Spectrochimica Acta Part A 90 (2012) 186–192

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Spectroscopic and theoretical insights on fullerene–octaethylporphyrin self assembled non-covalent conjugates studied in solution

Partha Mukherjee, Sumanta Bhattacharya*

*Department of Chemistry, The University of Burdwan, Golapbag, Burdwan 713 104, India*

ARTICLE INFO

*Article history:*
Received 8 September 2011
Received in revised form
22 December 2011
Accepted 16 January 2012

*Keywords:*
Fullerenes
Octaethylporphyrin free base
UV–Vis and fluorescence spectroscopic investigations
Binding constants
Quantum mechanical calculations

ABSTRACT

The present paper highlights the UV–Vis and fluorescence spectroscopic studies on spontaneous non-covalent interaction between a designed monoporphyrin, namely, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin (**1**) and fullerenes ($C_{60}$ and $C_{70}$) in toluene medium. While UV–Vis studies reveal considerable amount of fullerene/**1** interaction in ground state, steady state fluorescence study establishes remarkable quenching of fluorescence intensity of **1** in the presence of fullerenes $C_{60}$ and $C_{70}$. Stoichiometry of both the fullerene complexes of **1** is determined to be 1:1. The magnitude of average binding constant ($K$) values for $C_{70}$/**1** and $C_{60}$/**1** systems is estimated to be 8705 and 3440 $dm^3\,mol^{-1}$, respectively, which also prove that moderate value of selectivity in binding between $C_{70}$ and $C_{60}$ complexes of **1** is resulted in our present work. The genetics of the photo-physical characteristics of fullerene/**1** complexes get tremendous support from lifetime experiment, which signifies the importance of static quenching phenomenon for our presently investigated supramolecules. Life time experiment yields larger magnitude of charge separated rate constant for the fullerene/**1** species in toluene. Theoretical calculations at molecular mechanics level evoke the single projection geometric structures for the $C_{60}$/**1** and $C_{70}$/**1** systems in vacuo which also proves that interaction between $C_{70}$ and **1** is governed by the dispersive forces associated with $\pi$–$\pi$ interaction rather than electrostatic mechanism associated with charge transfer mechanism.

## 1. Introduction

The pioneering work by Kroto et al. [1] and Krätschmer et al. [2] regarding the initial discovery of fullerenes $C_{60}$ and $C_{70}$, and the development of a large-scale method for their preparation, have prompted a lively interest to employ these 3-dimensional carbon allotropes to undergo supramolecular interaction with various host molecules like calix[*n*]arene [3,4], crown ethers [5], cyclodextrin [6] and phthalocyanine [7–10]. Among various macrocyclic receptors, porphyrin molecule with highly delocalized $\pi$-electron systems, finds a unique place in forming host–guest or electron donor–acceptor complexes with fullerenes. Porphyrins are very much suited in energy and/efficient electron transfer process(s) due to the minimal structural change of such entity during the uptake or release of energy and/electrons, respectively. In order to understand the nature of interaction between fullerene and porphyrin chromophores, the topology of the two moieties in fullerene/porphyrin composite or dyad system has been systematically varied and a wide range of covalently and non-covalently linked such systems have been reported [11–18]. $\pi$-Conjugated molecules like fullerenes and porphyrins with tunable electronic properties may be employed as suitable building blocks for the construction of functional materials with exceptional electrochemical and photophysical properties [19]. One of the most interesting aspects of fullerenes and porphyrins is that they spontaneously attract to each other mainly through orbital interactions, as determined through experiment in solution [20,21], in the solid state [22,23] and also confirmed by high-level theoretical calculations [24]. A variety of covalently linked fullerene/porphyrin dyads of donor–acceptor type, have already been reported in this connection, in which the key feature is that the porphyrin loses its characteristic luminescence property as a result of light induced energy and/or electron transfer to the fullerenes [25]. The main objective of the present work is to study the extent of binding and selectivity of complexation of a newly designed monoporphyrin, namely, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin (**1**, Fig. 1) with fullerenes $C_{60}$ and $C_{70}$ in toluene. Spectroscopic investigations, viz., UV–Vis, steady state and time resolved fluorescence measurements have been employed to determine the extent of binding and some other physicochemical parameters related to fullerene/**1** complexation processes. The spectroscopic investigations enable us to determine the selectivity of binding between $C_{60}$/**1** and $C_{70}$/**1** complexes. Molecular mechanics force field (MMMF) calculations well

