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Synthesis of new porphyrin/fullerene supramolecular assemblies: a spectroscopic and electrochemical investigation of their coordination equilibrium in solution

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ABSTRACT

Two new fullerene ligands have been designed to provide relatively simple frameworks to build supramolecular systems containing both fullerene and Zn-porphyrin moieties. The coordination of the fullerene ligands to the Zn-porphyrin was supported by UV–vis titration, nuclear magnetic resonance and electrochemical data. The resulting spectrophotometric data were processed both graphically and computationally to yield the stoichiometry, stability constant, and molar absorptivity of the species in equilibrium.

1. Introduction

Porphyrin/fullerene systems and dyads have been extensively studied to examine donor/acceptor interactions.[1,2] Donor/acceptor interactions within fullerene/porphyrin assemblies are important for the design of multi-component model systems for photoactive materials[3] and light-harvesting devices.[4] Thus, chemists have increasingly sought to develop relatively simple donor/acceptor systems. Since Liddell and co-workers[5] reported the first synthesis of a C_{60} derivative covalently linked to a porphyrin, various other fullerene/porphyrin dyads have been synthesized based on covalently linked components.[6,7] Another attractive route to prepare such supramolecular assemblies has been the coordination of appropriately functionalized fullerene derivatives to metalloporphyrins, such as those containing zinc[8,9] or magnesium[10] as the metal center. In the latter route, the fullerene has often been functionalized with an *N*-heteroaromatic moiety. This metal/ligand coordination strategy provides a simple and versatile way to construct electron donor/acceptor assemblies, which may be of interest as mimics of the efficient biological electron transfer systems.[7]

With respect to the synthetic aspects, most of the fullerene ligands reported to date have been prepared by the functionalization of C_{60} in various steps in low-to-moderate yields. The prevailing strategy for the synthesis of fullerene ligands is via cycloaddition reactions.[11,12] For example, D'Souza and co-workers have synthesized fullerene ligands via [3+2] cycloadditions of azomethine ylides and C_{60}.[13,14] More recently, Deye and co-workers have designed a new ligand based on the Diels–Alder functionalization of C_{60}.[15] A less frequently used method to obtain fullerene ligands employs the Bingel's cyclopropanation reaction, which consists of the reaction of active methylene compounds with C_{60}.[16,17] The search for new fullerene/porphyrin supramolecular systems prompted us to design new functionalized fullerene ligands via the Bingel–Hirsch cyclopropanation of C_{60} and to evaluate the ability of these new ligands to assemble with a simple Zn-porphyrin, 5,10,15,20-tetraphenylporphyrinatozinc(II) (Zn(TPP)).

The accurate determination of the equilibrium constants (K) associated with dyad formation is often required in various chemical, biochemical, and pharmaceutical settings. In previous work, such constants for fullerene/porphyrin interactions have been determined by ^{1}H NMR,[18] UV–vis,[8,10,13,14,16,17,19] and fluorescence[9,10,17,18,21] spectroscopies. Whereas spectrophotometry has been the method of choice due to its simplicity, low cost, ease of adaptation, and high sensitivity (which allows the use of concentrations as low as 10^{-6} mol L^{-1}), it has also been limited to systems with minimal chromophore absorbance overlap.

In this contribution, we utilize a multiwavelength, multiple regression procedure for the determination of the equilibrium

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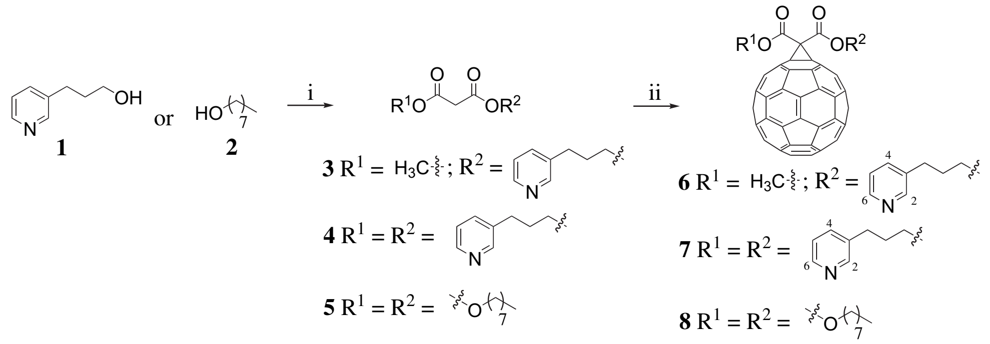
constant of complex absorbing mixtures in Zn-porphyrin/fullerene systems. Our protocol employs a computational approach rather than the usual graphical methods for treating spectrophotometric titration data; the software of choice was SQUAD (Stability Quotients from Absorbance Data).[22] This program is capable of calculating simultaneously, or individually, overall stability constants for any species formed in studied systems, as long as the species contributes to the total absorbance measured.[22] Early studies confirmed the ability of the program to evaluate the correctness of the equilibrium model proposed and the values of the refined equilibrium constants.[22] To the best of our knowledge, fullerene/porphyrin assembly coordination equilibrium data have been processed by only one computational (multiple regression) means.[17,20]

