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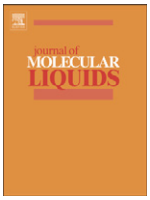

# Chemical physics behind inhibition in binding between fullerene and bisporphyrin in presence of gold nanoparticles: A new physical insight into fullerene-bisporphyrin complexation in solution

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ABSTRACT

The present paper reports supramolecular interaction between fullerenes ($C_{60}$ and $C_{70}$) and a designed bisporphyrin (**1**) in toluene in absence and presence of gold nanoparticles (AuNp) having diameter ~2–4 nm. UV–vis measurement reveals reduction in binding constant ($K$) value for both $C_{60}$-**1** ($K_{C60\text{-}\mathbf{1}} = 18{,}800\ dm^{3}\cdot mol^{-1}$) and $C_{70}$-**1** complexes ($K_{C70\text{-}\mathbf{1}} = 27{,}300\ dm^{3}\cdot mol^{-1}$) in presence of AuNp, i.e., $K_{C60\text{-}\mathbf{1}\text{-}AuNp} = 5000\ dm^{3}\cdot mol^{-1}$ and $K_{C60\text{-}\mathbf{1}\text{-}AuNp} = 3000\ dm^{3}\cdot mol^{-1}$ for $C_{60}$-**1**-AuNp and $C_{70}$-**1**-AuNp composite, respectively. Scanning electron microscope measurements reveal formation of nanorod in case of $C_{60}$-**1**-AuNp composite mixture. Both dynamic light scattering and transmission electron microscope experiment establish the role of electrostatic attraction between porphyrin-based supramolecule and AuNp in solution.

## 1. Introduction

There is an increasing interest among the chemists in finding the cooperative effect in non-covalent interactions, which can be successfully employed for the construction of quite complex structures [1]. Several classes of porphyrins and derivatized porphyrins have been used for this purpose and in many cases, the resulting systems have been served as models for the study of photo-induced energy [2,3] and electron transfer [4–7] process that mimic events occurring in natural photosynthesis. It is already reported that fullerene and porphyrin form naturally assembled co-crystallates, which are characterized by an unusually short fullerene-porphyrin distance (3.0–3.5 Å) [8,9] and that a number of fullerene-porphyrin systems form an emissive charge transfer (CT) state both in solutions [10,11] and in solid state [12]. Self-assembly of organic molecules on different substrates is one of the most studied approaches in order to obtain surface supported supramolecular nanostructures with controlled dimensions and innovative properties. Recently, self-assembled supramolecular methodology using axial coordination, hydrogen bonding, crown ether-ammonium cation complexation, rotaxane formation and additional studies, has been successfully utilized to construct fullerene-porphyrin assemblies [13–15]. Improved stability and control over the distance and orientation are achieved by utilizing multiple modes of binding, such as covalent-coordinate and coordinate-hydrogen bond formation in a few instances [16–18]. Here, we have adopted a two-point non-covalent bonding strategy for the construction of a highly stable fullerene-porphyrin supramolecular complex. The fullerene-porphyrin self-assembly phenomenon is monitored in absence and presence of gold nanoparticles (AuNp) having varying diameter of range between 2 and 4 nm which would yield donor(/host)-acceptor(/guest)-AuNp type nanocluster with an interpenetrating network. It is already explored by various researchers in recent past, that, combination of gold nanoparticles and porphyrins has yielded applications in photocurrent generation [19], catalysts [20] and in anion sensing [21]. Very strong interaction due to orbital overlap between porphyrin and gold nanoparticles is observed in porphyrins attached with multiple linkers parallel to the surface [22]. Fullerenes show high affinity for gold nanoparticles and mixing fullerene with TOABr-protected gold nanoparticles produces larger aggregates, where the individual particles are linked together by fullerenes [23]. Fullerenes modified with a thiol linker and attached to gold nanoparticles as mixed layers with dodecanethiols show energy transfer from photoexcited fullerene to the particle [24]. Photovoltaic cells are developed using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles [25]. Thus, fullerenes clearly interact with gold nanoparticles, but the nature of the interaction seems to be dependent on the structure of the fullerene-functionalized particles. Therefore, it would be a great idea to see whether any photophysical changes take place in the composite mixture containing fullerene and porphyrin when AuNp are added in such assembly. For the aforesaid reasons, we have chosen such a complex system which contains a bisporphyrin molecule, namely, **1** (Fig. 1) and to observe its

