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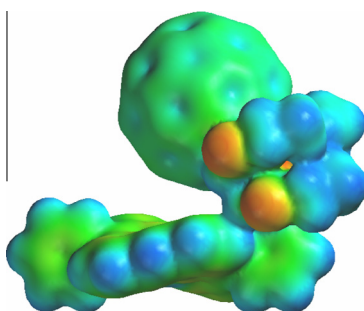
Role of charge transfer interaction and the chemical physics behind effective fulleropyrrolidine/porphyrin non-covalent interaction in solution

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HIGHLIGHTS

- First time report on CT interaction between PyC₆₀ and porphyrin in solution.
- Fluorescence study elicits efficient quenching of **1** in presence of PyC₆₀.
- Time-resolved emission study reveals formation of charge-separated state.
- DFT calculations explore electronic structure of PyC₆₀/**1** system in *vacuo*.
- Photoinduced electron transfer via ¹PyC₆₀ from **1** is confirmed.

GRAPHICAL ABSTRACT

PyC₆₀/**1** system

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ABSTRACT

The present paper reports the photophysical insights on supramolecular interaction of a monoporphyrin derivative, namely, **1**, with C₆₀ pyrrolidine tris-acid ethyl ester (PyC₆₀) in toluene and benzonitrile. The ground state interaction between PyC₆₀ and **1** is facilitated through charge transfer interaction. Both UV–Vis and steady state measurements elicit almost similar magnitude of binding constant for the PyC₆₀/**1** complex in toluene and benzonitrile, viz., 6825 and 6540 dm³ mol⁻¹, respectively. Life time measurement evokes that rate of charge separation is fast in benzonitrile. Both hybrid-DFT and DFT calculations provide very good support in favor of electronic charge-separation in PyC₆₀/**1** system in *vacuo*.

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Introduction

After the initial discovery in 1984 [1], the fortuitous contemporary growth of two apparently independent research lines, namely synthetic fullerene chemistry and supramolecular fullerene photochemistry, has been reciprocally beneficial and contributed to

boost activity in both fields. On the other hand, porphyrins are known to be one of the most common and versatile chromophores. Porphyrins offer a variety of desirable features such as a rigid and planar geometry, high stability, intense electronic absorption, strong fluorescence emission, and a small HOMO–LUMO energy gap [2]. For all this motivation, supramolecular architectures containing porphyrins and metalloporphyrins are particularly attractive. The molecular recognition process between fullerenes and porphyrins was recognized in a very unintentional way, prompting

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the birth of a new supramolecular recognition element [3]. The use of porphyrins and fullerenes in supramolecular chemistry is appreciated not only for the affinity that exists between the flat tetrapyrrole ring and the curved surface of the fullerene [4,5], but also for the capability that the fullerene/porphyrin assemblies possess to produce photoinduced charge-separated species mimicking the natural photosynthesis processes [6,7].

One of the main challenges in the field of supramolecular chemistry is the translation of molecular structure into function. In fact, synthetic multiporphyrin assemblies have been extensively investigated in materials science and nanotechnology and, in particular, its application to light-induced functions which attracted a great deal of interest [8–10].

The attainment of a better understanding of the dependence of photoinduced electron transfer reaction rates on the molecular structures of the donor and acceptor entities consisting fullerene/porphyrin and fullerene/phthalocyanine systems which resulted in improving the capture and storage of solar energy are nicely described by D'Souza et al. [11]. Very recently, Torres and co-workers have demonstrated that porphyrin- and phthalocyanine/carbon nanostructure ensemble(s) may be suitably utilized for the construction of artificial photosynthetic reaction center [12].

