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# Spectroscopic insights on energy transfer phenomenon from phthalocyanine to gold nanoparticle and role of phthalocyanine-gold nanoparticle conjugate over supramolecular interaction between fullerene and phthalocyanine in solution

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ABSTRACT

This letter envisages the photophysical insights on phthalocyanine (Pc)-gold nanoparticle (AuNp) conjugate in solution. Both steady state and time-resolved fluorescence studies evoke remarkable enhancement in energy transfer efficiency from ZnPc to AuNp in comparison to free-base Pc ($H_2Pc$) in toluene. It is observed that in presence of AuNp, selectivity in binding for the non-covalent complex of $H_2Pc$ with $PC_{70}BM$ (a fullerene derivative) is found to be ~3.0 times higher compared to ZnPc-$PC_{70}BM$ system. Dynamic light scattering, transmission electron microscope, atomic force microscope and fluorescence microscope measurements provide very good support in favour of the rationale behind Pc-AuNp interaction in solution.

## 1. Introduction

The extraordinary physicochemical properties of metal nanoparticles have become a blooming area of research in recent past since materials in the nanometer dimension display size-dependent optical, electronic, and chemical properties [1]. There are numerous possible applications for such nanoscale materials in developing nanosensors and nanodevices having possible application in biology [2] and optoelectronics [3]. Architecturing of the nanocluster surfaces with electro- or photoactive molecules can provide three-dimensional molecular arrangements around the nanoparticles. In this context, the ability of the gold surface to bind with some specific functional groups in colloidal gold nanoparticles (AuNp) has made the species suitable for possible optoelectronic applications in fluorescence patterning [4], for the development of bio-integrated nano-devices, high-performance sensors [5] and site-specific addressability of DNA nanostructures [6]. 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 [7], porphyrin [8], and fullerene [9].

Among porphyrinoids, phthalocyanines (Pc) have been used in a range of fields not only due to their unique properties such as their thermal and chemical stability, high degree of aromaticity, photophysical, photochemical, redox and coordination properties but also because of their tunable nature and designable structures [10,11]. Among Pc, zinc phthalocyanines (ZnPc) have intensive red-visible region absorption, high triplet and singlet quantum yields making them photoactive and valuable component as photosensitizers or photocatalysts [12]. For the above mentioned reasons, zinc is chosen as the central metal for this work along with free-base Pc, i.e., $H_2Pc$. Conjugates of Pc and AuNp have been reported for drug delivery applications [13]. Amendola et al. have nicely demonstrated that a AuNP solution shows very good nonlinear absorption properties in the nanosecond time regime at 532 nm when ZnPc are present [14]. Very recently, Noda et al. establishes that AuNp assemblies are stabilized by bis(phthalocyaninato)lanthanide(III) complexes through van der Waals interactions [15]. In most of the reported cases, however, the excitation of the chromophore is followed by energy transfer to the AuNp [16–18]. Thus it is clear from the literature that the fluorescence behaviour of Pc alone or in the presence of AuNp depends on the nature of the macrocycle. In this work, we compare the effects of AuNp on the photophysical behaviour of $H_2$- and ZnPc containing octyloxy group at the peripheries of the Pc (Scheme 1). Furthermore, we will explore the alluring physicochemical changes during non-covalent interaction between Pc (both $H_2$- and ZnPc) and a functionalized fullerene

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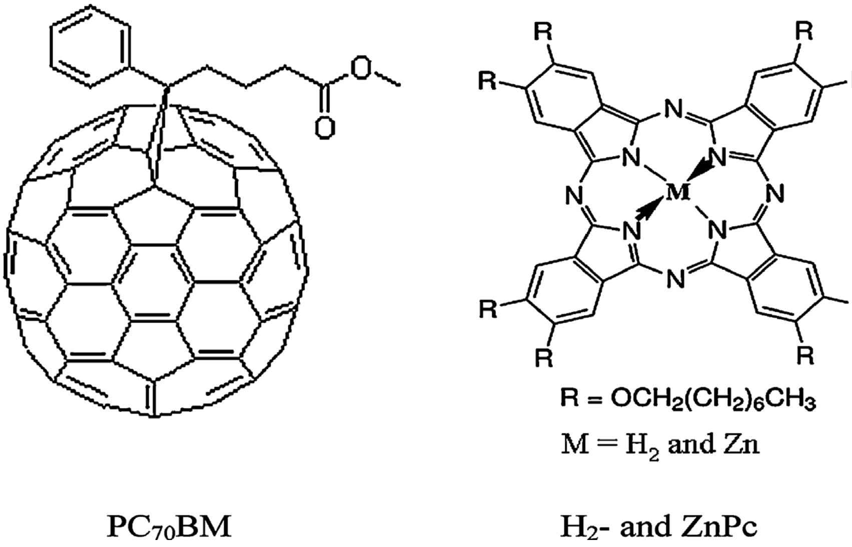

**Scheme 1.** Structures of $PC_{70}BM$ and phthalocyanines ($H_2$- and ZnPc).

derivative, namely, [6,6]-phenyl $C_{71}$ butyric acid methyl ester ($PC_{70}BM$, Scheme 1) in presence of AuNp. The reason behind selecting the $PC_{70}BM$ molecule as an electron acceptor comes from the work of Li et al. [19], in which they have utilized the narrow band gap of this particular molecule for enhancing the solar light harvest in the wavelength region of 350–500 nm [19].