2. Results and discussion

2.1. Synthesis

The strategy explored for the preparation of the fullerene derivatives **6**, **7**, and **8** was based on a Bingel-type reaction (Scheme 1).[23,24]

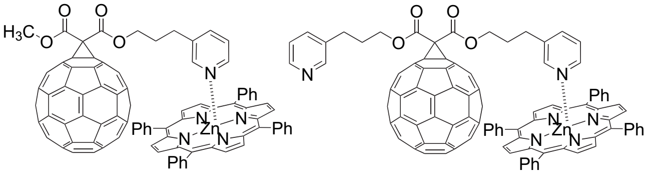


Scheme 1. Preparation of fullerene derivatives **6**, **7**, and **8**. Reagents and conditions: (i) methyl malonyl chloride or malonyl dichloride, pyridine, THF, room temperature, **3** (2 h, 83%), **4** (5 h, 57%), **5** (5 h, 74%); ii) C_{60}, I_2, DBU, toluene, room temperature, 8 h, **6** (50%), **7** (40%), **8** (50%).

The commercial alcohol **1** was esterified with commercial methyl malonyl chloride or malonyl dichloride in pyridine/THF mixtures at room temperature to yield the malonates **3** or **4** in 83% or 57% yield, respectively. The reaction of C_{60} with **3** or **4**, I_2, and DBU in toluene at room temperature afforded mono-adducts **6** or **7** in 50% or 40% yield, respectively, after purification by column chromatography. The advantages of this synthetic method for the preparation of the new compounds **6** and **7** include the overall simplicity of the procedure and the ready availability of the starting materials; additionally, this methodology can be easily adapted for the synthesis of other functionalized fullerenes. The fullerene derivative **8**, which does not contain the pyridyl moiety, was obtained from 1-octanol via the same method used for the synthesis of **6** and **7** (Scheme 1).

The applicability of the resulting compounds in supramolecular chemistry is demonstrated below by their ability to engage in coordination-type assemblies with metal complexes in solution, e.g., fullerene/Zn-porphyrin adducts. As a proof of concept, a study was undertaken to evaluate the ability of these new ligands **6** and **7** to assemble with Zn(TPP), to yield the corresponding Zn-porphyrin/fullerenes (Fig. 1) via the coordination route.

The structure and purity of the compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy (the spectra of the fullerene ligands are available in the Supplementary data). The ^{13}C NMR spectra of the fullerene ligands showed the characteristic signal[25] of the sp^3-hybridized fullerene C-atoms in the cyclopropane ring at ca. 71 ppm and the signals between 139 and 145 ppm corresponding to the sp^2-hybridized carbons of the fullerene sphere. The methano bridge signal was observed at 52 ppm. The molecular composition and the purity of the fullerene ligands **6** and **7** are also confirmed by ultra-high-resolution Fourier-transform mass spectrometry with electrospray ionization. Molecular masses of all isotopologue ions within the $[M+H]^+$ clusters agree well with calculated values.



Zn(TPP)/6 **Zn(TPP)/7**

Fig. 1. Structures of the 1:1 supramolecular complexes investigated in the present study.

2.2. Spectrophotometric titration

Zn-porphyrins are well-established, suitable spectroscopic probes for studying Lewis acid/base-type coordination equilibria in solution. The Zn(TPP) UV–vis absorption spectrum in hydrocarbon solvents, such as toluene, is characterized by a strong Soret band (λ=423 nm, in toluene) and a weaker Q band (λ=550 nm, in toluene). In the presence of a nitrogen/ligand (L), a rapid Lewis acid/base equilibrium is established to yield the Zn(TPP)/L adduct (ML) (where M=Zn(TPP) and L=ligand), according to Eq. 1. The formation of the ML species is accompanied by a red-shift of the Soret and the Q bands in a concentration-dependent manner, which makes UV–vis spectroscopy a suitable technique to study such systems. The spectrophotometric data are often analyzed graphically by a classical Benesi–Hildebrand (B–H) plot, given that there are only two absorbing species in equilibrium (i.e., M/ML or L/ML). Although this is usually the case for simple pyridine derivatives, fullerene-functionalized pyridines (such as **6** and **7**) absorb in the UV–vis region, which yields three chromophores (M, L, and ML) simultaneously in equilibrium and precludes the direct use of the B–H-type of analysis. To overcome these analytical issues, previous studies[8,10,17,18,20,21,26] on the coordination equilibrium of fullerenes to metalloporphyrins in solution are based on fluorescence data instead of UV–vis spectroscopy, as the fluorescence of Zn(TPP) (M) is quenched in a concentration-dependent manner by a non-fluorescent ligand (fullerene, L) to yield a non-fluorescent adduct (ML). We show here that the supramolecular assembly of functionalized fullerenes and Zn porphyrins may be conveniently measured by UV–vis spectrophotometry even in the case of strongly absorbing fullerene species, given that the data are appropriately treated by a multiwavelength spectrophotometric titration processing program, such as SQUAD. It is worth noting that, as