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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF A NOVEL PARACHUTE-SHAPED C₆₀-PORPHYRIN DYAD

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Abstract: A novel covalently linked C₆₀-porphyrin dyad has been prepared by cyclopropanation of C₆₀ with a strapped porphyrin malonate. Its fluorescence spectra show strong quenching of the porphyrin singlet excited state by the attached C₆₀.

INTRODUCTION

Photosynthetic model systems rely on spatially organized units with suitable photochemical and electronic properties. Recently much attention has been focused on using C₆₀ as an electron acceptor in donor-acceptor molecular systems due to its unique shape and redox properties (1,2). Our group has previously reported the synthesis and photophysical studies of a number of C₆₀-porphyrin hybrids (1). To continue this project aimed at studying interactions between the two chromophores in covalently linked C₆₀-porphyrin dyads with flexible and rigid tethers, we became interested in the synthesis of a novel parachute-shaped dyad in which the two π -systems are in a face-to-face arrangement.

The dyad **5** was synthesized in a total of 11 steps using the strapped porphyrin strategy (3). The major transformations are shown in Scheme 1. Esterification of 2-(3-hydroxypropyl)benzaldehyde with malonyl dichloride gave compound **2**. Condensation of the dialdehyde with 4 equiv. of benzyl 3,4-diethylpyrrol-2-carboxylate yielded compound **3**. Hydrogenation of **3** followed by reaction with methyl orthoformate catalyzed by trichloroacetic acid led to strapped porphyrin **4**, which was separated in 15% yield by flash column chromatography (silica gel, CH₂Cl₂-MeOH 20:1) after the insertion of zinc. The zinc porphyrin malonate was then attached to C₆₀ via Bingel cyclopropanation (4) accomplished by the action of I₂ and DBU. The dyad **5** was isolated in 40% yield from the reaction mixture by preparative TLC (silica gel, CH₂Cl₂-MeOH 25:1).

RESULTS AND DISCUSSIONS

Structure characterization

The structure of dyad **5** was confirmed by spectral data including ^1H , ^{13}C , UV/Vis and MALDI-TOF mass spectra. The ^1H NMR spectrum in CDCl_3 exhibits the expected features with correct integration ratios, which is similar to the spectrum of porphyrin **4** except for the disappearance of the two protons on the methylene carbon between the two carbonyl groups. The ^{13}C NMR spectrum of **5** shows a single resonance (δ 71.28) for the two sp^3 carbon atoms on the C-sphere, 25 of the 28 resonances in the region δ 97.0-160.0 arising from the sp^2 carbon atoms of the C_{60} moiety and the porphyrin as well as a resonance (δ 161.55) for the malonate carbonyl groups, clearly demonstrating that dyad **5** has C_{2v} symmetry. Interestingly, a dyad made from $^3\text{He}@C_{60}$ shows a resonance at -8.5 ppm relative to ^3He gas in ^3He NMR spectrum, whereas a typical 1,2-[di(ethoxycarbonyl)methano]-1,2-dihydro[60]fullerene **6** made from $^3\text{He}@C_{60}$ shows a peak at -8.1 ppm (**5**). The upfield shift is attributable to the shielding effect of the porphyrin ring current.

Electrochemical properties

In order to estimate the energies of charge-separated states formed after excitation, the first oxidation potential of the porphyrin moiety and first reduction potential of the C_{60} are required. They were determined by cyclic voltammetric experiments with dyad **5** in CH_2Cl_2 solution. Cathodic scans reveal the first reduction of the C_{60} moiety of zinc dyad **5** occurs at -1.09 V and the second at -1.45 V vs Fc/Fc^+ , which are ~ 30 mV more negative than those of the model C_{60} compound **6**. Anodic scans give the first oxidation potential of the porphyrin in the same dyad at $+0.13$ V, which is ~ 50 mV more positive than that of zinc porphyrin **4**. Similar shifts were also observed in the CV of metal-free dyad **5**. One can invoke interactions between the C_{60} and the porphyrin in the dyads to explain these observations. However, the actual mechanisms are not clearly understood.

Steady-state absorption spectra

The UV-vis spectrum of the dyad **5** displays strong absorption bands due to both the porphyrin and fullerene moieties. Figure 2 shows the UV-vis spectra of dyad **5** in CH_2Cl_2 together with that of porphyrin **4** and the model fullerene compound **6** for comparison. Since the porphyrin dominates the visible region whereas C_{60} dominates the UV region, the electronic spectrum of **5** is a virtual superimposition of the two independent chromophores present in the molecule, indicating no appreciable ground state interaction between the two π systems.

Steady-state fluorescence spectra

In CH_2Cl_2 , free base porphyrin **4** has fluorescence maxima at 635 nm and 698 nm. The metal-free dyad **5**, excited at 580 nm, shows an emission spectrum with characteristic features of the porphyrin. However, the porphyrin emission is efficiently quenched by the attached C_{60} by a factor of 70. Similarly, the zinc porphyrin emission is strongly quenched by the C_{60} by a factor of 100 in zinc dyad **5** (Figure 3).

