraphenylporphyrin−fullerene dyad. One of the possible isomers for the dyad **10** is shown in Figure 3 where it is shown that the fullerene ring is placed in a proximity to C10−H of purpurinimide, in agreement with the ^1H NMR experiments. Atropisomers are the consequence of significant torsional barrier along the rotation of a single bond. The structural characteristics contributing to the torsional barrier on the one side of the dyads **10**, namely,

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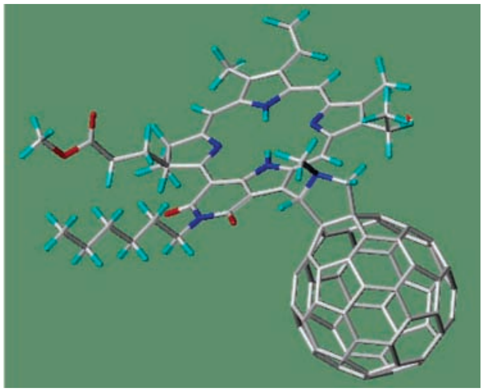

Figure 3. Structure of dyad.

the C10−H side, is identical to the structures found in dyads **1** and **5** in C5−H side and C10−H side, respectively. Compared to dyads **1** and **5**, for the dyads **10** the presence of a fused six-member imide ring with carbonyl substituents severely restricts the rotation of fullerene moiety along the C12−C2′ bond on this side of the molecule, whereas this obstacle is absent for the dyads **1** and **5**. Thus, certainly, the rotation along the C12−C2′ bond is much more restricted than that along the C3−C2′ and C8−C2′ bonds in dyads **1** and **5**, respectively. However, whether this restriction and a possible slightly larger energy difference between the atropisomers of **10** are sufficient to explain the most intriguing observation, namely, the apparent absence of atropisomers for dyads **10** despite the use of the same synthetic procedure, requires further investigation.

Thus another computational analysis was performed by examining the role of the intermediate state, or azomethine ylides, in the formation of 1,3 dipolar cycloaddition product. Various orientations of azomethine ylide moiety with respect to the chlorine ring are examined for the 12 position derivatives. The results at a semiempirical level showed that some configurations are not physically possible because the azomethine ylide moiety is too close to the chlorin ring.

In addition, because the 1,3-dipolar cycloaddition is a concerted reaction controlled by a HOMO (dipole)−LUMO (dipolarophile) or a LUMO (dipole)−HOMO (dipolarophile) interaction, we also examined the orientations of the HOMO/LUMO of ylides. The results indicate that some ylide structures are not suitable for the reaction because they leave no room for a bulky dipolarophile to approach. Thus it is possible that the presence of the fused imide ring will severely restrict the number of ylide structures utilized for 1,3 dipolar addition reaction among otherwise energetically viable structures, which prevents a formation of certain isomers. Unfortunately, the definite conclusion must await more sophisticated calculations including the determination of transition states and the reaction path.

For investigating the photophysical characteristics of metalated versus nonmetalated analogues, dyads **5**, **10a**, and **10b** were converted into the corresponding Zn(II) complexes **6**, **11a**, and **11b**. Compared to the fluorescence spectra of free base purpurinimides and the related zinc complexes, the corresponding purpurinimide−fullerene dyads exhibited a remarkable decrease in fluorescence intensity. The fluorescence intensity decreased by 74% from the free base purpurinimide **12** to the related fullerene dyad **1**, while from the zinc complex of purpurinimide **12** (i.e., compound **13**) to the related fullerene dyad **2** (i.e., Zn(II) complex of dyad **1**), a 98% decrease in fluorescence intensity was observed (Figure 4). Similar phenomena was also observed for dyads **5**, **6**, **10a**, **10b**, **11a**, and **11b**. These results indicate a rapid quenching of the chlorin excited singlet state by the fullerene moiety. The detailed photophysical studies (such as fluorescence lifetime measurements, time-resolved transient absorption spectroscopy, and the estimation of energy levels) of these novel structures are underway.

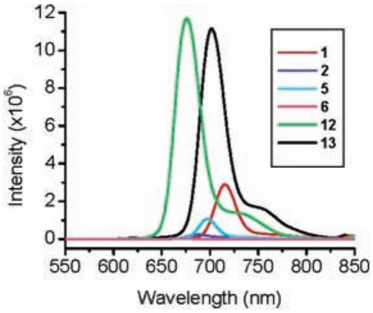

Figure 4. Fluorescence spectra of dyads **1**, **2**, **5**, and **6** and chlorins **12** and **13** (1.0 μM in $CHCl_3$). Excitation wavelengths: for **1**, 421 nm; **2**, 427 nm; **5**, 426 nm; **6**, 431 nm; **12**, 423 nm; **13**, 418 nm.)

In summary we have developed an efficient methodology for the introduction of a fullerene moiety at various peripheral positions of the purpurinimide system. The formation of only one atropisomer in purpurinimide−fullerene dyad **10** in which the fullerene is attached at position 12 is quite interesting. Although we were able to isolate both stereoisomers in pure form, the stereochemistry of the individual isomers could not be defined. Attempts are underway to crystallize these dyads for X-ray analyses.

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Supporting Information Available: The material is available free of charge via the Internet at http://pubs.acs.org.

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