## 2. Materials and methods

$PC_{70}BM$ is purchased from Aldrich, USA and used without further purification. Both $H_2$- and ZnPc are collected from Aldrich, USA and used without further purifications. The Gold nanoparticles, namely, AuNp, is procured from Sigma, USA having diameter of 3–6 nm (Catalogue no. 54349). UV–vis spectroscopic grade toluene (Merck, Germany) has been used as solvent to favour the non-covalent interaction between $PC_{70}BM$ and Pc and, at the same time, to ensure good solubility and photo-stability of the samples. Absorption spectrophotometric measurements are carried out in a UV-2450 Model spectrophotometer made by Shimadzu, Japan using quartz cell with 1 cm optical path length. Steady state fluorescence spectra have been recorded with a Hitachi F-7000 model spectrofluorimeter. Fluorescence decay curves are measured with a HORIBA Jobin Yvon single photon counting set up employing nanoled as excitation source. Fluorescence microscope is measured in a Leica DM1000 model (Germany) instrument. Dynamic light scattering (DLS) measurements have been done with Malvern Zeta Seizer instrument of Model No. NANOZS90. All the scattered photons are collected at 90° scattering angle. Transmission electron microscope (TEM) images have been obtained using a JEOL JEM1210 transmission electron microscope at 100 kV accelerating voltage. For the atomic force microscope (AFM) images, the images were obtained using a spring constant range of 20–80 $N\,m^{-1}$, and resonant frequency range of 210–280 Hz.

## 3. Results and discussions

### 3.1. UV–vis absorption studies

Absorption spectrophotometric investigations fingerprint interesting spectroscopic intuition when AuNp solution is added to $H_2$- and ZnPc in toluene. It is observed that in case of ZnPc-AuNp conjugate, a new broad absorption band is observed at 374 nm (Figure 1). For donor(porphyrin)-acceptor systems, red-shifted broad absorption bands has been already reported [20]. The broadening of the ZnPc absorption-band is attributed to a tight packing of the ZnPc on the gold surface [16]. It should be mentioned at this point that AuNps are coated with dodecanethiol and contains stabilizer which may play role in the observed modification of ZnPc spectrum. A more effect of surface binding is seen in the UV–vis spectrum of ZnPc. Little amount of blue shift (~2 nm) and moderate decrease in the intensity of the Q ($S_1 \leftarrow S_0$) absorption band maxima of ZnPc in presence of AuNp clearly suggests that the octyloxy groups are now engaged with AuNp reducing the electron donating ability of ZnPc. Similar sort of observation is reported by Kamat et al. for their study on organizing fluorophore molecules on the gold surface [4] and porphyrin-silver nanoparticle hybrid structure [21]. Complexation between ZnPc and AuNp is explained in terms of the following mechanism:

$$\text{ZnPc} + \text{AuNp} \rightarrow \text{ZnPc}\ldots\text{AuNp} \qquad (1)$$

Unlike ZnPc, $H_2$-Pc neither exhibits any broad red-shifted absorption band nor any shift (or split) in the absorption maxima at its Soret and Q absorption bands following the addition of AuNp in toluene (Figure 1S). The above observation clearly hints that there is no loss of symmetry in $S_1 \leftarrow S_0$ electronic transition indicating absence of surface binding in case of $H_2$Pc-AuNp system. All of the above findings prove that AuNp acts as a very good energy storage material in presence of ZnPc.

### 3.2. Steady state and time resolved fluorescence studies

To study the photo-induced behaviour of $H_2$- and ZnPc in absence and presence of AuNp and $PC_{70}BM$, steady-state fluorescence measurements are carried out in toluene. Fluorescence measurements would also reveal the effect of molecular structure on molecular and plasmonic resonances in Pc-AuNp interaction. Figure 2a shows the fluorescence spectrum of ZnPc in absence and presence of AuNp, $PC_{70}BM$ and AuNp + $PC_{70}BM$ mixture. It is clearly seen from Figure 2a that the fluorescence intensity of uncomplexed ZnPc suffers sharp quenching in presence of AuNp. The fluorescence quenching of ZnPc in the presence of AuNp may be attributed to energy transfer from photoexcited ZnPc to AuNp. Figure 2a also substantiates that the energy transfer efficiency is found to be formidable in case of ZnPc-AuNp conjugate. As expected, the fluorescence intensity of ZnPc gets maximum quenching when both AuNp and $PC_{70}BM$ are present in the mixture. The striking feature