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# Photophysical insights on effect of gold nanoparticles over fullerene–porphyrin interaction in solution

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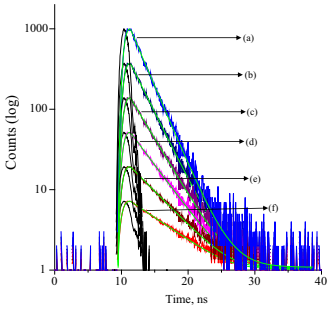
## HIGHLIGHTS

- Fullerene–porphyrin (**1**) complexation is examined in presence of AuNp in toluene.
- AuNp causes effective reduction in the value of binding constant for $C_{70}$–**1** system.
- Fluorescence studies elicit quenching of **1** in presence of fullerene-AuNp mixture.
- DLS study reveals increase in the particle size of $C_{70}$–**1**–AuNp nanocomposite.
- Energy transfer phenomenon takes place.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The present article reports the role of gold nanoparticles, i.e., AuNp (having diameter ~2–4 nm), in non-covalent interaction between fullerenes ($C_{60}$ and $C_{70}$) and a monoporphyrin (**1**) in toluene. Both UV–vis and fluorescence measurements reveal considerable reduction in the average value of binding constant ($K_{av}$) for the $C_{70}$–**1** system ($K_{C70-\mathbf{1}(av)} = 19{,}300\ dm^3\ mol^{-1}$) in presence of AuNp, i.e., $K_{C70-\mathbf{1}-AuNp(av)} = 13{,}515\ dm^3\ mol^{-1}$ although no such phenomenon is observed in case of $C_{60}$–**1** system, viz., $K_{C60-\mathbf{1}(av)} = 1445\ dm^3\ mol^{-1}$ and $K_{C60-\mathbf{1}-AuNp(av)} = 1210\ dm^3\ mol^{-1}$. DLS study reveals sizeable amount of increase in the particle size of $C_{70}$–**1**–AuNp nanocomposite, i.e., ~105 nm, compared to $C_{60}$–**1**–AgNp system, e.g., ~5.5 nm which gives very good support in favor of decrease in the value of $K_{av}$ for the former system. SEM study reveals that nanoparticles are dispersed in larger extent in case of $C_{70}$–**1**–AuNp system. Time-resolved fluorescence study envisages that deactivation of the excited singlet state of **1** by $C_{70}$ takes place at a faster rate in comparison to $C_{60}$ in presence of gold nanoparticles.



## Introduction

Gold (Au) nanoparticles (AuNp) play important roles in different branches of science, such as in nanoelectronics, nonlinear optics, biological labeling and oxidation catalysis [1–5]. The application of nanoparticles in nanoelectronic devices, exploiting the organoelectronic π-orbital interactions, which are generally used in electron-conductive polymers and organic transistors etc., are quite important in light of the reduction of the tunneling resistance of the surrounding ligands. In this sense, porphyrin is one of the most important π-conjugated compound and strong coupling between porphyrin and AuNp is observed due to orbital overlap in which porphyrin is attached with multiple linkers parallel to the surface [6]. Fullerenes also show high affinity for

