

π -Electronic Charge-Transfer Interactions in Inclusion Complexes of Fullerenes with Cyclic Dimers of Metalloporphyrins

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(Received: 15 July 2001; in final form: 31 August 2001)

Key words: charge-transfer interaction, fullerene, inclusion complex, porphyrin

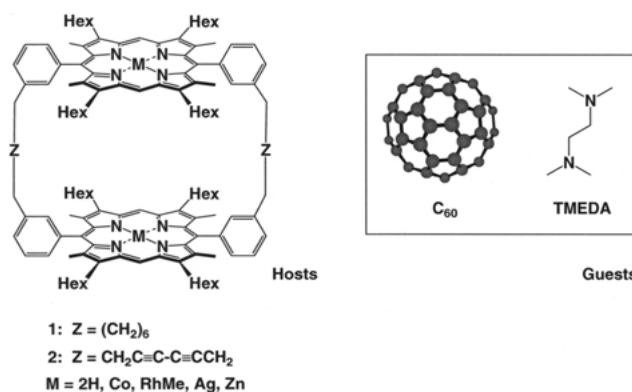
Abstract

Spectroscopic and voltammetric analyses on inclusion complexes of a fullerene such as C_{60} with a cyclic dimer of a free-base porphyrin (**1-M**; $M = 2H$) and its metal complexes ($M = Co, Ag, \text{ and } Zn$) showed that a charge-transfer interaction is partly responsible for the complexation.

Introduction

Host molecules for inclusion of fullerenes are of great importance because of their potential application to extraction and chemical modifications of fullerenes [1–6]. In particular, complexation via π -electronic interactions is highly interesting in view of possible supramolecular modulation of the electronic properties of fullerenes. From this point of view, porphyrin macrocycles are expected to serve as potential host molecules for fullerenes, where the resulting complexes possibly display unique electronic and magnetic properties. Recently, we have found that cyclic dimers of metalloporphyrins (**1-M**) form highly stable inclusion complexes with fullerenes such as C_{60} and C_{70} [7, 8], where the affinity of **1-M** can be tuned by the central metal ions (M). In particular, an extremely large binding constant (K_{assoc}) such as 10^8 M^{-1} (benzene, 25 °C) has been observed for C_{70} with a host molecule having a $Rh^{III}Me$ moiety at each porphyrin macrocycle. Such a high affinity of **1-Rh^{III}** is quite interesting, considering the fact that Rh^{III} complexes can form π -ethane complexes via charge-transfer interaction [9].

Here we report results of spectroscopic and voltammetric studies on the inclusion of C_{60} with a cyclic dimer of a free-base porphyrin (**1-2H**; $K_{\text{assoc}} = 7.5 \times 10^5 \text{ M}^{-1}$) and some of its metal complexes such as **1-Co** ($K_{\text{assoc}} = 2.1 \times 10^6 \text{ M}^{-1}$), **1-Ag** ($K_{\text{assoc}} = 1.2 \times 10^5 \text{ M}^{-1}$), and **1-Zn** ($K_{\text{assoc}} = 6.7 \times 10^5 \text{ M}^{-1}$) [7, 8], in order to investigate if charge-transfer interactions are also operative in inclusion complexes other than **1-Rh^{III}** \supset fullerenes.

