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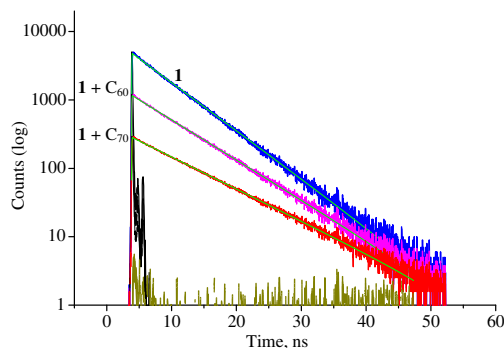
Photophysical investigations on supramolecular fullerene/phthalocyanine charge transfer interactions in solution

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HIGHLIGHTS

- CT interaction between a free-base phthalocyanine (**1**) and fullerene in solution.
- Fluorescence study elicits efficient quenching of **1** in presence of C₆₀ and C₇₀.
- Time-resolved emission study reveals formation of charge-separated state.
- Photoinduced electron transfer from **1** to fullerene is confirmed.
- PM3 calculations establish side-on binding motif of C₇₀ towards **1** in *vacuo*.

GRAPHICAL ABSTRACT



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ABSTRACT

The photophysical features of non-covalently linked fullerenes C₆₀ and C₇₀ with a designed free-base phthalocyanine, namely, 2,3,9,10,16,17,23,24-octakis-(octyloxy)-29H,31H-phthalocyanine (**1**) have been investigated employing various spectroscopic tools like UV–vis absorption spectrophotometry, steady state and time resolved fluorescence along with proton NMR measurements in toluene. The ground state interaction between fullerenes and **1** is nicely demonstrated with the appearance of well defined charge transfer absorption bands in the visible region of the electronic spectra. Steady state fluorescence experiment reveals efficient quenching of the excited singlet state of **1** in presence of both C₆₀ and C₇₀. The average values of binding constants for the non-covalent complexes of C₆₀ and C₇₀ with **1** are determined to be ~18,150 and ~32,000 dm³ mol⁻¹, respectively. The magnitude of *K* suggests that **1** preferentially binds C₇₀ in comparison to C₆₀ although average value of selectivity in binding is measured to be low (~1.75). Time resolved emission measurements establish photoinduced energy transfer from the excited singlet state of **1** to fullerene in toluene. Measurements of free energy of electron transfer and free energy of radical ion-pair formation elicit that C₇₀/**1** complex is stabilized more in comparison to C₆₀/**1** complex regarding generation of charge-separated state. Proton NMR studies provide very good support in favor of effective ground state complexation between fullerenes and **1**. Semi empirical theoretical calculations on fullerene/**1** systems in *vacuo* substantiate the stronger binding between C₇₀ and **1** in comparison to C₆₀/**1** system in terms of heat of formation value of the respective complexes, and determine the orientation of bound guest (here C₇₀) towards the plane of **1** during complexation.

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Introduction

Non-covalent forces are key to maintain molecules together in supramolecular chemistry; likewise the covalent bond is the essence of the link between atoms in molecules [1,2]. As much of the inspiration and origins of non-covalent or supramolecular chemistry comes from the chemistry found in living biological systems, many studies have been focused on developing artificial photosynthetic systems to achieve light-to-energy conversion similar to the natural photosynthetic system that converts solar energy into chemical energy very efficiently and is regarded as one of the most elaborate nano-biological machines [3–5]. Now-a-days, one of the main challenges in the field of supramolecular chemistry is the construction of artificial photosynthetic reaction center through rational design of donor–acceptor ensemble capable of producing light induced charge separation over a long distance [6,7].

Phthalocyanines (Pcs) [8–12], structural analogues of porphyrins, exhibit several outstanding physicochemical properties, which render them of great interest in a variety of scientific and technological areas. Particularly, promising application of Pcs appears in the field of photovoltaics [13,14]. The strong absorption of Pcs in the solar spectrum with very high molar extinction coefficients together with their rich redox chemistry, provides both excellent light-harvesting and electron-donor features and prompts to their potential. Pcs can also function as electron acceptors [15] and it is verified that the peripheral substituents in the Pcs influence the properties for both Pc and metalloPc [16–18].

Fullerenes, C_{60} and C_{70} , are charming and valuable third generation carbon allotropes with low reduction potentials and strong electron acceptor properties [19–23]. Fullerenes are employed as suitable building blocks for the development of multi-component supramolecular systems because of their three dimensional structure [24] and energetically favorable first reduction potentials

[25]. Low reorganization energy [26,27] of fullerenes is responsible very much for the acceleration of the photo induced charge separation and deceleration of charge recombination [28].

