



CHEMICAL PHYSICS BEHIND NON-COVALENT INTERACTION BETWEEN FULLERENE AND A MONOPORPHYRIN IN ABSENCE AND PRESENCE OF SILVER NANOPARTICLES

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Abstract- The present article reports the supramolecular interaction between fullerenes (C_{60} and C_{70}) and a designed monoporphyrin, e.g., parafluorotetraphenylporphyrin (1), in presence of silver nanoparticles (AgNp) having diameter of ~3-7 nm in toluene. UV-Vis studies reveal an interesting new physicochemical aspect. It is observed that in presence of C_{60} and C_{70} solution (in toluene), reduction in the absorbance value of the Soret band of 1 takes place; however, increase in the absorbance value of 1 occurs when the same experiment is performed in presence of silver nanoparticles. The most remarkable feature of the UV-Vis studies is that in presence of AgNp, all the species, i.e., 1, 1 + C_{60} and 1 + C_{70} mixtures, undergo first order exponential decay and the rate constant values are estimated to be 0.068, 0.084 and 0.060 min⁻¹, respectively. Steady state fluorescence measurement reveals that reduction in the binding constant (K) value takes place for both C_{60} -1 ($K = 1065 \text{ dm}^3 \times \text{mol}^{-1}$) and C_{70} -1 systems ($K = 12585 \text{ dm}^3 \times \text{mol}^{-1}$) in presence of AgNp ($K_{C_{60}-1} = 890$ & $K_{C_{70}-1} = 11975 \text{ dm}^3 \times \text{mol}^{-1}$). Conductance measurements evoke that AgNp particle reduces the magnitude of conductance value for the fullerene-1 systems in presence of AgNp. Dynamic light scattering and scanning electron microscope measurements demonstrate that the electrostatic attraction between porphyrin-based supramolecules and AgNp is very much responsible behind the formation of nanorod in case of C_{60} -1-AgNp composite.

Keywords- C_{60} and C_{70} , designed monoporphyrin (1), silver nanoparticles, UV-Vis and fluorescence investigations, conductance studies, DLS and SEM measurements.

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Introduction

Photoactive supramolecular systems, in which a donor and an acceptor moieties are non-covalently linked, are particularly appealing either as models for natural photosynthesis or for the conversion of light into electric current [1,2]. Toward constructing such systems, fullerenes [3] and porphyrins [4-6] have been utilized as important constituents owing to their rich redox [7], optical [8] and photochemical [9] properties. After the first reports of the co-crystallization of C_{60} or C_{70} with the porphyrin unit, the search for highly efficient porphyrin receptors has become intensified [10,11]. A number of porphyrin receptors have been developed [12-18] and the resulting fullerene-porphyrin assemblies have brought forward many interesting photophysical properties [19,20]. In general, fullerenes are considered as excellent electron

acceptors in forming electron donor-acceptor or charge transfer (CT) complexes for their ability to accept multiple electrons [21]. The primary component of the fullerene-porphyrin interaction is, therefore, driven by the dispersive forces associated with interaction, which is augmented by weak electrostatic or donor-acceptor stabilization. For efficient recognition of spherical guests like fullerenes, the recognition sites in the synthetic receptor are pre-organized for favorable interaction [22]. Taking into account the fact that fullerene and porphyrin undergo spontaneous interaction through self-assembly leading to make a supramolecular complex in solutions as well as in the solid state [23-26], and as this type of model system is of great importance not only in opto-electronic technologies [27] but also in life science in relation to respiration [28], photosynthesis [29] and photomedicine [30], it would be a

great idea to see whether any photophysical changes take place in the composite mixture containing fullerene and porphyrin when silver nanoparticles (AgNp) are added in such assembly. For the aforesaid reasons, we have selected a monoporphyrin molecule, namely, parafluorotetraphenylporphyrin (**1**) (Fig. 1) to find out its intermolecular interaction with fullerenes C_{60} and C_{70} in absence and presence of AgNp. Metal nanoparticles have size dependent optical and electrical properties [31]. In this respect, an important feature of metal nanoparticles is the localized surface plasmon resonance [32], 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. Applications utilizing the surface plasmon resonances of metal nanoparticles include imaging, sensing, medicine, photonics and optics [33,34]. Although there are some reports on interaction between fullerene and gold nanoparticles (AuNp) in presence of porphyrin in recent past [35,36], there is no such investigation on non-covalent interaction between fullerene and porphyrin in presence of silver nanoparticles (AgNp). In recent past, a novel two-step bottom-up approach to construct a 2-dimensional long-range ordered, covalently bonded fullerene-porphyrin binary nanostructure is presented in presence of Ag (110) [37]. However, we anticipate that the combination of photoactive molecules, like fullerene and porphyrin, into formation of non-covalent assembly in presence of AgNp may lead to some new physicochemical aspects. The motivation of the present work, therefore, deals with the non-covalent interaction between fullerenes and monoporphyrin in presence of AgNp. Binding and selectivity in binding between fullerenes and **1** is one of the goals of our present studies, other than to envisage various physicochemical aspects on host-guest chemistry of fullerene and porphyrin in presence of AgNp.