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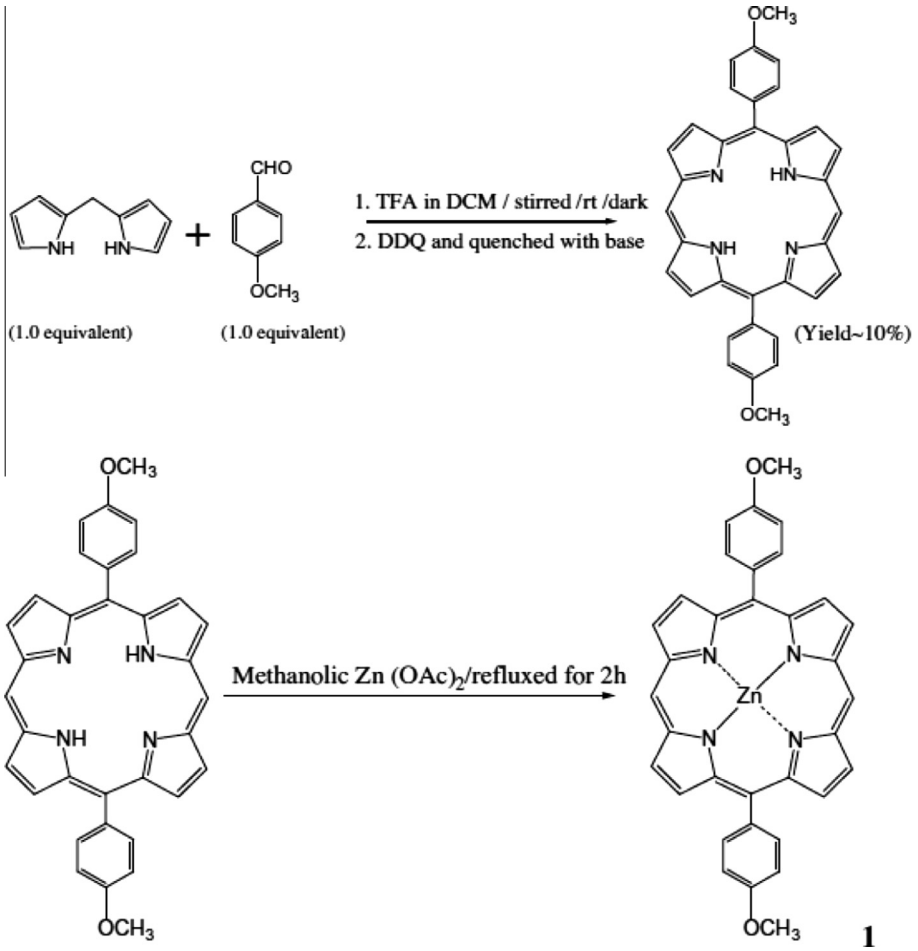
AuNp and mixing of fullerene with TOABr-protected AuNp produces larger aggregates, where the individual particles are linked together by fullerenes [7]. Fullerenes modified with a thiol linker and attached to AuNp as mixed layers with dodecanethiols show energy transfer from photoexcited fullerene to the particle [8]. As a result of this, photovoltaic cells are developed using composite nanoclusters of porphyrins and fullerenes in presence of AuNp [9].

When a nanosize metal particle is activated by light, the collective oscillation of conduction electrons occurs on the particle surface, which is called localized surface plasmon resonance (SPR) [10,11]. It exhibits unique phenomena such as intense absorption at a wavelength resonant with the electronic transition of molecules in the ultraviolet–visible (UV–vis) region. While the analogies between nano particulate building blocks at the nanoscale and the atomic building blocks at the molecular-scale appear appealing [12,13], it must be remembered that nanoparticles – unlike atoms, are never mono dispersed, and no two particles are ever identical. This inherent polydispersity proves self-assembly, and affects the overall characteristics deriving from the size-dependent properties of individual NPs (e.g., SPR) [14,15] or magnetic susceptibility [16].

In spite of several appealing properties, researchers did not pay their attention in exploring the photophysical insights during self-assembly phenomenon between fullerene and porphyrin in presence of AuNp in past few decades. Only very recently, our research group have explored that the binding between fullerene and a monoporphyrin, namely, **1** (Scheme 1), is reduced considerably in presence of silver nanoparticle (AgNp) in solution [17]. In continuation of our earlier work [17], we have presented the photophysical insights on non-covalent interaction between **1** and fullerenes ($C_{60}$ and $C_{70}$) in presence of AuNp (having diameter in the range of 2–4 nm) in toluene. We anticipate that there is a strong possibility that fullerenes may undergo interaction with AuNp, but the nature of the interaction seems to be dependent on the nature of solvent matrix, structure of the fullerene-complexes of porphyrin and concentration of all the interacting species like fullerene, porphyrin and AuNp. Other than binding studies employing absorption spectrophotometric and steady state fluorescence methods, we have employed time-resolved fluorescence, dynamic light scattering (DLS) and scanning electron microscope (SEM) probes to study the physicochemical insights behind fullerene–porphyrin interaction in presence of AuNp.

## Materials and methods

$C_{60}$ and $C_{70}$ are purchased from Sigma–Aldrich, USA and used without further purification. **1** is synthesized according to the method reported in literature [17]. 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 favour 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. Fluorescence decay curves have been obtained with a HORIBA Jobin Yvon Single Photon Counting Setup employing Nanoled as excitation source. DLS




**Scheme 1.** Synthesis of Zn-5, 15-di (para- methoxy phenyl)-porphyrin.