Journal of Molecular Liquids 220 (2016) 92–100

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Spectroscopic and theoretical insights on non-covalent interaction between fullerenes and Xantheno-linked benzo-15-crown-5 receptor in solution

Anamika Ray [a], Kusumita Kundu [a], Kshama Kundu [b], Sandip K. Nayak [b], Sumanta Bhattacharya [a,*]

[a] Department of Chemistry, The University of Burdwan, Golapbag, Burdwan, 713 104, India
[b] Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

ARTICLE INFO

Article history:
Received 26 February 2016
Accepted 6 April 2016
Available online xxxx

Keywords:
Fullerenes
Xantheno-linked benzo-15-crown-5
Charge transfer
Binding constant
Solvophobic effect

ABSTRACT

This paper envisages the spectroscopic insights behind supramolecular interaction between xantheno-linked benzo-15-crown-5 (**1**) and fullerenes in solution. Estimation of binding constants (K) in various solvents gave rise to the highest binding affinity for C_{70} complex of **1** in toluene, i.e., $K = 133.000\ dm^3 \cdot mol^{-1}$. Studies of binding as a function of solvent ($K_{1,2\text{-dichlorobenzene}} < K_{chlorobenzene} < K_{toluene}$) correlates inversely with fullerene solubility, indicating that desolvation of fullerene is a major factor for determining the magnitude of K. DFT calculations provide convincing support in favor of high value of K for C_{70}-**1** system.

1. Introduction

The search for proper macrocyclic receptors with complimentary sites for efficient binding of fullerenes is gaining current impetus [1,2] as fullerene-based supramolecular complexes have attracted immense attention for the construction of photosynthetic systems and photonic devices [3–5]. An interesting aspect of the chemistry of fullerenes and various macrocyclic receptors is that they are spontaneously attracted to each other, as a result of ground state complexation. From the viewpoint of stability of host-guest complexes of fullerene, various host molecules have been designed in recent past — for example, calixarene [6], crown ether [7], cyclodextrin [8], resorcarene [9], cyclotriveratrylene [10] and carbon nanoring [11]. Very recently, phosphorus containing chiral molecules are designed for fullerene recognition based on concave/convex interaction [12]. Among all the receptors reported so far, porphyrin [13–16] and phthalocyanine (Pc) [17–19] occupy the major part of the literature in terms of their unique binding motif as well as appealing photophysical properties. Very recently, we have demonstrated very high selectivity in binding (~10.0) between C_{70} and C_{60} complexes of chiral monoporphyrin estimated in toluene [20]. Moreover, chemical physics behind gold nanoparticle (AuNp)-Pc conjugate is explored very recently, and its effect over supramolecular interaction between a functionalized fullerene and Pc is studied in detail by various spectroscopic techniques [21,22]. Other than AuNp, silver nanoparticle is also found to be very much effective in increasing the electrostatic interaction between fullerene and Pc in solution [23]. In recent past, we have also reported supramolecular interaction between fullerene and porphyrazine in solution [24]. It is already reported that both C_{60} and C_{70} form ground state molecular complexes with crown ether [25,26] as a result of electron donor-acceptor or charge transfer (CT) phenomena. However, the estimated binding constant (K) values for the fullerene-crown ether complexes are not so significant in comparison to what fullerene exhibits with other host molecule as mentioned above. For example, the K values for C_{60}-benzo-15-crown-5 and C_{70}-benzo-15-crown-5 complexes are estimated to be ~50 [25] and 116 $dm^3 \cdot mol^{-1}$, respectively [25,26]. However, large fullerene binding constants are necessary for meaningful photophysical studies because such measurements must be done at low concentrations, where undesired dissociation becomes favored. Therefore, we have chosen the route of supramolecualr assembly due to its versatility and simplicity. Our approach, in this paper, is to concentrate on design and synthesis of xantheno-linked benzo-15-crown-5 (**1**) host and then, examine its binding affinity and photophysical properties towards fullerene guests in solvents having varying polarity.

2. Materials and methods

The acceptors, namely, C_{60} and C_{70}, are collected from Aldrich, USA. UV–Vis spectroscopic grade toluene, chlorobenzene and 1.2-dichlorobenzene (DCB) are purchased from Spectrochem, India and used as solvent to favor non-covalent interaction between

* Corresponding author.
E-mail address: sum_9974@rediffmail.com (S. Bhattacharya).

http://dx.doi.org/10.1016/j.molliq.2016.04.010
0167-7322/

fullerene and **1** and, at the same time, to ensure good solubility and photo-stability of the samples. UV–Vis spectral measurements are performed on a Shimadzu UV-2450 model spectrophotometer using quartz cell with 1 cm optical path length. Emission spectra have been recorded with a Hitachi F-7000 model spectrofluorometer. Theoretical calculations are performed with a using SPARTAN'14 Windows version software. Fluorescence microscope is measured in a Leica DM1000 model (Germany) instrument.