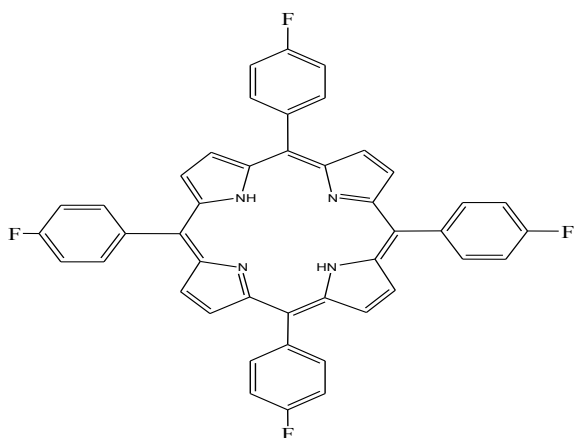


Fig. 1 -

Materials and methods

C_{60} - and C_{70} are purchased from Sigma-Aldrich, USA and used without further purification. **1** is synthesized in our laboratory according to the method reported in literature [38]. 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 photostability 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. Steady state emission spectra are recorded with a Hitachi F-4500 model fluorescence spectrophotometer. 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.

Results and discussions

A. UV-Vis investigations

The ground state absorption spectrum of **1** (4.50×10^{-6} mol \times dm $^{-3}$, Fig. 2(a)) in toluene recorded against the solvent as reference displays one broad Soret absorption band ($I_{\max} = 417$ nm) corresponding to the transition to the second excited singlet state S_2 . As for the Q absorption bands, **1** shows two major absorption bands at 510 and 588 nm along with two minor absorption bands at 543 and 655 nm (Fig. 2(a)). Q absorption bands in metalloporphyrin correspond to the vibronic sequence of the transition to the lowest excited singlet state S_1 . Fig. 2(b) shows the electronic absorption spectrum of 0.02 ml AgNp solution in 4 ml toluene measured against toluene. The distinctive colour of AgNp is due to a phenomenon known as plasmon absorbance. Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed. The spectrum of the clear yellow colloidal silver shows one broad absorption band near the region of 451 nm due to its surface plasmon band resonance character [39]. When 0.02 ml solution of AgNp is added to the solution of **1** (4.50×10^{-6} mol \times dm $^{-3}$) and the electronic absorption spectrum of the mixture is recorded against the same concentration of AgNp in toluene, the intensity of the Soret absorption band is found to decrease from absorbance value of 1.395 to 1.190 (Fig. 2(c)). Evidence in favour 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} (2.10×10^{-5} mol \times dm $^{-3}$) and/ C_{70} solution (2.10×10^{-5} mol \times dm $^{-3}$) to a toluene solution of **1** (4.50×10^{-6} mol \times dm $^{-3}$, Fig. 3) decreases the absorbance value of **1** at its Soret absorption maximum (Fig. 3) recorded against the pristine acceptor solution as reference; the extent of decrease is considerably larger in magnitude compared to AgNp in toluene. 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. Another important feature of the UV-Vis investigations is the larger extent of decrease in the absorbance value of **1** in presence of C_{70} in comparison to C_{60} . This spectroscopic observation suggests greater amount of interaction between C_{70} and **1**. However, measurements of UV-Vis spectrum of the C_{60} (2.10×10^{-5} mol \times dm $^{-3}$) + **1** (4.50×10^{-6} mol \times dm $^{-3}$) and C_{70} (2.10×10^{-5} mol \times dm $^{-3}$) + **1** (4.50×10^{-6} mol \times dm $^{-3}$) mixtures in presence of AgNp recorded against the same concentration of fullerene in presence of AgNp, make new physical insight. It is observed that in presence of AgNp, the intensity of the Soret absorption peak of the C_{60} + **1** and C_{70} + **1** mixtures increase (Fig. 3), in comparison to the situation

when complexation takes place between **1** and fullerenes in absence of AgNp. From the above observations we may infer that binding phenomenon between C₆₀ and **1** takes place at less extent in presence of AgNp. Similar observation is observed in case of C₇₀-**1** complexation process. This new photophysical feature of the fullerene-**1** mixtures in presence of AgNp prompt us to measure the quantitative estimation of the binding phenomenon between fullerenes and **1** in absence and presence of AgNp employing steady state fluorescence spectroscopic tool.

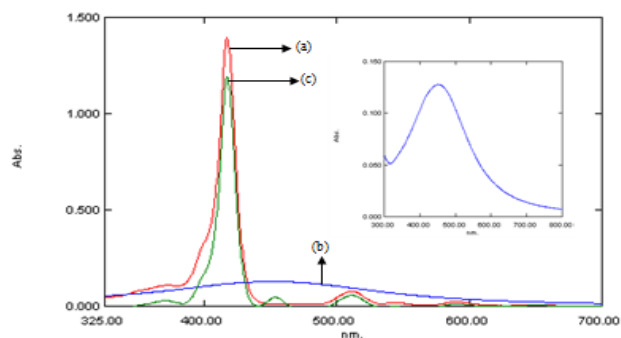


Fig. 2-

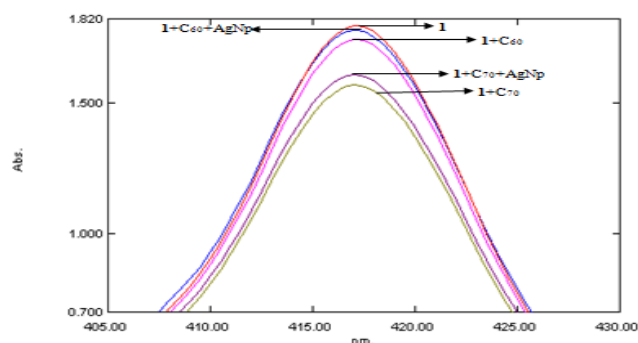


Fig. 3-

$$\text{Absorbance} = (0.92616 \pm 0.00733) + (1.1773 \pm 0.02958) \exp\left\{-\frac{\text{Time}}{(11.8737 \pm 0.5634)}\right\} \quad (2)$$