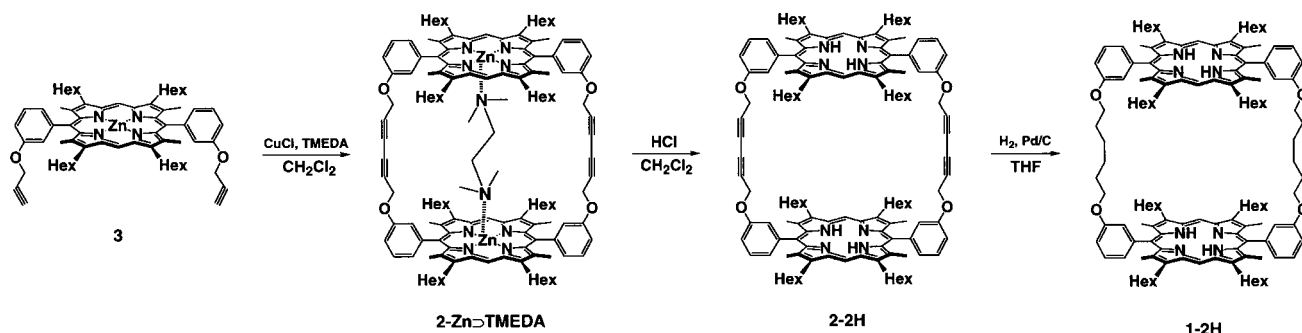


Experimental

Host molecules **1-M** were synthesized by a Cu^I -mediated coupling of the acetylenic terminals of a precursor monomeric zinc porphyrin **3** in the presence of N, N, N', N' -tetramethylethylene diamine (TMEDA) as a template, followed by treatment of the resulting **2-Zn** \supset TMEDA with aqueous HCl to give **2-2H**, whose diacetylenic spacers were then hydrogenated with Pd/C (Scheme 1) [7, 8]. The product (**1-2H**) was metallated to give **1-Co**, **1-Ag**, and **1-Zn**. C_{60} (>99%, TermUSA) was used as received.

Absorption spectra were measured in toluene at 25 °C on a JASCO V-570 spectrometer. Cyclic voltammetry was performed on a BAS CV-27 voltammetry controller under Ar at room temperature, using platinum wire working and counter electrodes, and a silver wire pseudo-reference electrode. A CH_2Cl_2 solution (0.1 mM) of an equimolar mixture of **1-Zn** and C_{60} , containing 0.1-M Bu_4NPF_6 as a supporting electrolyte, was subjected to several freeze-pump-thaw-cycles in a 5-mL round-bottomed Schlenk flask for CV analysis, where the redox potentials were referenced to the redox couple for internal ferrocene.

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Scheme 1.

Results and discussion

Armaroli and coworkers have reported that a face-to-face fullerene-porphyrin dyad, in which C_{60} is located on a porphyrin macrocycle, shows at a near-IR region a broad absorption band from the tail-up of a Q-band absorption to 800 nm, which has been assigned as a charge-transfer band [10]. As we have already reported, host molecules such as **1-2H**, **1-Co**, **1-Ag**, and **1-Zn**, upon mixing with C_{60} , all showed red-shifted absorption bands in the visible region, due to the formation of inclusion complexes. At the same time, **1-Zn**, for example, also showed a broad absorption band centered at 744 nm (Figure 1d). Likewise, other host molecules (**1-2H**, **1-Co**, and **1-Ag**), upon mixing with C_{60} , showed similar spectral profiles in the near-IR region (Figures 1a–1c). On the other hand, in the ^{13}C NMR spectrum in C_6D_6 at 30 °C, inclusion complex **1-Zn** \supset C_{60} showed a signal due to the included C_{60} at δ 140.10 ppm (Figure 2b), which is shifted toward an upfield region by 3.11 ppm from free C_{60} (Figure 2a). All the above observations indicate a charge-transfer interaction between the porphyrin moieties of the host molecules and the included C_{60} . Of interest, in the presence of excess C_{60} in toluene below 20 °C, signals due to the free and included C_{60} were separately observed, whereas at 30 °C, only one signal due to C_{60} was observed as the result of a faster exchange of C_{60} than the NMR timescale.

In relation to the charge-transfer complexation, cyclic voltammetry of an equimolar mixture of **1-Zn** and C_{60} in CH_2Cl_2 showed that the first reduction of C_{60} occurs at -1.11 V vs. Fc/Fc^+ (Figure 3b). Comparison of the observed redox potential with that of free C_{60} ($E_{1/2} = -1.05$ V; Figure 3a) indicates that C_{60} becomes less subject to reduction upon complexation with **1-Zn**. Taking into accounts also the upfield shift of the ^{13}C NMR signal due to C_{60} upon inclusion with **1-Zn**, C_{60} is likely to serve as electron acceptor in the charge-transfer complexation. On the other hand, the second reductions of C_{60} with and without **1-Zn** took place at the same electrochemical potential. This observation suggests that C_{60} upon electrochemical reduction may dissociate from inclusion complex **1-Zn** \supset C_{60} . Therefore, one may electrochemically switch on and off the complexation between **1-Zn** and C_{60} .