Time-resolved fluorescence studies

Additional information concerning the fate of the excited states of the dyad **5** was obtained from time-resolved fluorescence studies carried out by a single-photon counting method. A solution of zinc-containing dyad **5** in benzene was excited at 550 nm, and emission time profiles were collected at 587, 644 and 704 nm. Global analysis yielded two exponential decay components with lifetimes of 9 and 45 ps. However, the model fullerene **6** and the zinc porphyrin **4** have singlet lifetimes of 1.3 and 1.8 ns, respectively, in this solvent. Thus, both the porphyrin and C_{60} singlet states in the dyad are strongly quenched. Similar experiments were carried out with free-base dyad. The decay curves were fitted by two exponential decays with lifetimes of 14 and 57 ps, also indicating a strong quenching of singlet states of both the porphyrin and C_{60} . Similar results were obtained in using THF as solvent. These data suggest that in both polar and nonpolar solvents lowest singlet excited states of the porphyrin in the dyads are quenched by electron transfer to the C_{60} . This decay pathway needs to be further confirmed by transient absorption studies.

Determination of the quantum yield of singlet oxygen production

The treatment of various cancers by photosensitization in the presence of oxygen, known as photodynamic therapy (PDT), has been an active field of investigation since the early 1970's. It is generally agreed that singlet oxygen is the key agent of cellular damage. Ever since it was discovered that the efficiency of formation of $^1\text{O}_2$ upon electronic excitation of C_{60} was essentially unity, potential application of fullerenes in PDT were considered. C_{60} -porphyrin compounds provide new opportunities to overcome two major problems of directly using C_{60} as a sensitizer in PDT, namely, limited solubility in aqueous media and small absorption in the red end of the visible spectrum. We are interested in the formation of $^1\text{O}_2$ upon irradiation of our parachute-shaped C_{60} -porphyrin dyad.

The singlet oxygen quantum yields (Φ_Δ) were determined by the comparative method using 5,10,15,20-tetraphenylporphyrin (TPP), $\Phi_\Delta(\text{CH}_2\text{Cl}_2)=0.8$, $\Phi_\Delta(\text{toluene})=0.67$, as the standard. In CH_2Cl_2 , both free-base dyad **5** and zinc dyad **5** have singlet oxygen quantum yields less than 0.01; whereas in toluene, singlet oxygen quantum yield of free-base dyad is 0.22 and that of zinc dyad is less than 0.01. These results are consistent with the results obtained from time-resolved fluorescence studies.

CONCLUSIONS

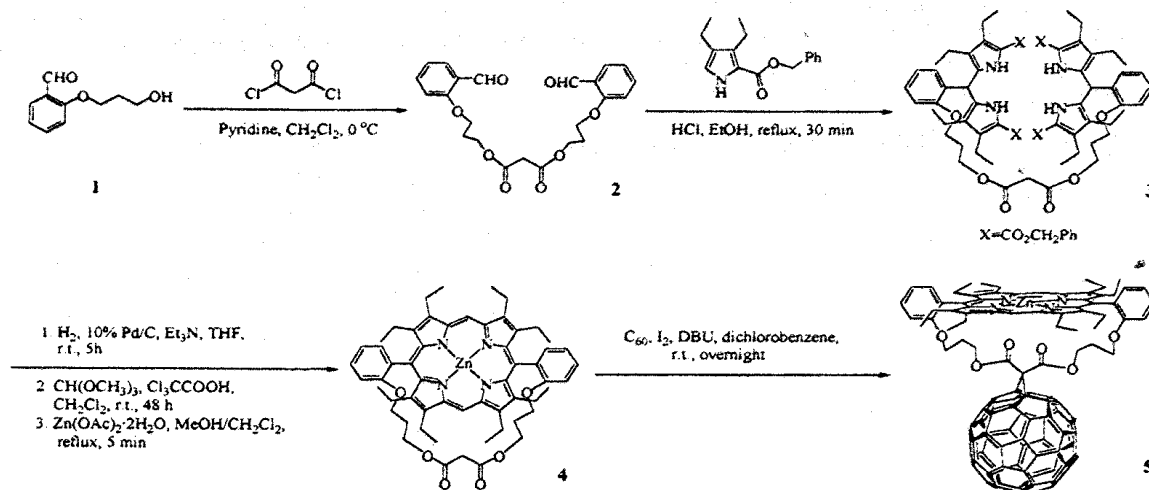
We have synthesized a novel covalently linked C₆₀-porphyrin dyad whose structure resembles the shape of a parachute. The steady-state fluorescence studies indicate that the singlet excited state of the porphyrin in the dyad is strongly quenched by the attached C₆₀. The detailed photodynamics studies of this dyad are still underway and the results will be reported in due course.