C₇₀-**1**-AgNp system:

$$\text{Absorbance} = (0.59060 \pm 0.00742) + (1.4314 \pm 0.02112) \exp\left\{-\frac{\text{Time}}{(16.5900 \pm 0.5900)}\right\} \quad (3)$$

k for C₆₀-**1**-AgNp and C₇₀-**1**-AgNp systems are estimated to be 0.084 and 0.060 min⁻¹, respectively; the exponential plots are demonstrated in Figs. 3S(b) & 4(b), respectively.

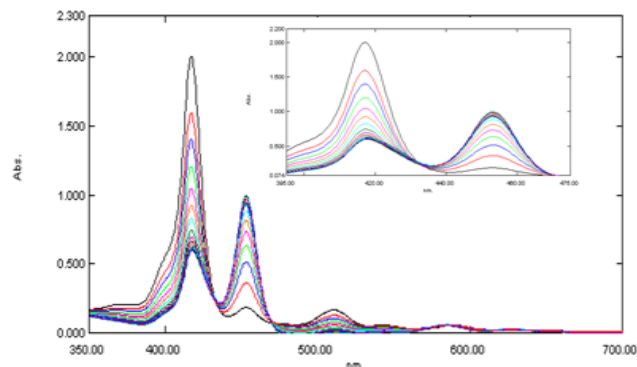


Fig. 4a-

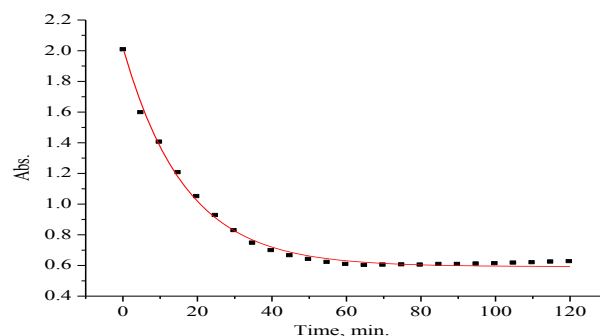


Fig. 4b-

B. Kinetic studies

Absorption spectrophotometric investigations evoke a new physical insight on interaction between monoporphyrin, i.e., **1** with AgNp in absence and presence of fullerenes C₆₀ and C₇₀. It is observed that when AgNp solution in toluene is added to the solution of **1** in same solvent, peak intensity of **1** at its electronic transition, i.e., Soret and Q absorption maximum, found to decrease with increasing time (Fig. 1S). For example, the absorbance value at 417 nm (Soret peak) suffers considerable extent of decrease from 2.1720 (0 minute) to 0.5638 in 130 minutes. Plot of absorbance value against time fits excellently well according to the following equation:

$$\text{Absorbance} = (0.55343 \pm 0.00785) + (1.7027 \pm 0.02752) \exp\left\{-\frac{\text{Time}}{(14.5815 \pm 0.4530)}\right\} \quad (1)$$

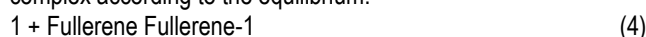
From Eq. (1), the rate constant (*k*) for above process is estimated to be 0.068 min⁻¹. Plot of Eq. (1) for **1**-AgNp system is demonstrated in Fig. 2S. In case of C₆₀-**1** and C₇₀-**1** composite mixtures, when AgNp solution is added similar sort of spectral observations are noticed as depicted in Figs. 3S(a) & 4(a), respectively. Variation of absorbance value with time is found to obey the following equations:

C₆₀-**1**-AgNp system:

C. Steady state fluorescence investigations

It is observed that the fluorescence of **1** upon excitation at Soret absorption band diminishes gradually during titration with C₆₀ and C₇₀ solutions in toluene (Figs. 5(a) & 5(b), respectively). This indicates that there is a relaxation pathway from the excited singlet state of the porphyrin to that of the fullerene in toluene. It is already reported that charge separation can also occur from the excited singlet state of the porphyrin to the C₆₀ in toluene medium [40]. Competing between the energy and electron transfer processes is a universal phenomenon in donor molecule-fullerene complexes [41], solvent dependent photo physical behavior is a typical phenomenon of the most fullerene-porphyrin dyads studied to date [42]. Photo physical studies already prove that in conformationally flexible fullerene/porphyrin dyad, π-stacking interactions facilitate the through space interactions between these two chromophores which is demonstrated by quenching of ¹porphyrin* fluorescence and formation of fullerene excited states (by energy transfer) or generation of fullerene-porphyrin* ion-pair states (by electron transfer) [43]. However, in non-polar solvent, energy transfer generally dominates (over the electron transfer process) the photo physical behavior in deactivating the photo excited chromophore ¹porphyrin* of fullerene-porphyrin dyad.