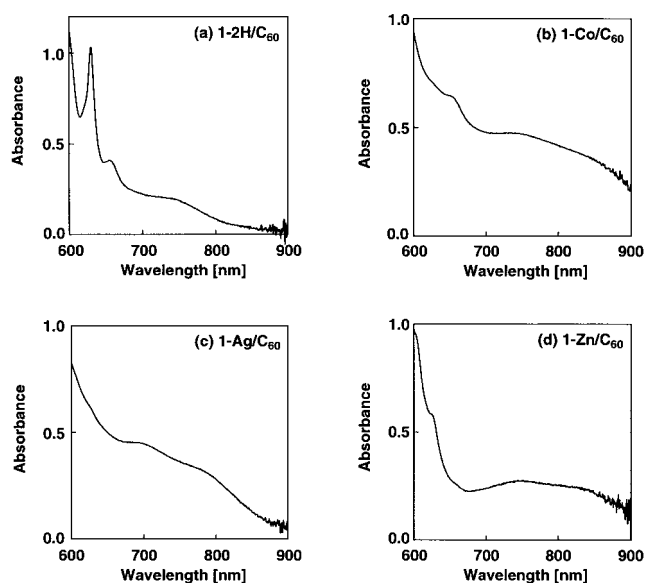


Figure 1. Absorption spectra of (a) **1-2H**/ C_{60} , (b) **1-Co**/ C_{60} , (c) **1-Ag**/ C_{60} , and (d) **1-Zn**/ C_{60} at 600–900 nm in toluene at 25 °C.

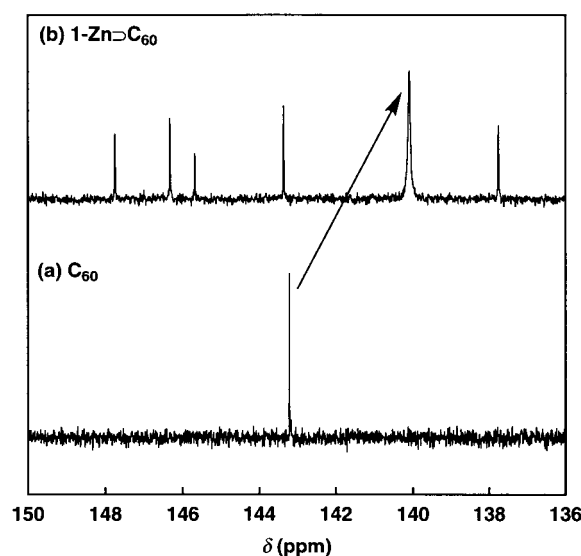


Figure 2. ^{13}C NMR spectra of (a) C_{60} and (b) **1-Zn** \supset C_{60} in C_6D_6 at 30 °C.

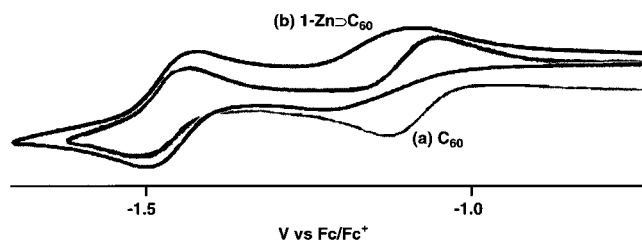


Figure 3. Cyclic voltammograms of (a) C_{60} and (b) $1\text{-Zn} \supset C_{60}$ in CH_2CL_2 at 25°C .

Conclusions

By absorption and ^{13}C NMR spectroscopies and voltammetry analyses, we have indicated herein that charge-transfer interactions as well as van der Waals interactions are operative in the inclusion complexes between 1-M ($M = 2\text{H}$, Co , Ag , and Zn) and C_{60} . Further studies on photochemical properties of the inclusion complexes are in progress.

Acknowledgment

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 13450367) from the Ministry of Edu-

cation, Science, Sports, and Culture, Japan. We are grateful to Prof. K. Yamaguchi and S. Sakamoto of Chiba University and Prof. K. Saigo of the University of Tokyo for their active collaboration.

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