3. Results and discussions

3.1. Synthesis of *1*

It is given in Appendix **B**.

3.2. UV–vis absorption studies

Absorption spectrophotometric investigations fingerprint new photophysical insight when solution of C_{60} and C_{70} are added to **1** in DCB. New absorption bands are observed in the visible region between 380 and 410 nm. This may be attributed as CT absorption bands (Fig. 1). Similar absorption spectral feature is observed when complexation between **1** and other electron acceptors like tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), *p*-chlornail and 2.3-dichloro-5.6-dicyano-*p*-benzoquinone (DDQ) is monitored in DCB (Figs. 1S—4S). To obtain the CT bands, spectra of above solutions (in DCB) have been recorded against the pristine acceptor solution as reference to cancel out the acceptor's absorbance. The solvent DCB does not absorb in the visible region. For the detection of CT absorption bands in solution, the donor (in

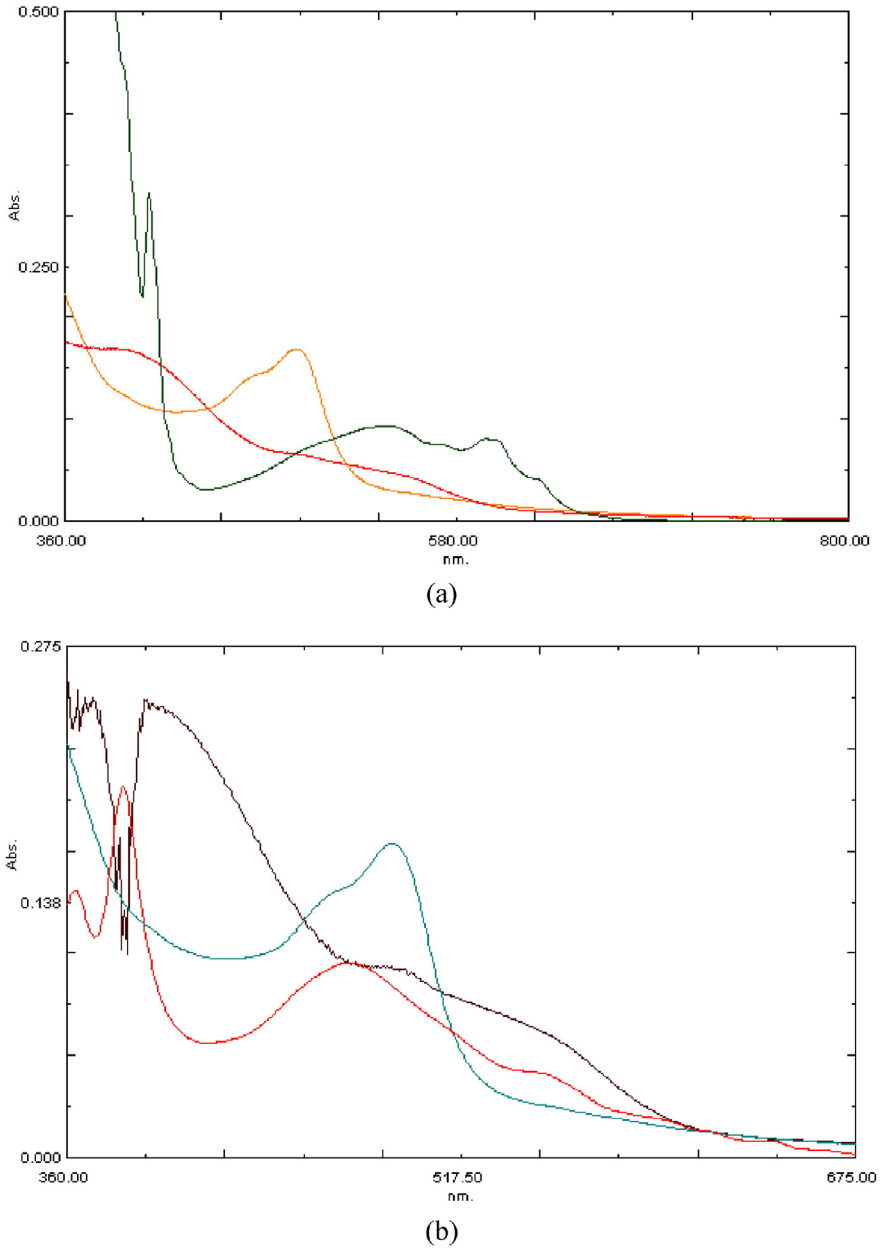

Fig. 1. (a) UV–vis absorption spectra of uncomplexed **1** (yellow color) and free C_{60} (green color) recorded in DCB against the solvent as reference along with mixture of C_{60} and **1** (red color) recorded in DCB against the pristine C_{60} as reference; (b) UV–vis absorption spectra of uncomplexed **1** (blue color) and free C_{70} (red color) recorded in DCB against the solvent as reference along with mixture of C_{70} and **1** (grey color) recorded in DCB against the pristine C_{70} as reference. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)