Similar sort of rationale is already proved by Yin *et al.* for their particular *cis*-2,5-dipyridylpyrrolidino[3,4:1,2]C₆₀-zinc tetraphenylporphyrin supramolecule [44]. In the present investigation, therefore, the quenching phenomenon can be ascribed to photoinduced energy transfer from porphyrins to fullerenes. As we use the Soret absorption band as our source of excitation wavelength in fluorescence experiment, the 2nd excited singlet state of **1** is deactivated by singlet-singlet energy transfer to the fullerene. Although **1** exhibits fluorescence quenching upon the addition of fullerenes, the quenching efficiency of C₇₀ is higher than that of C₆₀. As ground state complex formation between **1** and fullerenes is evidenced from the steady state fluorescence studies, let us consider the formation of a non-fluorescent 1:1 complex according to the equilibrium:



The fluorescence intensity of the solution decreases upon addition of fullerenes C₆₀ and C₇₀. Using the relation of binding constant (*K*) we obtain,

$$K = \frac{[\text{Fullerene-1}]}{[1][\text{Fullerene}]} \quad (5)$$

Using the mass conservation law, we may write

$$[1]_0 = [1] + [\text{Fullerene-1}] \quad (6)$$

where [1]₀, [1] and [Fullerene-1] are the initial concentrations of **1**, **1** in presence of fullerene, and Fullerene-1 complex, respectively.

Eq. (6) can be rearranged as

$$\frac{[1]_0}{[1]} = 1 + \frac{[\text{Fullerene-1}]}{[1]} \quad (7)$$

Using the value of *K* in place of [Fullerene-1]/[1] from Eq. (5), we can write the Eq. (7) as follows

$$\frac{[1]_0}{[1]} = 1 + K [\text{Fullerene}] \quad (8)$$

Considering the fluorescence intensities are proportional to the concentrations, Eq. (8) is expressed as

$$F_0/F = 1 + K [\text{Fullerene}] \quad (9)$$

where, F₀ is the fluorescence intensity of **1** in the absence of fullerene and F is the fluorescence intensity of **1** in the presence of quencher (i.e., fullerene). In our present investigations, steady-state fluorescence quenching studies afforded excellent linear plot for both the C₆₀-**1** and C₇₀-**1** systems as demonstrated in Figs. 6 (a) & 6(b), respectively, which is explained by fluorescence of **1** is being quenched only by static mechanism, as opposed to diffusional quenching process. Eq. (9), therefore, represents a Stern-Volmer (SV) type plot for investigated supramolecules. *K* values of the C₆₀-**1** and C₇₀-**1** systems are given in Table 1. The binding constant is determined by the Eq. (9) for the C₆₀-**1** and C₇₀-**1** systems are estimated to be 1065 and 12585 dm³mol⁻¹, respectively. It is interesting to note that the increase in magnitude of binding constant led to increase of the fluorescence quenching efficiency. The steady state fluorescence emission measurements of C₆₀-**1** and C₇₀-**1** systems in presence of AgNp, however, evoke new physicochemical insight regarding perturbation in binding between fullerenes and **1** in solution.

Table 1- Binding constants (*K*) for the non-covalent complexes of **1** with C₆₀ and C₇₀ in absence and presence of AgNp recorded in toluene Temp. 298K

System	In absence of AgNp		In presence of AgNp	
	K, dm ³ ×mol ⁻¹	Selectivity in binding	K, dm ³ ×mol ⁻¹	Selectivity in binding
C ₆₀ -1	1065 ± 55	11.8	890 ± 45	13.4
C ₇₀ -1	12585 ± 630		11975 ± 600	

It is observed that the *K* value of C₆₀-**1** and C₇₀-**1** systems in presence of AgNp are estimated to be 890 and 11975 dm³×mol⁻¹, respectively, which are found to be lower in absence of AgNp (see Table 1). The steady state fluorescence quenching spectral variation of **1** by C₆₀ and C₇₀ in presence of AgNp are given as Figs. 5(c) & 5(d), respectively; corresponding SV type plots are provided in Figs. 6(c) & 6(d), respectively.

