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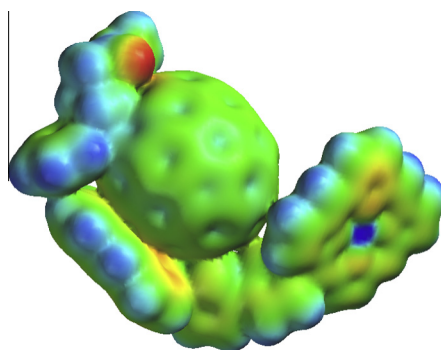
Absorption spectrophotometric, fluorescence and quantum chemical investigations on non-covalent interaction between PC₇₀BM and designed diporphyrin in solution

Anamika Ray^a, Ajoy Bauri^b, Sumanta Bhattacharya^{a,*}^aDepartment of Chemistry, The University of Burdwan, Golapbag, Burdwan 713 104, India^bBio-organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

HIGHLIGHTS

- PC₇₀BM/diporphyrin non-covalent interaction is established in solution.
- Carbazole spacer diporphyrin exhibits largest value of binding constant with PC₇₀BM.
- High selectivity of binding is observed in polar solvent.
- *Ab initio* calculations establish size selective orientation during complexation.

GRAPHICAL ABSTRACT

MEP of PC₇₀BM/**1** system (end-on orientation of PC₇₀BM) done by *ab initio* calculation in *vacuo*.

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ABSTRACT

Present work reports the photophysical insights on supramolecular interaction of a C₇₀ derivative, namely, [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₀BM), with two designed diporphyrin molecules having dithiophene (**1**) and carbazole (**2**) spacer in toluene and benzonitrile. Both absorption spectrophotometric and steady state fluorescence investigations reveal efficient complexation of PC₇₀BM with **1** and **2** in both toluene and benzonitrile. The magnitude of average value of binding constant, viz., K_{av} , for the complexes of PC₇₀BM with **1** and **2** in toluene (benzonitrile) are estimated to be $2.185 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ ($3.215 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$) and $10.180 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ ($25.405 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$), respectively. Selectivity in binding for the complexation process of PC₇₀BM with **1** and **2** is estimated to be ~ 4.6 and ~ 7.90 as observed in toluene and benzonitrile, respectively. The complexation between PC₇₀BM and diporphyrin is well accounted by a theoretical model which takes into account the electronic subsystems of both acceptor and donor. *Ab initio* calculations in *vacuo* establish that size selective orientation pattern of PC₇₀BM towards the cavity of diporphyrin dictates the magnitude of binding and electronic structure of the PC₇₀BM/diporphyrin complexes.

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Introduction

Self-assembled donor–acceptor nanohybrids are considered to be a viable alternative for the covalently linked molecular polyads in order to achieve an increased rate and yield of the

* Corresponding author. Tel.: +91 9433962777; fax: +91 342 2530452.
E-mail address: sum_9974@rediffmail.com (S. Bhattacharya).

charge-separation process and at the same time, prolongation of the lifetime of the charge separated state. Nanohybrid systems that combine the favorable features said above, for example, fullerenes and porphyrins as electron acceptors and electron donors, respectively, have received considerably interest in recent past [1–7]. As a consequence, new materials with a wide range of unique and spectacular physicochemical properties have resulted in noteworthy advances in the areas of light induced electron transfer chemistry and solar energy conversion [8–10]. It is mainly the small reorganization energy that fullerenes exhibit in electron transfer reactions, is accountable for a significant breakthrough [11–12]. One of the commonly used strategies to achieve the formation of charge-separated states during photo induced electron and/ energy transfer in fullerene/porphyrin systems involves promoting multi-step electron transfer reactions along well-defined redox gradients [13,14]. The most important and unprecedented finding is that electronic communication between the porphyrin donor and fullerene acceptor is even possible through a considerable number of σ - and hydrogen bonds. This is expected to open new avenues of approaches for the inexpensive and efficient construction of new prototypes of supramolecular recognition element.

The intention of this work is to develop and to analyze novel electron donor–acceptor systems consisting designed diporphyrin molecules and a C_{70} derivative, namely, [6,6]-phenyl C_{70} butyric acid methyl ester ($PC_{70}BM$; Fig. 1). For enhancing the solar light harvest, the soluble C_{70} derivative, i.e., $PC_{70}BM$ has been used as electron acceptor in recent past [15,16]. The most important character of $PC_{70}BM$ is based upon narrow band gap for enhancing the solar light harvest in the wavelength region of 350–500 nm [17–19]. Starting from our well established supramolecular approaches in solution [20,21], non-covalent directed recognition motif is chosen to construct self-assembled fullerene/diporphyrin architecture with designed diporphyrin receptor, e.g., diporphyrins having dithiophene (**1**) and carbazole spacer (**2**) unit between two monoporphyryns [22,23] (Fig. 1). We anticipate that the introduction of suitable spacer (or group) between two monoporphyrin units would lead to gable type diporphyrin receptors with selective recognition ability towards $PC_{70}BM$ in solvent having varying polarity. UV–vis and steady state fluorescence spectroscopic tools supported by *ab initio* calculations in *vacuo* give credence to the relation between molecular complex formation and stability.