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intermolecular interaction with fullerenes ($C_{60}$ and $C_{70}$) in absence and presence of AuNp. Metal nanoparticles have size dependent optical and electrical properties and in this respect, an important feature of metal nanoparticles is the localized surface plasmon band resonance [26], which is seen as high extinction coefficients of metal nanoparticles. As a result of this, smaller sizes of metal nanoparticles absorb light intensively, whereas scattering of light becomes an important factor for bigger nanoparticles. The surface plasmon band resonance causes enhancement of electromagnetic field near the metal nanoparticles. Application utilizing the surface plasmon resonances of metal nanoparticles includes imaging, sensing, medicine, photonics and optics [27]. Although there are some reports on interaction between fullerene and gold nanoparticles (AuNp) in presence of porphyrin in recent past [28,29], as far we know, there is no such work on non-covalent interaction between fullerene and bisporphyrin in presence of gold nanoparticles (AuNp). Very recently, we have monitored the non-covalent interaction between fullerene and a monoporohyrin in absence and presence of silver nanoparticles (AgNp) [30]. In this work, we have determined the binding constant ($K$) of the fullerene-monoporphyrin complexes in absence and presence of AgNp [30]. The motivation of the present work, therefore, deals with the binding studies of fullerenes and **1** in presence of AuNp. We anticipate that the combination of photoactive molecules, like fullerene and bisporphyrin, into formation of non-covalent assembly in presence of AuNp may lead to some new physicochemical aspects. Other than binding studies employing absorption spectrophotometric method, we have employed dynamic light scattering (DLS), scanning electron microscope (SEM) and transmission electron microscope (TEM) probes to see the nature of intermolecular interaction persists between fullerenes and **1** in presence of AuNp.

## 2. Materials and methods

$C_{60}$ and $C_{70}$ are purchased from Sigma-Aldrich, USA and used without further purification. **1** is obtained as a gift item from Prof. H. Uno of Ehime University, Japan and used without further purification. AuNp (~2–4 nm) is purchased from Sigma-Aldrich, USA (Catalogue No. 660426) and used without further purifications. UV–vis spectroscopic grade toluene (Merck, Germany) is used as solvent to favor the intermolecular interaction between fullerene and **1**, as well as to provide good solubility and photo-stability of the samples. UV–vis spectral measurements have been performed on a Shimadzu UV-2450 model spectrophotometer using quartz cell with 1 cm optical path length. DLS measurements have been done with Nano S Malvern instrument employing a 4 mW He-Ne laser ($\lambda = 413$ nm) equipped with a thermostated sample chamber. All the scattered photons are collected at 173° scattering angle. SEM measurements are done in a S-530 model of Hitachi, Japan instrument having IB-2 ion coater with gold coating facility. Transmission electron microscopy (TEM) has been used for estimating the core diameter of the gold nanoparticle. In a TEM measurement, an electron beam from an electron gun is guided into the sample using condenser lenses. The electrons are scattered from the sample atoms, mainly elastically, while passing through it. After this, the transmitted electrons are detected by a charge coupled device camera. The spatial distribution of the scattered electrons is called electron diffraction patterns and provides information about the structure of the sample, that is, arrangement of the atoms.