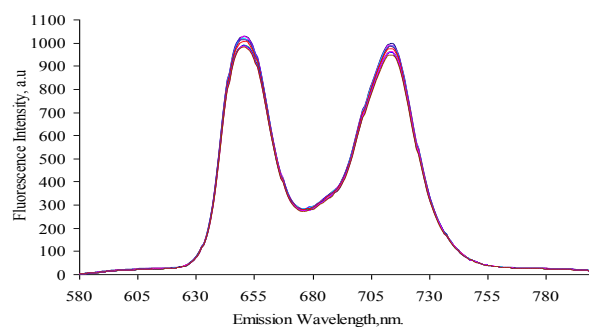


Fig. 5a-

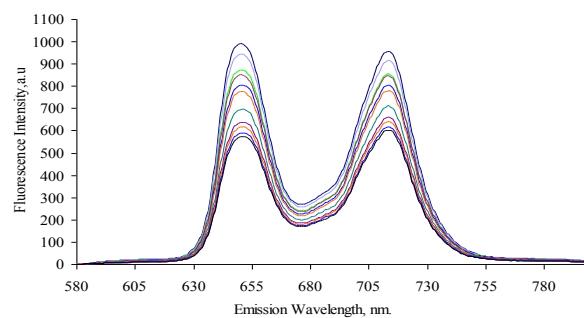


Fig. 5b-

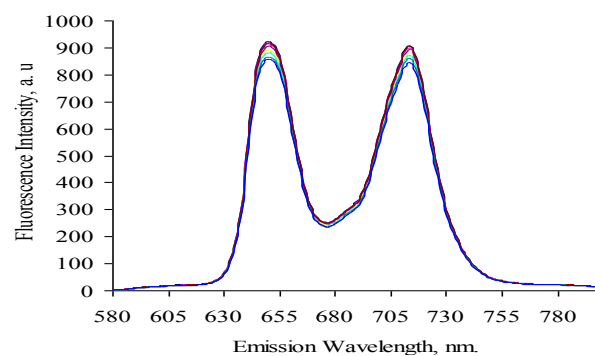


Fig. 5c-

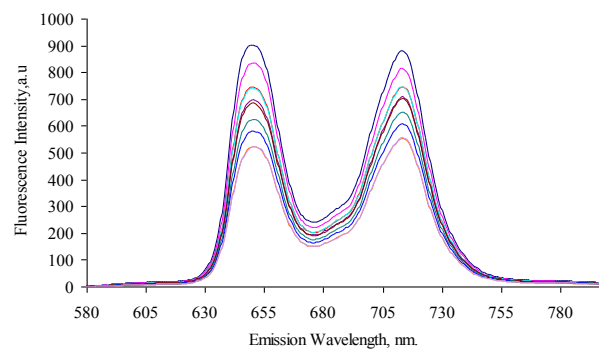


Fig. 5d-

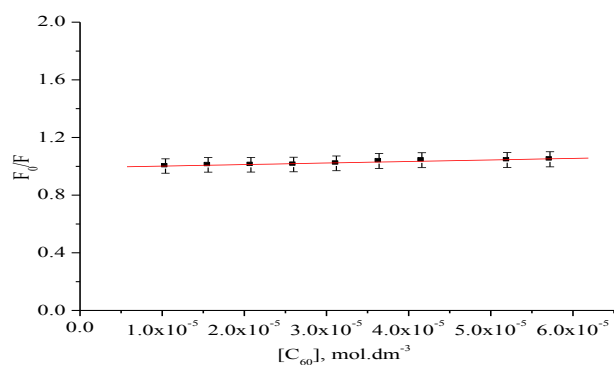


Fig. 6a-

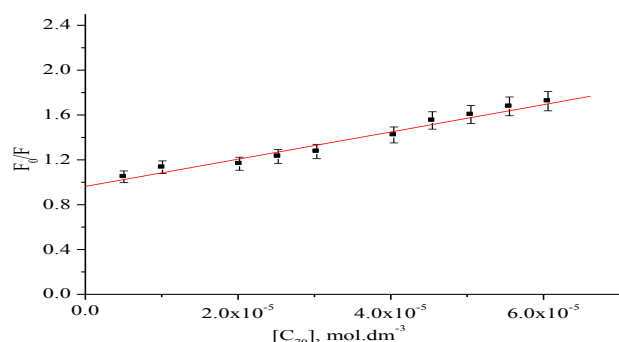


Fig. 6b-

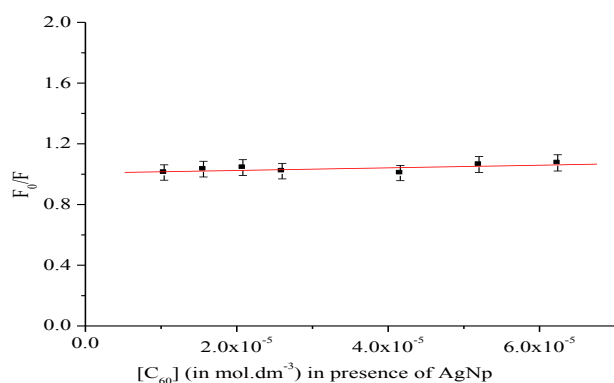


Fig. 6c-

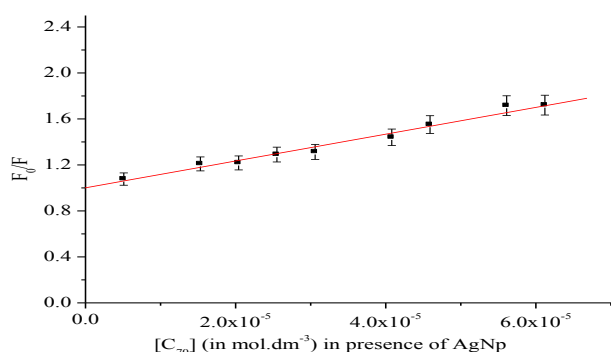


Fig. 6d-

In our present investigations, DLS measurements clearly demonstrate that in presence of C_{60} and C_{70} , the size of the nanoparticles do not change much. Figs. 7(a)-7(c) show the variation of scattering intensity vs. size of the nanoparticles for various systems. It shows that size of the nanoparticles remains within the limit of ~ 4.8 nm (Fig. 7(a)) when fullerenes are not present in the mixture of **1** + AgNp. In presence of C_{60} (Fig. 7(b)) and C_{70} (Fig. 7(c)), the particle size of AgNp becomes ~ 4.35 nm. The above findings provide strong support in favor of the evaluation of K value of fullerene-**1** systems in absence of AgNp, i.e., slight reduction in the K value of fullerene-**1** systems takes place in presence of AgNp. It also envisages that AgNp partially covers the surface area of porphyrin, which renders the fullerene molecule to undergo interaction with the whole surface area of **1** leading to the reduction in the binding constant value for fullerene-**1** systems.