---

* Corresponding author. Tel.: +91 332 6327254; fax: +91 342 2530452.
*E-mail address:* sum_9974@rediffmail.com (S. Bhattacharya).

1386-1425/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2012.01.031

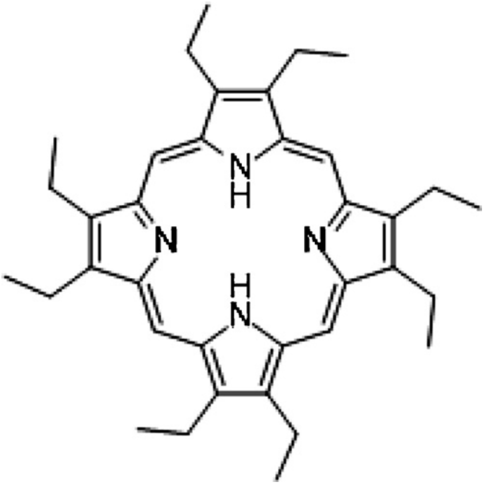

**Fig. 1.** Structure of **1**.

interpret the stability difference between complexes $C_{60}$/**1** and $C_{70}$/**1**.

## 2. Experimental

$C_{60}$, $C_{70}$ and **1** have been purchased from Aldrich, USA. Toluene (spectroscopic grade, Merck) is used as solvent, because it is sufficiently apolar to favor non-covalent interaction between fullerene and porphyrin and, at the same time, ensures good solubility and photo-stability of the samples. UV–Vis spectral measurements are performed on a Shimadzu UV-2450 spectrophotometer using quartz cell with 1 cm optical path length. Steady state fluorescence spectral measurements are recorded in a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence decay curves are measured with a HORIBA Jobin Yvon Single Photon Counting set up employing nanoled as excitation source. Theoretical calculations are done using SPARTAN'06 software.

## 3. Results and discussions

### 3.1. UV–Vis absorption studies

**Table 1**
Binding constants ($K$) and the selectivity in binding, i.e., $K_{C_{70}/\mathbf{1}}/K_{C_{60}/\mathbf{1}}$, of the fullerene/**1** complexes at 298 K.

| System | $K$ (dm$^3$ mol$^{-1}$) | | $K_{C_{70}}/K_{C_{60}}$ | |
|---|---|---|---|---|
| $C_{60}$/**1** | 5600 (UV–Vis) | 1280 (fluorescence) | 1.9 | 5.2 |
| $C_{70}$/**1** | 10,710 (UV–Vis) | 6680 (fluorescence) | (UV–Vis) | (fluorescence) |

