Molecular tetrads comprised of Zinc porphyrin-boron dipyrrin-triphenylamine triad to probe sequential energy/electron transfer events via axial ligation with C_{60}imidazole entity

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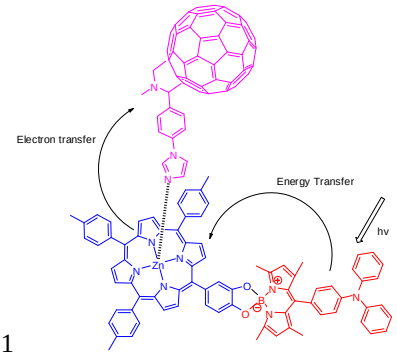
Abstract. There is a growing interest to mimic major processes in natural photosynthesis via artificial systems in order to harvest solar energy.
In the present study, we wish to report newly synthesized molecular triads comprised of Zinc porphyrin-boron dipyrrin-triphenylamine entities.Further, supramolecular tetrad is formed by axial ligation of imidazole functionalized fullerene. Systematic spectral, electrochemical and emission studies are performed to probe sequential energy transfer followed by electron transfer events in the newly synthesized triads. Computational studies using B3LYP/3-21G* are performed to arrive at the geometry and electronic structures. Photochemical study using time-resolved emission is performed to probe electron transfer events. Further, organic photocells are being built to directly convert light energy into electricity.

1. Introduction

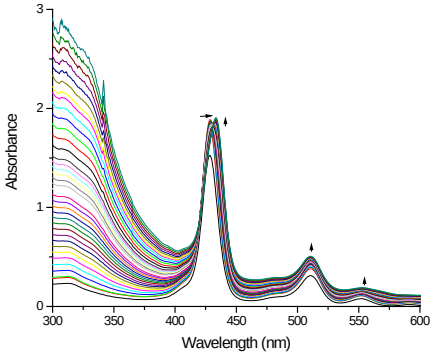
Green plants, algae and certain types of bacteria are capable of converting light energy into chemical energy. This light harvesting process is known as photosynthesis and it involves two main processes, transportation of absorbed light energy by antenna molecules to the reaction center and generating a charge separated entities via photo induced electron transfer (PET) [1]. In natural systems the antenna and reaction center entities are arranged in non-covalent fashion in order to achieve efficient solar energy conversion [2].
Mimicking the fundamental processes involved in natural photosynthesis using model systems is an interesting, challenging and demanding area of research in modern sciences. Many artificial systems have been studied to mimic antenna-reaction center functionality using porphyrin as an electron donor and fullerene as an electron acceptor linked via either covalent or non-covalent approach [3].
In present study we report artificial model system (Scheme 1) to mimic antenna –reaction center functionality using non- covalent supramolecular approach.



Scheme 1

In scheme 1, triphenylamine(TPA) appended borondipyrrin (BDP) acts as an energy absorbing and transferring antenna and Zinc-porphyrin (ZnP) acts as energy acceptor from antenna and promotes electron to electron accepting fullerene moiety (C60-Im) using absorbed energy. TPA-BDP is used stabilize charge separated entities other than antenna functionality. ZnP-C60-Im is used due to their characteristic properties in electron transfer reactions.

2. Experiment, Results, Discussion, and Significance.



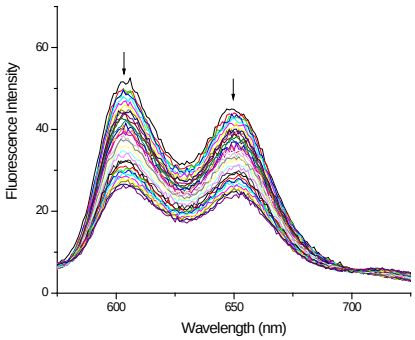


Fig.1**.** Optical absorption spectral changes of C60Im with the TPA-BDP-ZnP triad.

Fig. 2. Steady state fluorescence spectral changes of C60Im with TPA-BDP-ZnP triad.

In order to study ground state interactions between TPA-BDP-ZnP triad and C60-Im UV-Visible titration was performed (Fig.1) in o-dichlorobenzene. Spectral changes (425 nm band) were observed during addition of C60-Im and binding constants were calculated. These results indicate stable supramolecular tetrad formation by the axial ligation approach.

Steady state fluorescence studies were carried out to investigate electron transfer events between TPA-BDP-ZnP triad and C60-Im. Upon photo excitation of 550 nm band corresponds to ZnP, emission spectra were observed during addition of C60-Im. The quenching of fluorescence emission (605 and 650 nm bands) attributed to electron transfer reaction from ZnP moiety to C60-Im entity.

3. Conclusions

As revealed by the absorption and emission studies a stable supramoleculartertad is formed between TPA-BDP-ZnP and C60-Im via axial coordination and TPA-BDP moiety acts as an antenna in this tetrad and ZnP-C60-Im moiety functions as reaction center entity. However further studies are going on to get more data to support these conclusions.

4. Acknowledgment

The authors are thankful to National Science Foundation, NSF EPSCOR for funding and Dr. Nikolai V.Tkachenko for collaborating with this project.

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