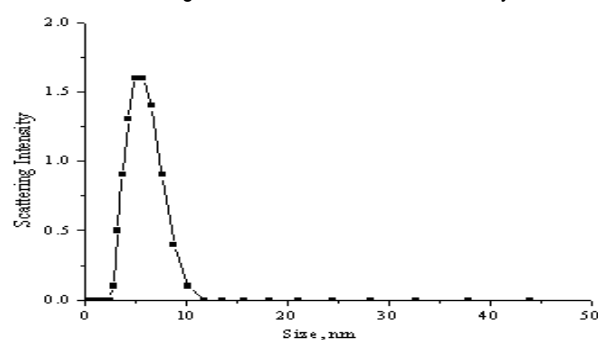


Fig. 7a-

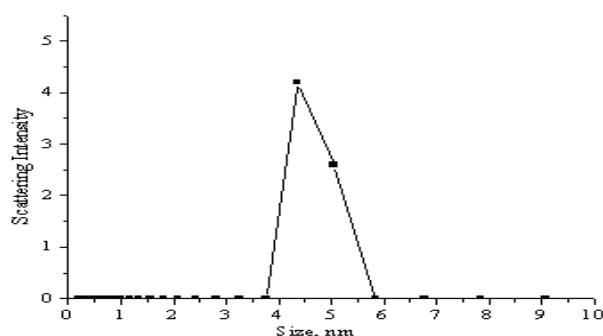


Fig. 7b-

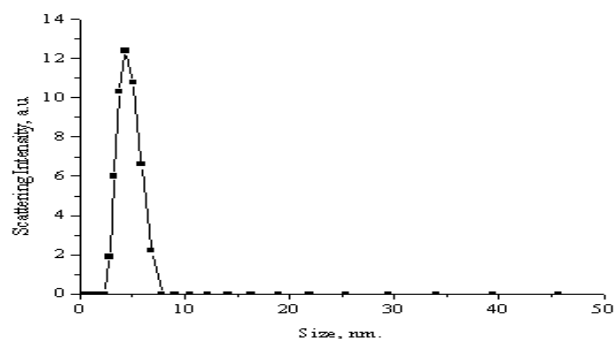


Fig. 7c-

C. Dynamic light scattering experiment

Dynamic light scattering (DLS) is the most versatile and useful set of techniques for measuring *in situ* on the sizes, size distributions, and (in some cases) the shapes of nanoparticles in liquids [45-48].

D. Conductance measurements

Conductance measurements of the **1** in presence of only AgNp, only C_{60} , only C_{70} , C_{60} + AgNp and C_{70} + AgNp mixtures reveal

very important new physicochemical aspect. It is observed that in presence of AgNp, the conductance value of **1** in toluene gets very little change with increasing time. After ~2 hours of measurement, the conductance value of **1** + AgNp mixture in toluene is determined to be 1.6 mS compared to the initial value of 0.2 mS in absence of AgNp (see Table 1S); from this observation, it may be inferred that AgNp molecule generates some degree of photocurrent in **1** + AgNp mixture due to electrostatic deposition of silver nanoparticles over the surface of **1**. The most promising aspect of the present investigations is that in presence of C₆₀ and C₇₀, the composite solution containing C₆₀ + **1** + AgNp and C₇₀ + **1** + AgNp mixtures do not produce any great degree of photocurrent. For example, after ~2 hours of measurement, the conductance value of C₆₀ + **1** + AgNp mixture in toluene (Table 2S) is determined to be 0.4 mS compared to the initial value of 0.2 mS. This is very much comparable with the C₆₀ + **1** system in absence of AgNp (Table 3S); the conductance value gets little shifted from 0.1 mS to 0.3 mS. In case of C₇₀, however, slight increase in the value of conductance is observed both in absence (Table 4S) and in presence of AgNp (Table 5S). This is quite consistent with the fact that C₇₀ forms much stronger complex with **1** either AgNp is absent or present in the solution.

E. SEM Measurements

SEM measurements of **1** in presence of AgNp reveals uneven sized particles (Fig. 8(a)). The SEM image of (C₆₀ + **1** + AgNp) composite mixture (Fig. 8(b)) obtained from drop-casted films of the clusters ([**1**]:[C₆₀]=1:1) on a stab made of copper reveals the formation of rod-like clusters with a well-controlled size (4-5 mm in the long axis). In sharp contrast, the SEM image of the clusters of (C₇₀ + **1** + AgNp) composite mixture (Fig. 8(c)) shows ill-defined sizes and shapes. In particular, the SEM image of clusters consisting of (C₆₀ + **1** + AgNp) reveals both rods of different sizes and small random-shaped structures. In addition, variation of the [**1**]:[C₆₀] ratio is found to affect the cluster size and shape (Fig. 8(b)). This trend is consistent with the size of the large and bucket-shaped surface holes, which are expected to incorporate up to as many as C₆₀ molecules. These results clearly demonstrate that the shape and the size of the surface holes on the 1-C₆₀/C₇₀-AgNp structure play an important role in controlling the formation of molecular clusters with either C₆₀ or C₇₀ molecules.

