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Photophysical insights behind zinc naphthalocyanine-gold nanoparticle interaction and its effect over supramolecular interaction between zinc napthalocyanine and PyC_{60} in solution

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ABSTRACT

This work envisages an efficient energy transfer phenomenon from zinc naphthalocyanine (**1**) to dodecanethiol functionalized gold nanoparticles (AuNp) having size of 3–6 nm in toluene. Significant enhancement in singlet energy transfer efficiency is observed for **1**-AuNp conjugate. Role of AuNp over the non-covalent interaction between **1** and C_{60} pyrrolidine tris-acid ethyl ester (PyC_{60}) is studied by various spectroscopic tools; considerable reduction in the magnitude of binding constant for **1**-PyC_{60} supramolecule is observed in presence of AuNp. Dynamic light scattering, atomic force microscope and scanning tunneling microscope measurements give clear evidence in favour of the surface binding of **1** to AuNp.

1. Introduction

The concept of non-covalent interaction in forming supramolecular structure is promising for having a large impact on nanoscience if adequate nanoscale manipulation methods are used. Gold nanoparticles (AuNp) have unusual optical, electronic and chemical properties, for which researchers are seeking to put to use in a range of new technologies, starting from nanoelectronics to biomedical applications [1,2]. The physical properties like stability and size distribution of AuNp are determined by stabilization mechanism through interacting with organic molecules. In this connection, many different kinds of chromophores have been assembled on surfaces of AuNp, including pyrene [3], porphyrin [4], and fullerene [5]. Among porphyrinoids, phthalocyanines (Pc) have been used in a range of fields not only due to their unique properties such as thermal and chemical stability, high degree of aromaticity, photophysical, photochemical, redox and coordination properties but also because of their tunable electronic character and designable structures [6,7]. On the other hand, fullerenes are also employed as suitable building blocks for the development of multicomponent systems because of their three dimensional structure [8]. As a result of this, combination of fullerene and Pc can be a promising candidate for possible application in optoelectronics and in organic solar cells [9]. An interesting aspect of the chemistry of fullerenes and Pc's is that they undergo spontaneous self-assembly phenomenon with each other as a result of ground state complexation in solution [10,11]. Accordingly, both covalent and non-covalently connected Pc-fullerene dyads and triads have been designed and studied to understand the mechanistic details behind construction of the artificial photosynthetic reaction centre [12–14]. In a Pc-fullerene dyad, the role of the Pc is dual: first it is to function as an antenna and the second to act as a donor molecule once photo-excited. Among Pc, zinc naphthalocyanine (ZnNc) has good solubility in many organic solvents and an intense absorption band in near infrared region, in addition to the possible tuning of its optical [15] and electronic properties [16]. For the above mentioned reasons, zinc 2,11,20,29-tetra-*tert*-butyl-2,3-naphthalocyanine (**1**, Scheme 1) is chosen as a donor molecule for this work. Although **1** possesses excellent electron-donating properties compared to porphyrins and Pc, the studies of ZnNc-based dyads and triads are rare [17–19]. Moreover, there is no such investigation on non-covalent interaction between fullerene and ZnNc in presence of metal nanoparticles in solution, although there are some reports on interaction between fullerene and Pc in presence of Ag- and AuNp in recent past [20,21]. The objective of the present research work is to envisage electronic interaction between **1** and AuNp and to utilize self-assembly protocols to monitor **1**-fullerene complexation in presence of AuNp in solution. The motivation behind selecting the PyC_{60} (Scheme 1) molecule as electron acceptor in our present

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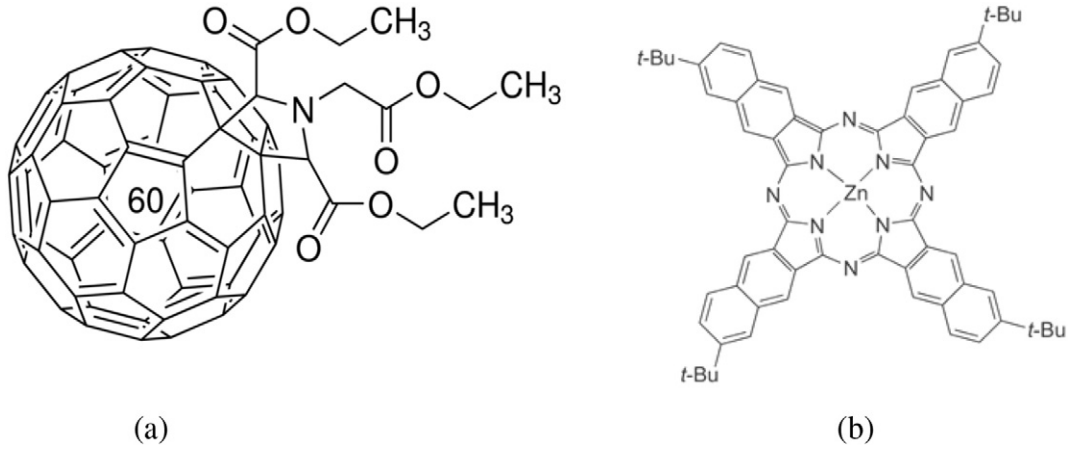