The molecular recognition process between fullerenes and Pcs was, therefore, recognized through examination of the photo-physical behavior of various covalently linked fullerene/Pc dyad [29–34], prompting the birth of a new supramolecular recognition element. The study on non-covalently linked fullerene/Pc system, however, is rare despite the long-standing interest in these versatile and unique materials. Only in recent past, we explored that electrostatic interaction plays key role behind fruitful non-covalent interaction between fullerenes and Pc in solution through systematic photophysical studies on fullerene/Pc (free-base) and fullerene/ZnPc systems [35]. Very recently, Abe et al. have nicely demonstrated the photo-anodic characteristics of an organic p/n bilayer of fullerene (C_{60} , n-type semiconductor) and metal-free phthalocyanine (H_2Pc , p-type semiconductor) in water phase [36]. As previously told [16–18], insertion of long chain alkyl groups in the periphery of metalloPc (here ZnPc) molecule results formation of size-selective non-covalent complexes with fullerenes C_{60} and C_{70} in solution [37]. In this case [37], the presence of eight numbers of octyloxy group made an octopus like embrace surrounding the ZnPc molecule which resulted large-driving forces for the charge recombination and small reorganization energies in presence of fullerenes. Therefore, the ZnPc molecule (Fig. 1(a)) plays the role of an antenna (i.e., absorbing very efficiently light in the visible region of the solar spectrum) and also as a donor molecule in $C_{60}/ZnPc$ and $C_{70}/ZnPc$ non-covalent systems. Considering these results, the possibility of using this kind of supramolecular recognition element(s) as material(s) for photovoltaic devices has come. However, the successful utilization of these systems into devices is strongly related to the possibility to control the spatial arrangement of these molecules with respect to each other, since a high degree of order of these molecules at the molecular level is often accompanied by an improvement in the device's performance. To achieve this goal then, it is necessary to carefully design and prepare fullerene/Pc systems capable to self-organize spontaneously into highly-ordered supramolecular structures. For these reasons, we have undertaken a more detailed study with the free-base analogue of ZnPc, i.e., **1** (Fig. 1(b)) to study various physicochemical properties reaching from UV–vis, steady state and time-resolved fluorescence to NMR and quantum chemical calculations. We anticipate that the present work might bring very interesting and new photo-physical insights on $C_{60}/\mathbf{1}$ and $C_{70}/\mathbf{1}$ supramolecular assemblies in solution.

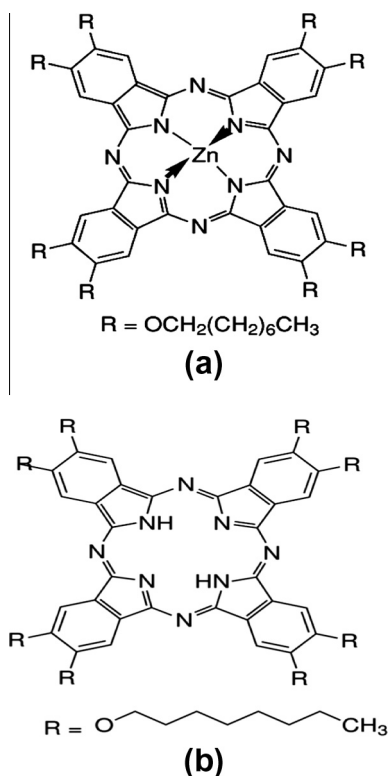


Fig. 1. Structure of (a) ZnPc and (b) **1**.

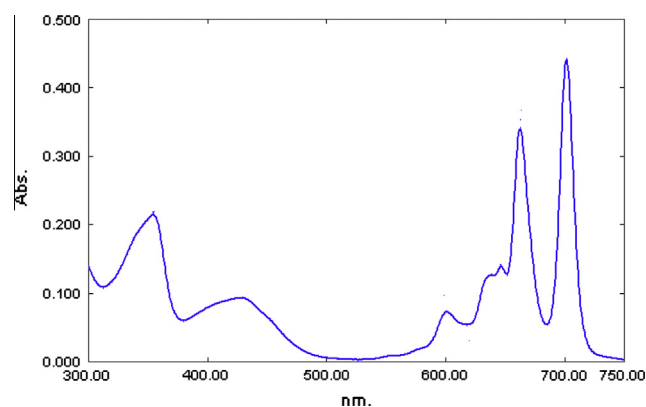


Fig. 2. UV–vis absorption spectrum of **1** (2.15×10^{-6} mol dm⁻³) recorded in toluene medium.

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