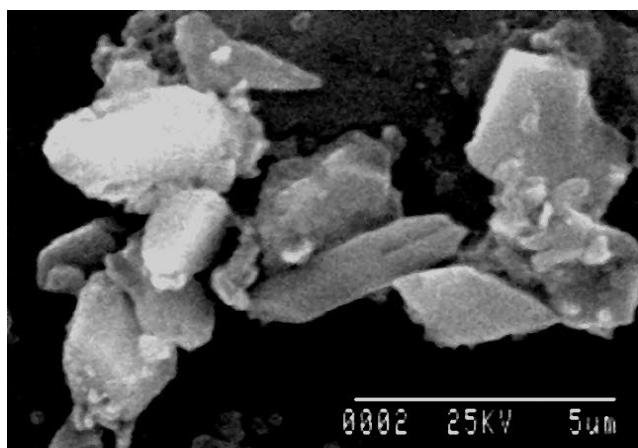


Fig. 8a-

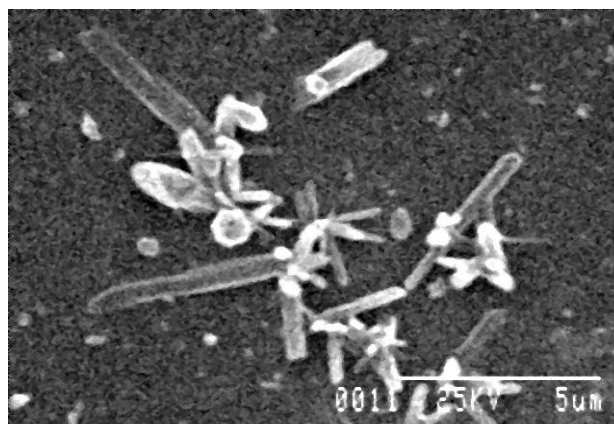


Fig. 8b-

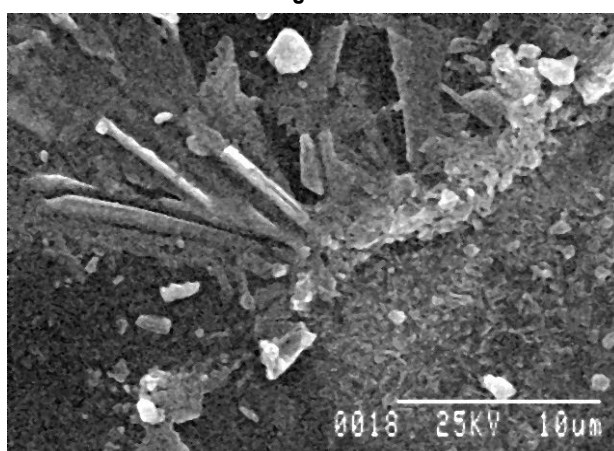


Fig. 8c-

Conclusions

The main findings of our attempt to develop a new and improved methodology of characterization of fullerene-porphyrin non-covalent assembly in presence of silver nanoparticles are summarised as follows:

- The absorbance value of the Soret absorption peak gets reduced when fullerene-**1** non-covalent complexation process is monitored in presence of AgNp in solution.
- It is observed that the quenching efficiencies of both C₆₀ and C₇₀ have been reduced in presence of AgNp in toluene.
- Estimation of binding constants applying steady state fluorescence spectroscopic techniques reveal that **1** could not serve as an efficient complexing agent towards C₆₀ and C₇₀ in presence of AgNp; however, **1** serves as a better discriminator molecule towards C₇₀ in presence of AgNp.
- Conductance measurements evoke that AgNp particle reduces the magnitude of conductance value for the fullerene-**1** systems in presence of AgNp.
- DLS studies establish the fact that particle size of AgNp becomes shorter when complexation takes place between fullerenes and **1**, and it is the primary reason behind getting lesser magnitude of *K* value for fullerene-**1** systems.
- SEM measurements, for the first time, establish the formation of C₆₀-porphyrin-AgNp nanorod and prove that the shape and the size of the surface holes on the fullerene-porphyrin-AgNp

structure play an important role in controlling the formation of molecular clusters with fullerenes.

- The results emanating from present investigations would be of potential interest in studying the interaction between fullerenes and diporphyrin in presence of gold and silver nanoparticles in near future.

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Supporting information available

UV-Vis absorption spectral variation in the kinetics experiment of **1** in presence of AgNp, plot of absorbance vs. time for **1**-AgNp kinetics experiment, UV-Vis absorption spectral variation in the kinetics experiment of **1** in presence of C₆₀ + AgNp and plot of absorbance vs. time for C₆₀-**1**-AgNp system, conductance value of **1** + AgNp mixture in toluene, conductance value of C₆₀ + **1** + AgNp mixture in toluene, conductance value of C₆₀ + **1** system in absence of AgNp, conductance value of C₇₀ + **1** + AgNp mixture in toluene and conductance value of C₇₀ + **1** system in absence of AgNp are given as Figs. 1S-3S and Tables 1S-5S, respectively. Figures 1S-3S and Tables 1S-5S are provided as supporting information. Supporting information associated with this paper are available free of charge via the internet.

