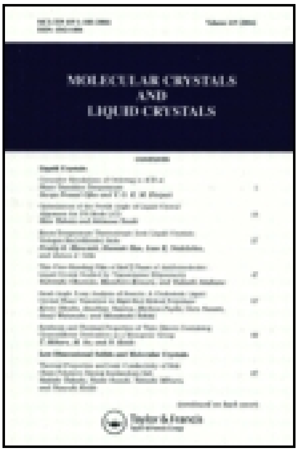

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Inclusion Properties of a New Metallo-Porphyrin Dimer Derived from a Calix[4]arene: Tweezers for C 70

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Inclusion Properties of a New Metallo-Porphyrin Dimer Derived from a Calix[4]arene: Tweezers for C_{70}

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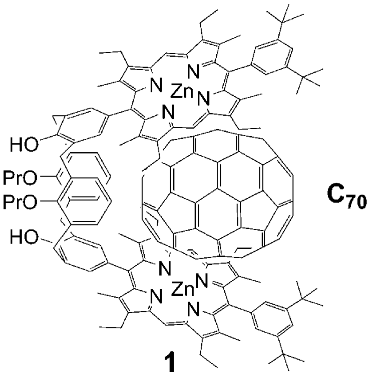
For the selective binding of the fullerene C_{70}, we report here on the inclusion properties of a novel metallo-porphyrin dimer **1** which entails the functionalization of the basic supramolecular frame of a calix[4]arene. First, the electrochemical property of **1** was evaluated by a voltammetric method. The redox potential for reduction is – 0.46 V vs. Fc/Fc^+, and those for the first and second oxidation are 0.14 V and 0.32 V vs. Fc/Fc^+, respectively. These results show two porphyrin moieties of **1** are essentially unperturbed each other. Second, the selectivity factor of C_{70} for **1** is remarkably large as compared with competing C_{60}, because evidence for the formation of the complex came from ^1H NMR and fluorescence spectroscopic studies. In any event, the present work shows two porphyrin groups of **1** serve as tweezers to capture C_{70} by two-point fixation.

Keywords: porphyrin; supramolecular chemistry; fullerene; redox potential; tweezers; calixarene

INTRODUCTION

Metallo-porphyrin dimer derivatives constitute interesting models of biological systems of vital importance, like the ones involved in the photosynthetic machinery[1]. The considerable progress achieved in porphyrin chemistry can be attributed to the extensive studies carried out on the syntheses of variously substituted porphyrin derivatives[2]. We have recently reported on the syntheses and photophysical properties of calixarene-porphyrin conjugates[3], pointing out some interesting features in terms of a directional, efficient electron transfer. On the other hand, fullerenes along with their unique electronic properties, have been used extensively as the electron acceptor from which well-defined three-dimensional architectures containing specific functional groups have been built[4]. In this paper, we describe a novel porphyrin dimer derived from a calix[4]arene show selective binding properties from a fullerene C_{70}. Compound **1** serves as tweezers for C_{70} selectively, which led to the formation ensemble **I**.



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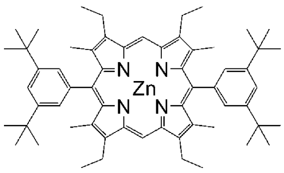

2

Ensemble I

EXPERIMENTAL

The preparation of Zn(II) porphyrin di-substituted calix[4]arene **1** was described in a previous paper of this series[5]. The cyclic voltammetric studies were performed with BAS-100 electrochemical analyzer and a typical three electrodes electrochemical cell. A 1.6 mm diameter disk platinum electrode were used as the working electrode, while a platinum wire and sodium chloride saturated Ag/AgCl electrode served as the

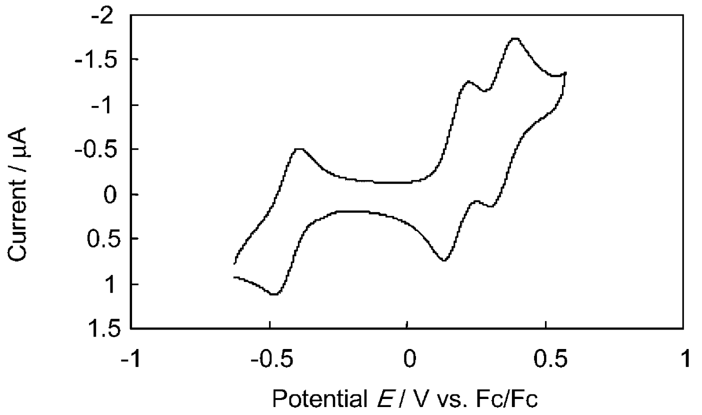

FIGURE 1 Cyclic voltammogram of 1 in 0.5 M TBAP, CH_2Cl_2. Scan rate 100mV/s. [**1**] = 2.0 x 10^{-4} M.

auxiliary and reference electrodes, respectively. A ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as an internal standard of potentials. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at 300 MHz at room temperature (20 °C) in the Fourier transform mode. Tetramethylsilane was used as an internal reference for ^1H NMR measurement. UV-visible spectra were obtained with a Shimadzu UV-3101PC spectrometer. Steady-state fluorescence spectra were taken on and a Shimadzu RF-5301PC spectrofluorimeter.