The ground state electronic absorption spectrum of **1** (Fig. 2(a)) in toluene shows one intense absorption band, i.e., B or Soret band, at 401 nm corresponding to the transition to the second excited singlet state ($S_0 \leftarrow S_2$) and four absorption bands of lower intensity at 500 nm, 530 nm, 560 nm and 623 nm corresponding to the vibronic sequence of transition to the lowest excited singlet state ($S_0 \leftarrow S_1$). According to the Gouterman's four-orbital model, the intensity of the Q band is directly related to the energy separation between the nearly degenerate ($a_{1u}$,$e_g$) and ($a_{2u}$,$e_g$) one-electron excited configuration [26]. Evidence in favor of ground state electronic interaction between fullerenes and **1** come from UV–Vis titration experiment. It is observed that the gradual addition of a $C_{60}$ solution to a toluene solution of **1** decreases the absorbance of the Soret band and it suffers little amount of red-shift, i.e., from 401 to 402 nm (Fig. 2(b)). However, no additional absorption peaks are observed in the visible region. The former observation extends a good support in favor of the complexation between $C_{60}$ and **1** in ground state. The latter observation imparts that the interaction is not primarily controlled by charge transfer (CT) type transition in ground state. The stoichiometry of the $C_{60}$/**1** complex is found to be 1:1 as confirmed by Jobs plot of continuous variation experiment (Fig. 3(a)). Similar sort of absorption spectral features are observed in case of $C_{70}$/**1** system (Fig. 1S), though the Soret absorption band has been red-shifted by 2 nm. Jobs plot of continuous variation indicates the 1:1 stoichiometry for $C_{70}$/**1** complex (Fig. 2S). All of the above phenomena prove that **1** undergoes substantial amount of interaction with both $C_{60}$ and $C_{70}$ solution. The gradual decrease in the absorbance value at the Soret band of **1** has been utilized to determine the binding constant ($K$) of $C_{60}$/**1** and $C_{70}$/**1** systems using Benesi–Hildebrand (BH) equation [27] of following type:

$$\frac{[A]_0[D]_0}{d'} = \frac{[D]_0}{\varepsilon'} + \frac{1}{K\varepsilon'} \qquad (1)$$

Here $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor (i.e., $C_{60}$ and $C_{70}$) and donor or host (**1**) solutions (in toluene), respectively; $d'$ is the corrected absorbance of the fullerene/**1** mixture at the wavelength of measurement (i.e., 401 nm, Soret absorption band of **1**) recorded against the same concentration of **1** as reference. The quantity $\varepsilon'$ means the corrected molar absorptivity of the complex. $K$ is the binding constant of the fullerene/**1** complex. Eq. (1) is valid under 1:1 approximation for fullerene/**1** systems. It should be mentioned at this point that the corrected molar extinction coefficient, $\varepsilon'$, is not quite that of the complex. The BH method [27] is an approximation that we have used many times, and it gives decent answers. But the extinction coefficient is really a different one between the complex and free species that absorbs at the same wavelength. Data for spectrophotometric determination of stoichiometry of the $C_{60}$/**1** and $C_{70}$/**1** systems recorded in toluene medium are provided in Tables 1S and 2S, respectively. The most formidable support in favor of evaluation of $K$ by BH method comes from the work of Haino et al. on fullerene encapsulation by various types of calix[5]arene derivatives [28] and also from CT complexation of $C_{60}$ with some amines reported by Mizyed et al. [29]. In all the cases studied, very good linear plots have been obtained according to the present data. Typical BH plots for $C_{60}$/**1** and $C_{70}$/**1** systems in toluene medium are shown in Figs. 3(b) and 3S, respectively. Values of $K$ determined from BH method for the fullerene/**1** complexes are listed in Table 1. The larger extent of decrease in the absorbance value of the Soret absorption band for $C_{70}$/**1** system exemplifies the strong interaction between $C_{70}$ and **1** compared to $C_{60}$ and **1**. The most important observation in the present investigation is that the Soret absorption bands get affected more than the Q-absorption bands, which is already observed by Guldi et al. [30] for their particular fullerene/porphyrin systems.

### 3.2. Fluorescence investigations

#### 3.2.1. Steady state

The photo-induced behavior of the fullerene complexes of **1** has been investigated by steady-state emission measurements, which also accounts the binding of **1** with fullerenes. The large molar extinction coefficient value of **1** with respect to the fullerenes in the UV–Vis spectral region allows us to preferentially excite **1**, keeping the porphyrin concentration at much lower level compared to fullerenes. In toluene solution, upon excitation at 401 nm, **1** exhibits two emission bands at 623 and 690 nm corresponding to (0, 0) and (0, 1) transitions, respectively. According to Gouterman [26], the (0, 0) band results from a transition between the ground state and the lowest exited state, and the (0, 1) band is related to the transition between the lowest exited state and the vibronic state involving the most active vibrations. The fluorescence spectral