Scheme 1. Structures of (a) PyC_{60} and (b) **1**.

studies comes from the work of work of Sessler et al. in which they have employed fulleropyrroline bearing a guanosine moiety as a recognition motif for the construction of Pc–C_{60} dyad system [22].

2. Materials and methods

1 is purchased from Aldrich, USA having product no. 432210. The acceptor, namely, PyC_{60}, is collected from Aldrich, USA having product no. 709093. The Gold nanoparticles, namely, AuNp, is procured from Sigma (Catalogue no. 54349). UV–Vis spectroscopic grade toluene (Merck, Germany) has been used as solvent to favour non-covalent interaction between 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-4500 model spectrofluorimeter. Fluorescence decay curves are measured with a HORIBA Jobin Yvon Single Photon Counting Setup employing Nanoled as excitation source. Theoretical calculations are performed using SPARTAN'14 Windows version software. DLS measurements have been done with Malvern Zeta Seizer instrument of Model No. NANOZS90. All the scattered photons are collected at 90° scattering angle.

3. Results and discussions

3.1. UV–Vis absorption studies

Absorption spectrophotometric investigations fingerprint new photophysical insight when AuNp solution is added to **1** in toluene. A new broad absorption band is observed around 400 nm (Fig. 1). Red-shifted broad absorption bands have been already reported for donor (porphyrin)-acceptor systems [23]. It should be mentioned at this point that AuNp is coated with dodecanethiol and may contain stabilizer which may play role in the observed modification of **1** spectrum. Interesting feature is noted in case of Q-absorption band of **1** resulted from $S_1 \leftarrow S_0$ transition; significant blue shift (~7 nm) in Q absorption band of **1** (from 769 to 762 nm) in presence of AuNp clearly hints possibility of energy transfer from **1** to AuNp in toluene. All of the above

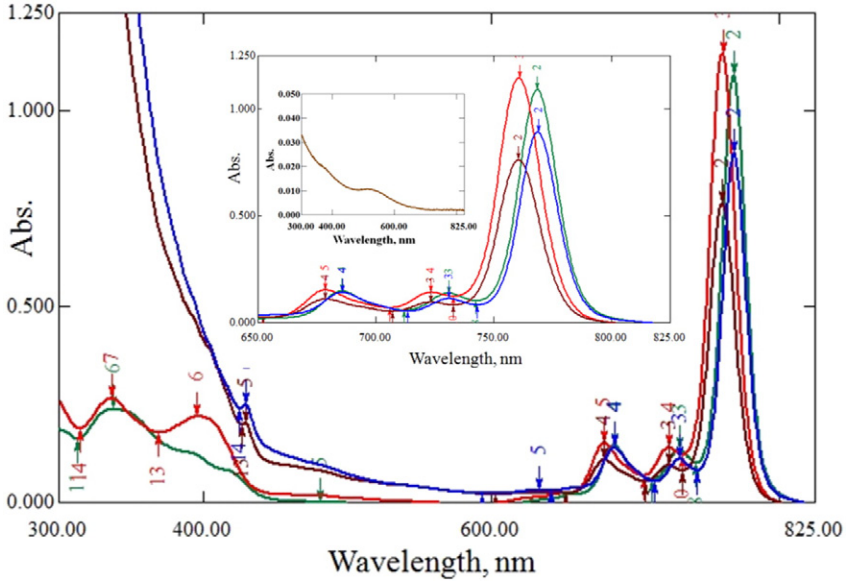

Fig. 1. UV–Vis spectral feature of **1** (4.75×10^{-6} mol·dm^{-3}, green colour line) in presence of AuNp (red colour line), PyC_{60} (3.30×10^{-5} mol·dm^{-3}, blue colour line) and PyC_{60} (3.30×10^{-5} mol·dm^{-3}) + AuNp mixture (brown colour line) recorded in toluene at 298 K against the solvent as reference. In inset of this figure, the shift in Q absorption band along with the absorption spectrum of AuNp (brown colour line) is clearly demonstrated.