

Design and Studies of a Self-Assembled Cofacial Zinc Phthalocyanine Dimer Complexed with Fullerene(s)

Eranda Maligaspe *, Francis D'Souza

Department of Chemistry, Fairmount College of Liberal Arts and Sciences

Abstract. Biomimetic bacterial photosynthetic reaction center complexes have been constructed using well-defined self-assembled supramolecular approaches. The “special pair” donor, a cofacial phthalocyanine dimer, was formed via potassium ion induced dimerization of tetra-(benzo-[15]crown-5) phthalocyanine. The dimer was subsequently self-assembled with functionalized fullerene(s) via axial coordination. The utilization of such well-defined multiple modes of binding in a controlled fashion results in the formation biomimetic supramolecular complexes which further allows to probe the photoinduced charge separation. These complexes were fully characterized using ¹H NMR, UV-Vis, electrochemical and mass spectrometric methods. The evidence for interaction in the ground state systems was obtained from spectroscopic and computational studies. Electron transfer from the excited zinc phthalocyanine to fullerene was revealed by steady and time-resolved emission studies.

1. Introduction

Self-assembly directed constructed of supramolecules capable of mimicking biological functions is one of the fastest growing areas of research. The potential applications of these self-assembly techniques to the design of molecular systems include light energy harvesting and nanotechnology.

The sequential multi-step electron transfer of the bacterial photosynthetic reaction centers realizes the efficient conversion of light energy into chemical energy. However, modeling the primary electron donor, as a ‘special pair’ has been limited to only a few studies due to the complexity in synthesizing such molecules. In the present study, building novel supramolecular ‘special pair’ donor-acceptor conjugates is presented. These complexes are ideal candidates for light harvesting devices (photovoltaic devices) to create a green environment.

2. Experiment, Results, Discussion, and Significance

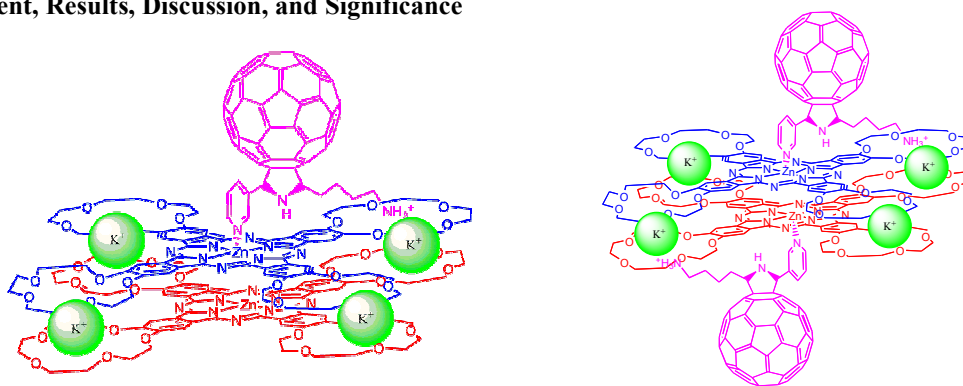


Figure 1. Construction of the supramolecular “special pair” porphyrin dimer-fullerene triad and tetrad.

Phthalocyanines with four crown-ether voids are known to dimerize by encapsulating K^+ cations to form dimer species. [1] In electronic absorption spectroscopy, this was monitored as a decrease in the Q band peak of monomer (around 675 nm) and concomitant increase of absorption intensity to shorter wavelength region (*ca.* 630 nm, the so-called dimer peak). Addition of functionalized fullerene, $PyC_{60}NH_3^+$ (Figure 1) to potassium induced zinc tetrakis (benzo-[15]crown-5) phthalocyanine dimer ($K_4[ZnTCPC]_2$) formation, which resulted in a

decreased dimer peak at 630 nm with a small red shift, typical of that expected axial coordination of pyridine to zinc phthalocyanine.