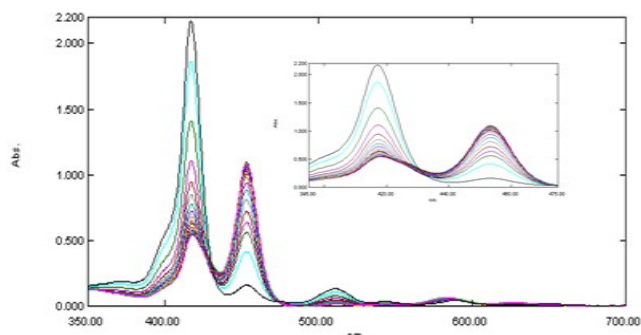


Fig. 1S- UV-Vis absorption spectral variation of the **1** ($4.75 \times 10^{-6} \text{ mol} \times \text{dm}^{-3}$)-AgNp system recorded in toluene with time; the inset of Fig. 1S demonstrates the clear view of such spectral variation at two different wavelengths, namely, 417 nm and 453 nm

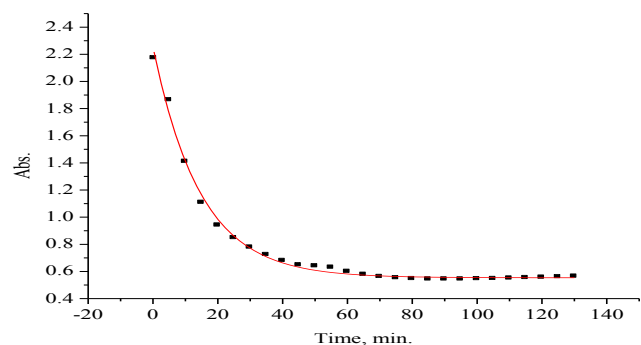


Fig. 2S- Plot of the variation of the absorbance vs. time for **1**-AgNp system recorded in toluene

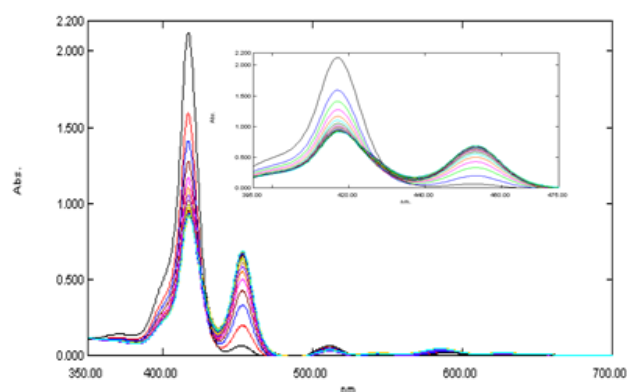


Fig. 3S(a)-

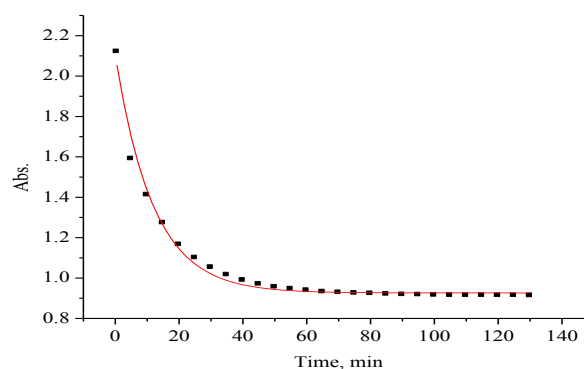


Fig. 3S(b)-

Fig. 3S- (a) UV-Vis absorption spectral variation of the C₆₀($2.0 \times 10^{-5} \text{ mol} \times \text{dm}^{-3}$)-**1**($4.75 \times 10^{-6} \text{ mol} \times \text{dm}^{-3}$)-AgNp system recorded in toluene with time; the inset of Fig. 3S(a) demonstrates the clear view of such spectral variation at two different wavelengths, namely, 417 nm and 453 nm; and (b) plot of the variation of the absorbance vs. time for C₆₀-**1**-AgNp system

Table 1S- Conductance value of **1** + AgNp mixture in toluene. Temp. 298K

Conductance	Time
0.2ms	0 min
0.3ms	3.84 min
0.4ms	11.54 min
0.5 ms	20.1 min
0.6 ms	28.75 min
0.7 ms	37.00 min
0.8 ms	44.67 min
0.9 ms	52.84 min
1.0 ms	61.67 min
1.1 ms	78.17 min
1.2 ms	83.48 min
1.3 ms	92.34 min
1.4 ms	102.217 min
1.5 ms	109.084 min
1.6 ms	116.44 min

Table 2S- Conductance value of C₆₀ + **1** + AgNp mixture in toluene. Temp. 298K

Conductance	Time
0.2ms	0 min
0.3ms	54.4 min
0.4ms	127.97 min

Table 3S- Conductance value of $C_{60} + 1$ mixture in toluene. Temp. 298K

Conductance	Time
0.1ms	0 min
0.2ms	25.54 min
0.3ms	124.07 min

Table 4S- Conductance value of $C_{70} + 1$ mixture in toluene. Temp. 298K

Conductance	Time
0.1ms	0 min
0.2ms	1.11 min
0.3ms	37.0 min
0.4 ms	70.87 min
0.5 ms	115.67 min

Table 5S- Conductance value of $C_{70} + 1 + AgNp$ mixture in toluene. Temp. 298K

Conductance	Time
0.1ms	0 min
0.2ms	31.88 min
0.3ms	80.75 min
0.4 ms	139.74 min

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