RESULTS AND DISCUSSION

As for the redox potentials of **1**, Figure 1 shows the cyclic voltammograms of **1** in CH_2Cl_2 containing 0.05 M tetra-n-butylammonium perchlorate (TBAP) as supporting electrolyte. Within the accessible potential window of the solvent, a total of the three reversible redox processes were observed. The first redox potentials corresponding to the reduction of Zn(II) porphyrin were located at $E_{1/2}$ = - 0.46 V vs. Fc/Fc^+, while the second and third redox corresponding to the oxidation of Zn(II) porphyrin were located at $E_{1/2}$ = 0.14 and 0.32 V

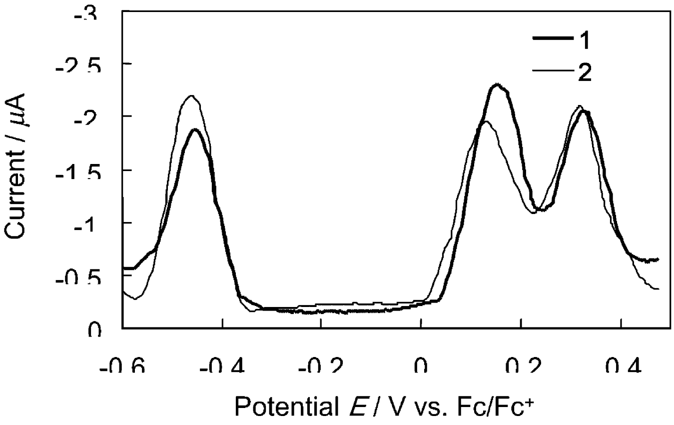

FIGURE 2 Differential pulse volammograms of **1** and **2** in 0.5 M TBAP, CH_2Cl_2. Scan rate 20mV/s, pulse amplitude: 50 mV, pulse width: 50 ms. [**1**] = [**2**] = 2.0 x 10^{-4} M.

vs. Fc/Fc^+, respectively. These potentials were almost same as those for **2**. Figure 2 shows the differential pulse voltammograms of **1** and **2**. Both of them were virtually identical and three redox processes were observed as shown in their cyclic voltammograms of Figure 1. This indicates that each redox process of **1** and **2** is one electron reaction. In other words, one out of two porphyrin of **1** might involve the redox reaction. These results show two porphyrin moieties of **1** are essentially unperturbed each other.

Evidence for the formation of ensemble **I** in C_6D_6 came from ^1H NMR spectroscopic studies. Upon addition of C_{70}, *meso* proton signals of **1** were shifted 0.1 ppm upfield, while the other porphyrinic signals remain unperturbed. No chemical shift changes of **1** were observed in the presence of C_{60}. Moreover, ^1H NMR shift changes of the control system **2** were not observed in the presence of C_{60} and C_{70}. Analysis of the increasing C_{70} concentration by standard curve fitting methods[6] provided support for a 1 : 1 binding model and yielded an association constant K_a of ca. 5000 M^{-1}.

The fluorescence spectra of **1** and **2** in benzene (2.0 x 10^{-5} M) exhibit maxima at 580 and 630 nm with excitation at 540 nm. Furthermore, one can directly compare these fluorescence intensities,

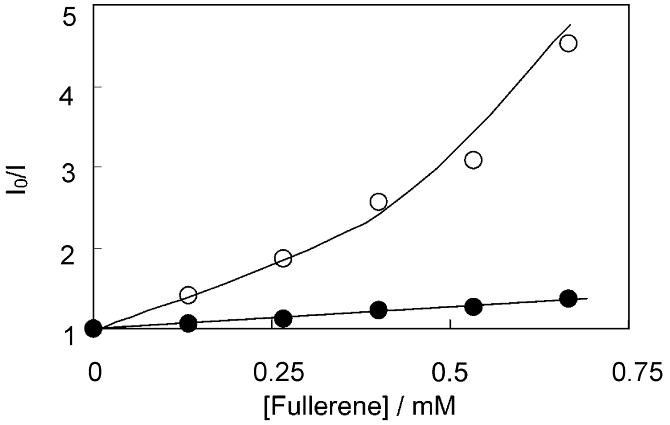

FIGURE 3 Stern-Volmer plots for the fluorescence quenching of 1 with C_{60} (●) and C_{70} (○) in benzene. The sample was excited at 540 nm with emission being integrated from 550 to 700 nm. [**1**] = 2.0 x 10^{-5} M.

because not only the UV-visible absorbance of each is similar at this wavelength but also is essentially perturbed in the presence of the fullerenes (C_{60} and C_{70}).

First, analysis of **1** and C_{60} were carried out. In this instance, steady state fluorescence quenching studies afforded a linear Stern-Volmer plot (Figure 3), a finding that was explained by fluorescence of the porphyrin **1** being quenched only by a diffusional, as opposed to a static, mechanism[7]. In the case of ensemble **I**, the species produced by mixing **1** with C_{70}, the corresponding plot was found to be curved upward (Figure 3). Such non-linear curvature suggests that the porphyrin excited state of **1** is being quenched by both static and dynamic processes. In other words, we interpret the fluorescence of **1** in ensemble **I** as being partially quenched by an intra-ensemble electron transfer process involving a complexed C_{70}. On the other hand, as to analysis of **2** and fullerenes (C_{60} nor C_{70}), the fluorescence intensities were scarcely decreased by the addtion of the fullerenes, This indicates **2** does not form the complexes with either C_{60} nor C_{70}.

The present paper outlines that two porphyrin moieties of the calix[4]arene derivative **1** serve as tweezers to capture C_{70} selectively by two-point fixation.

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