The motivation behind selecting the PyC_{60} molecule as an electron acceptor comes from the pioneering work of Prato and Maggini on the synthesis and photophysical properties of such molecule [13]. Later, Sessler et al. successfully employed fulleropyrroline bearing a guanosine moiety as a recognition motif for the construction of C_{60} -phthalocyanine (Pc) dyad system [14]. Very recently, we have got enough evidences behind effective non-covalent interaction between PyC_{60} and various Pc derivatives in solution [15]. The basic intention of the present work, therefore, is to find out the possibility of ground state non-covalent interaction between PyC_{60} and a designed monoporphyrin derivative, namely, **1** (Fig. 1), in solution having varying polarity. The motivation behind selecting monoporphyrin having coumarin unit comes from the fact that metal-free organic dye present very attractive candidate for the construction of de sensitized solar cell, with some significant advantage over the organometallic complexes. This include the ease with which they can be synthetically modified, low production cost, the absence of often scare metal elements and much higher extinction co-efficient [16]. Coumarin [17] is amongst the first organic species to demonstrate high device efficiency and having displaying good log-term ability. Various spectroscopic tools like absorption spectrophotometric, steady state fluorescence, time-resolved fluorescence and transient absorption studies are employed to find out the extent of such interaction. Quantum chemical calculations at hybrid-DFT and DFT levels of theory are performed to investigate the possibility of electronic redistribution between PyC_{60} and **1** during complexation. We

anticipate that the use of functionalized form of fullerene C_{60} to undergo non-covalent type of interaction with donor molecules having photoactive and electroactive units would certainly generate some new and interesting photophysical features in supramolecular photochemistry of fullerenes.

Materials and methods

PyC_{60} is purchased directly from Aldrich, USA and used without further purification. The monoporphyrin, **1**, is obtained as a gift material from Dr. A. Bauri, BARC, India. The synthetic procedures and related spectroscopic data on this compound will be published in some other journal, very soon. UV–Vis spectroscopic grade toluene (Merck, Germany) has been used as solvent to favor non-covalent interaction between PyC_{60} 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-7000 model spectrofluorimeter. Fluorescence decay curves are measured with a HORIBA Jobin Yvon single photon counting set up employing nanoleo as excitation source. PyC_{60} is selectively excited by 532 nm light from a Nd:YAG laser (6 ns fwhm) with 7 mJ power. For the transient absorption spectra in the visible region, a photomultiplier tube has been used as a detector for the continuous Xe-monitor light (150 W). Theoretical calculations are performed with a Pentium IV computer using SPARTAN'06 V1.1.0 Windows version software.

Results and discussions

UV–Vis absorption studies

The extensively conjugated aromatic chromophoric system of porphyrin generates intense bands in its absorption spectrum. The stronger and the most well-resolved absorption band of **1** is detected in the visible region (ranging from 375 to 580 nm (Fig. 2). Generally, in case of porphyrin, one intense absorption band is noticed around ~ 400 nm due to $S_2 \leftarrow S_0$ transition (Soret band) and Q-absorption bands are observed in the region of 475–650 nm due to $S_1 \leftarrow S_0$ transition. In our present case, **1** exhibits the Soret absorption band at 412 nm and Q-absorption peaks 503, 542 and 577 nm in toluene against the solvent as reference (Fig. 2). When the spectrum is recorded in benzonitrile, peak shift is observed in the longer wavelength region due to the increase in the polarity of the solvent. The Soret and Q-absorption peaks are shifted to 415, 504, 544 and 579 nm, respectively (Fig. 2). The first evidence in favor of ground state complexation between PyC_{60} and

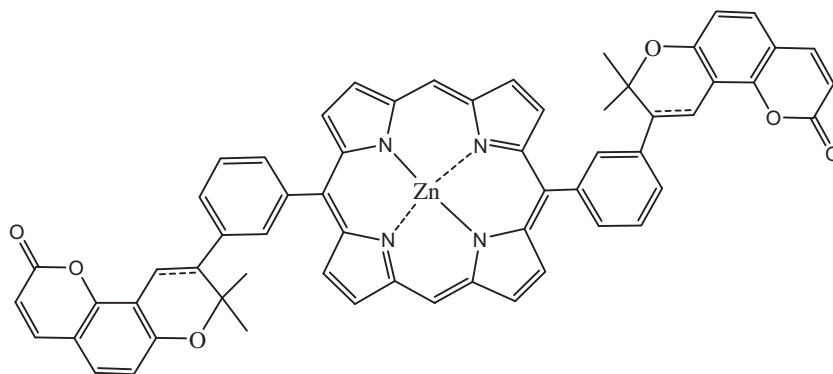


Fig. 1. Structure of **1**.

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