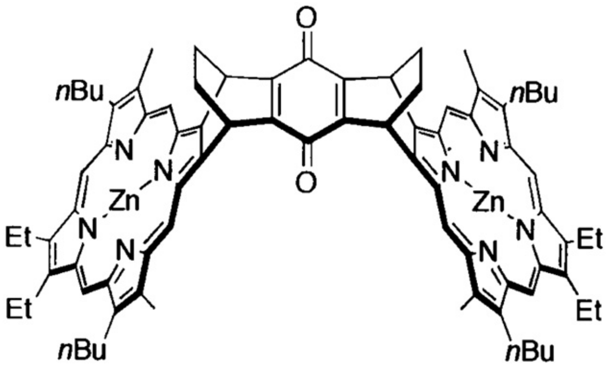

**Fig. 1.** Structure of **1**.

## 3. Results and discussion

### 3.1. UV–vis investigations

The ground state absorption spectrum of **1** ($1.50 \times 10^{-6}$ mol·dm$^{-3}$, Fig. 1S(a) in toluene recorded against the solvent as reference displays one broad Soret absorption band ($\lambda_{max} = 402$ nm) corresponding to the transition to the second excited singlet state $S_2$. As for the Q absorption band, **1** shows two absorption bands at 530 at 570 nm (Fig. 1S(a)). Q absorption bands in metalloporphyrin correspond to the vibronic sequence of the transition to the lowest excited singlet state $S_1$. Fig. 1S(b) shows the electronic absorption spectrum of 0.02 ml AuNp solution in 4 ml toluene measured against the solvent as reference. Gold nanoparticle is generally identified by beautiful red color. More recent results have shown that the color is due to the collective oscillations of the electrons in the conduction band, known as surface plasmon oscillation. The oscillation frequency is usually in the visible region for gold giving rise to strong surface plasmon resonance absorption [31]. The spectrum of the deep red colloidal gold shows one broad absorption band near the region of 508 nm (Fig. 1S(b)). When 0.02 ml solution of AuNp is added to the solution of **1** ($1.5 \times 10^{-6}$ mol·dm$^{-3}$) and the electronic absorption spectrum of the mixture is recorded against the same concentration of AuNp in toluene, the intensity of the Soret absorption band is found to decrease from absorbance value of 0.730 to 0.695 (Fig. 1S(a)). Evidence in favor of ground state electronic interaction between fullerenes and **1** first comes from the UV–vis titration experiment. It is observed that addition of a $C_{60}$ (0 to $9.22 \times 10^{-5}$ mol·dm$^{-3}$, Fig. 2S(a)) and/ $C_{70}$ solution (0 to $9.18 \times 10^{-5}$ mol·dm$^{-3}$, Fig. 2(a)) to a toluene solution of **1** ($1.5 \times 10^{-6}$ mol·dm$^{-3}$) decreases the absorbance value of **1** at its Soret absorption maximum recorded against the pristine acceptor solution as reference. However, no additional absorption peaks are observed in the visible region. The former observation extends a good support in favor of the non-covalent complexation between fullerenes and **1** in ground state. The latter observation indicates that the interaction is not controlled by charge transfer (CT) transition. Isobestic point is observed at 410 nm and 412 nm for $C_{60}$-**1** and $C_{70}$-**1** systems, respectively. Appearance of isobestic point proves that both fullerenes and **1** form 1:1 complexes in solution and maintain the condition of perfect reversible equilibrium [32]. Another two important features of the UV–vis investigations are the larger extent of decrease in the absorbance value of **1** in presence of $C_{70}$ in comparison to $C_{60}$ as well as larger extent of shift in the wavelength maximum of the Soret absorption peak for $C_{70}$-**1** complexation process in comparison to $C_{60}$-**1** system. These spectroscopic observations clearly suggest greater amount of interaction between $C_{70}$ and **1** in toluene. However, measurements of UV–vis spectrum of the $C_{60}$ (0 to $9.22 \times 10^{-5}$ mol·dm$^{-3}$) + **1** ($1.5 \times 10^{-6}$ mol·dm$^{-3}$) and $C_{70}$ (0 to $9.27 \times 10^{-5}$ mol·dm$^{-3}$) + **1** ($1.5 \times 10^{-6}$ mol·dm$^{-3}$) mixtures in presence of AuNp recorded against the solvent as reference, make new physical insight. It is observed that in presence of AuNp, the intensity of the Soret absorption peak of the $C_{60}$ + **1** and $C_{70}$ + **1** mixtures increase (Figs. 3S(a) & 4S(a)) in comparison to the situation when complexation takes place between **1** and fullerenes in absence of AuNp. Thus, we may infer that binding between fullerenes and **1** is inhibited at lesser extent in presence of AuNp. This new photophysical feature of the fulllerene-**1** mixtures in presence of AuNp prompt us to measure the binding strength of fullerene-**1** complexes in solution in absence and presence of AuNp; the gradual decrease in the absorbance