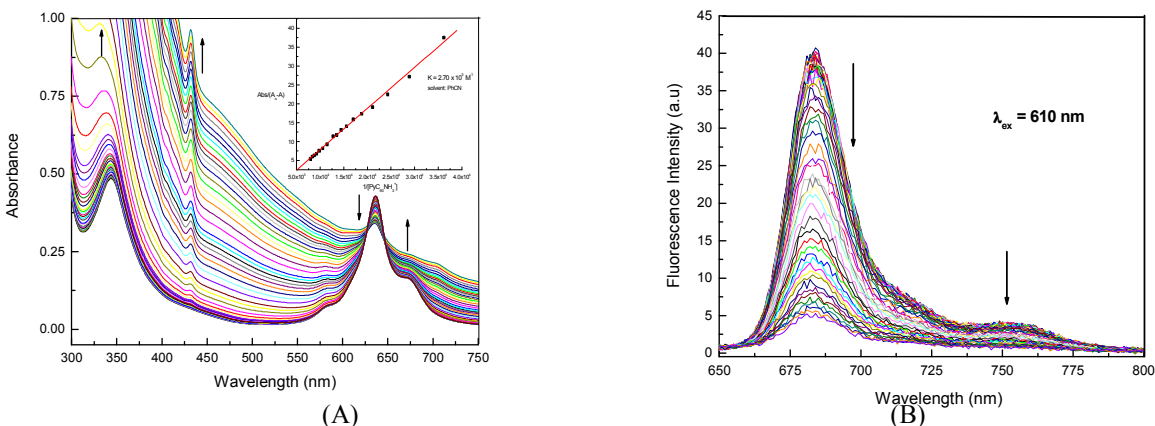


Figure 2. (A) UV-Visible spectra of $K_4[ZnTCPC]_2$ upon addition of $PyC_{60}NH_3^+$ in benzonitrile. The inset shows a Benesi-Hildebrand plot constructed for evaluating the binding constants. (B) Fluorescence spectral changes observed on increasing addition of $PyC_{60}NH_3^+$ to solution of $K_4[ZnTCPC]_2$ in benzonitrile.

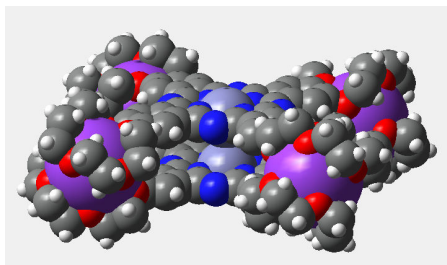
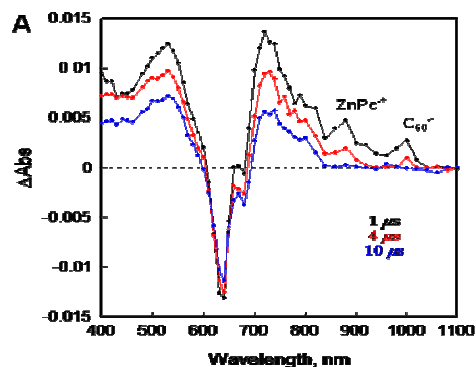


Figure 3. Ab initio B3LYP/3-21G(*) optimized geometries of $K_4[ZnTCPC]_2$

The computational studies were performed using density functional methods (DFT) at B3LYP/3-21G(*). In the dimer structure, the two phthalocyanine rings were stacked with a Zn-Zn distance of 4.77 Å.

The confirmation of the charge –separated state and evaluation of the charge recombination rate were performed by the nanosecond transient absorption spectral technique. Upon forming the supramolecular triad, the transient absorption spectrum revealed the characteristic band at 1000 nm of fulleropyrrolidine anion radical and 875 nm of Zn phthalocyanine cation radical, serving as a direct proof of charge separation within the supramolecular triad.

Figure 4. Femtosecond transient absorption spectra of $K_4[ZnTCPC]_2$ (10 μ M) with $PyC_{60}NH_3^+$ (100 μ M) in benzonitrile observed by 426 nm laser irradiation



3. Conclusions

Efficient charge separation from singlet excited Zn phthalocyanine dimer, $K_4[ZnTCPC]_2^*$ to the complexed fullerene within supramolecular triad and tetrad was observed. Hence, these complexes are real candidates for study of photo-induced charge transfer processes.

4. Acknowledgements

We are thankful to Navaneetha Krishnan, Melvin E. Zandler and Shunichi Fukuzumi. The authors are thankful to donor of National Science Foundation for a PR fellowship.

[1] N. Kobayashi, M. Togshi, T. Osa, K. Ishii, S. Yamauchi and H. Hino, *J.Am.Chem.Soc.* **1996**, 118, 1073-1085