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Scheme 1. Synthesis of the parachute-shaped C_{60} -porphyrin dyad

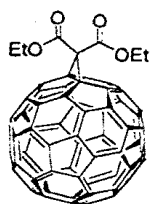


Figure 1. Structure of 1,2-[di(ethoxycarbonyl)methano]-1,2-dihydro[60]fullerene

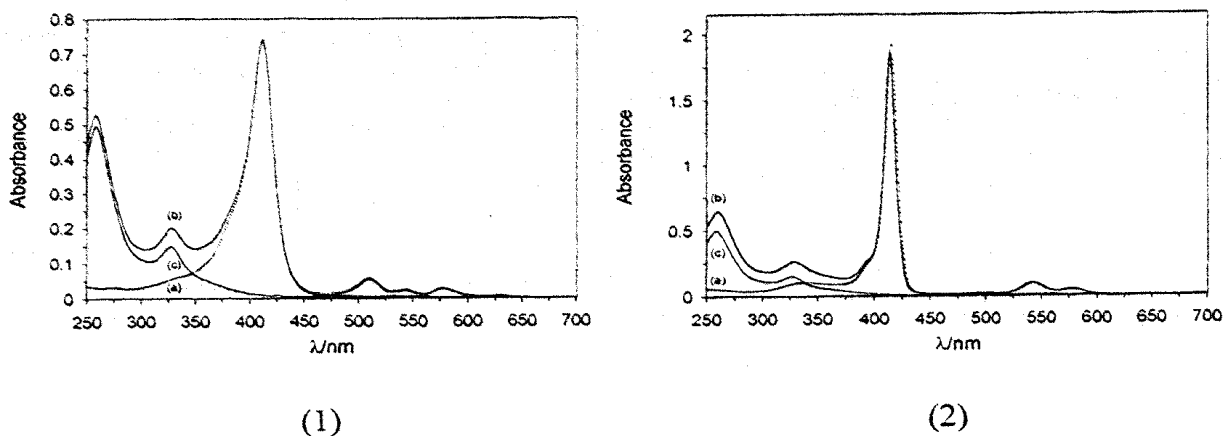


Figure 2. (1) UV-vis spectra of (a) free base porphyrin **4**, (b) free base dyad **5** and (c) **6** in CH_2Cl_2 ($5.0 \times 10^{-6} \text{ mol dm}^{-3}$);
 (2) UV-vis spectra of (a) zinc porphyrin **4**, (b) zinc dyad **5** and (c) **6** in CH_2Cl_2 ($5.0 \times 10^{-6} \text{ mol dm}^{-3}$)

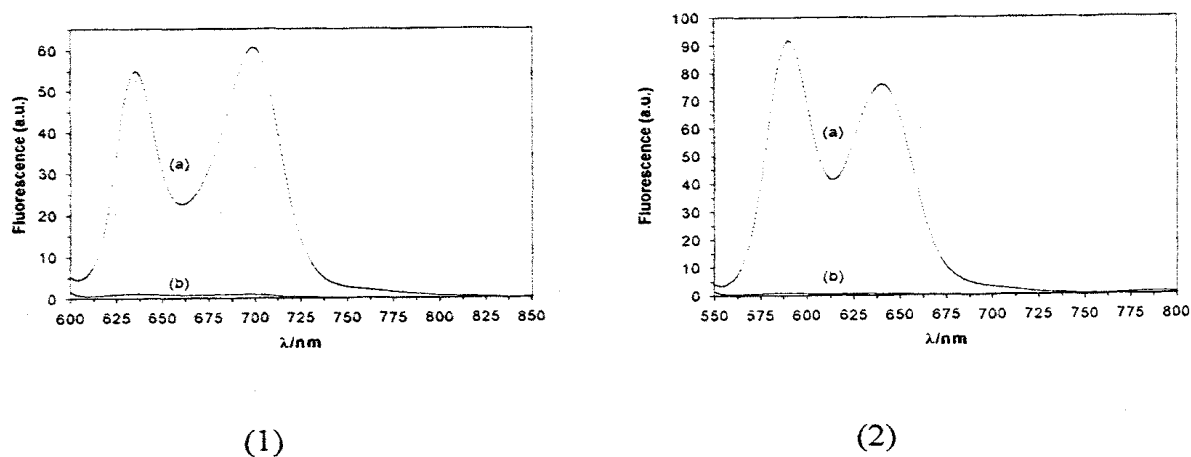


Figure 3. (1) Fluorescence spectra of (a) free base porphyrin **4** and (b) free base dyad **5** in CH_2Cl_2 ($5.0 \times 10^{-6} \text{ mol dm}^{-3}$, excited at 580 nm);
 (2) Fluorescence spectra of (a) zinc porphyrin **4** and (b) zinc dyad **5** in CH_2Cl_2 ($5.0 \times 10^{-6} \text{ mol dm}^{-3}$, excited at 530 nm)