Materials and methods

$PC_{70}BM$ is purchased from Aldrich, USA. **1** and **2** have been synthesized according to the method described in literature [22,23]. UV–vis spectroscopic grade toluene and benzonitrile (Merck, Germany) have been used as solvent to favor non-covalent interaction between fullerene and diporphyrin 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. Fluorescence spectra have been recorded with a Hitachi F-7000 model spectrofluorimeter. Theoretical calculations are performed in 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 the diporphyrins, namely, **1** and **2**, generate intense bands in their absorption spectra. The stronger and the most well-resolved absorption bands of **1** and **2** have been detected in the visible region (ranging from 350 to 600 nm (Fig. 2(a)) and popularly

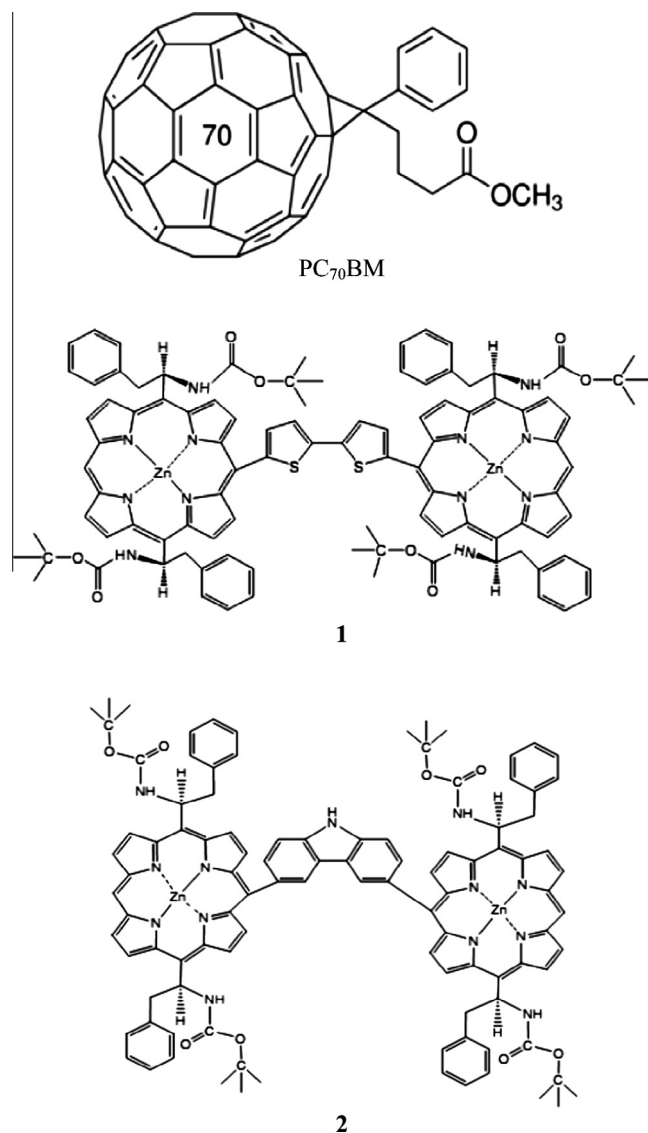


Fig. 1. Structures of $PC_{70}BM$, **1** and **2**.

known as Soret (or B) and Q peaks. For metalloporphyrin, generation of Q and B bands follow the orbital model proposed by Gouterman et al. [24,25]. B and Q absorption bands in metalloporphyrin correspond to the vibronic sequence of the transition from the ground singlet S_0 to 2nd (S_2) and 1st excited singlet states (S_1), i.e., $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$, respectively. The position of the B and Q bands of the diporphyrins are listed in Table 1. Table 1 clearly demonstrates with increasing the solvent polarity from toluene ($\epsilon = 2.4$) to benzonitrile ($\epsilon = 25.2$), considerable amount of red shift of the absorption bands takes place for both **1** and **2**. $PC_{70}BM$ shows main absorption peaks at 375, 407 and 463 nm in toluene, which suffers very little peak shift as observed in benzonitrile (Fig. 2(b)). Evidence in favor of ground state complexation phenomenon between $PC_{70}BM$ and **1** comes from UV–vis absorption spectrophotometric titration measurements. Addition of varying concentration of $PC_{70}BM$ (in toluene and benzonitrile) [26,27] to **1** (fixed concentration) produces considerable change in the absorbance value of the uncomplexed diporphyrin solution (i.e., A_0) at its B absorption band. A systematic relative decrease in the absorbance value of **1** (ΔA) in presence of $PC_{70}BM$ takes place in $PC_{70}BM$ /**1** mixture with increasing concentration of acceptor solution (Fig. 3(a) and (b) for $PC_{70}BM$ /**1** mixture in toluene and benzonitrile, respectively). Here, $\Delta A = A_0 - A$, and A signifies the

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