

Design and studies of photo-induced electron transfer in ‘Pacman’ type porphyrin-fullerene conjugates

Eranda Maligaspe*, Francis D’Souza

Department of Chemistry, College of Liberal Arts and Sciences

Abstract. The design of donor-acceptor systems and the study of their photo-induced electron transfer processes are of current interest in artificial photosynthesis and solar energy conversion. Among donor-acceptor conjugates, systems with defined intramolecular distances and orientations are of particular importance to manipulate the efficiency of the electron transfer processes. These newly synthesized compounds were fully characterized using ¹H NMR, UV-Vis, electrochemical and mass spectrometric methods. Evidence for interaction in the ground state systems was obtained from spectroscopic and computational studies. Electron transfer from the excited zinc porphyrin to fullerene was revealed by steady and time-resolved emission studies.

1. Introduction

Studies on photoinduced charge transfer in organic molecular donor-acceptor systems have witnessed a rapid growth in recent years [1]. In our systems, an efficient donor, zinc porphyrin (ZnP), was functionalized with an elegant acceptor, fullerene, through a series of rigid linkers, resulting in a so-called ‘Pacman’ porphyrin-fullerene conjugate.

2. Experiment, Results, Discussion and Significance

Porphyrin-fullerene dyads involved in this study are presented in Figure 1.

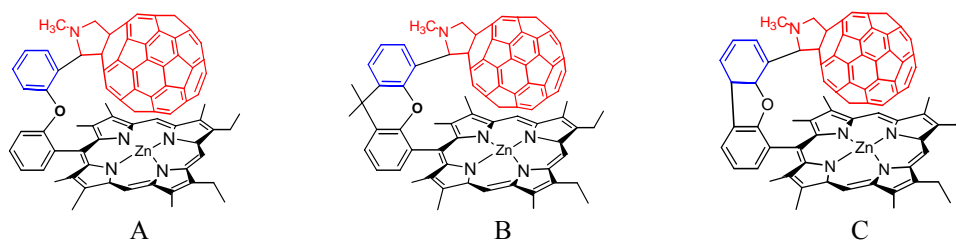


Fig. 1. A) 13,17-diethyl-2,3,7,8,12,18-hexamethyl-5-[8-(fulleropyrrolidine)diphenyl ether] zinc porphyrin B) 13,17-diethyl-2,3,7,8,12,18-hexamethyl-5-[8-(fulleropyrrolidine)-9,9-dimethyl-9H-xanthene] zinc porphyrin C) 13,17-diethyl-2,3,7,8,12,18-hexamethyl-5-[8-(fulleropyrrolidine)dibenzofuran] zinc porphyrin

The spectral features corresponding to Zn octaethyl porphyrin were seen in the visible region while these corresponding to fullerene were clearly envisioned around 330 nm in the UV region (Fig. 2). Evidence for the ground state interactions between porphyrin and fullerene moieties was provided by a weak CT (Charge Transfer) broad band around 680 nm that appeared at high concentrations of the compound (see as shown in Fig. 2a.) Steady state emission studies of flexible bridge porphyrin C₆₀ revealed a band around 826 nm. This can be attributed to the CT emission. The presence of a highly intense charge transfer band of the complex in polar solvents like DMF confirmed the efficient charge transfer process between the Zn porphyrin and C₆₀ moieties.

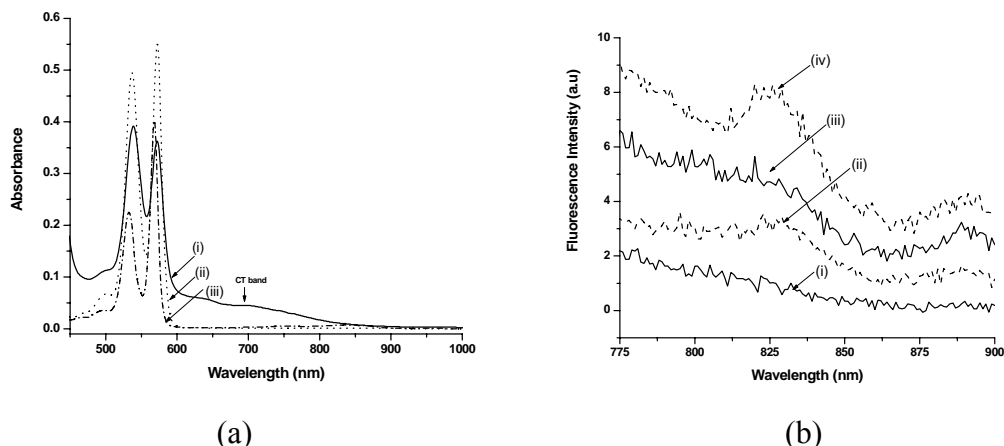


Fig. 2. (a) Absorption spectra of (i) flexible bridge porphyrin-C₆₀ (A), (ii) flexible bridge porphyrin aldehyde, and (iii) Octaethyl Zn porphyrin. The concentrations were held at constant at 3.68×10^{-5} M in *o*-DCB) (b) Fluorescence emission spectra of flexible bridge porphyrin-C₆₀ (A) in (i) *o*-DCB, (ii) acetonitrile, (iii) benzonitrile, and (iv) DMF. ($\lambda_{\text{ex}} = 680$ nm)

The computational studies were performed using density functional methods (DFT) at the B3LYP/ 3-21G level. The structures of rigid and flexible pacman porphyrin-fullerene compounds were optimized to a stationary point on the Born-Oppenheimer potential energy surface.



Fig. 3. *Ab initio* B3LYP/3-21G(*) optimized geometries of flexible bridge porphyrin-C₆₀ (a) HOMO and (b) LUMO

Electrochemical studies were performed to evaluate the redox potentials of the donor acceptor entities and free energy changes pertaining to charge separation and charge recombination processes were deduced.

3. Conclusion

The results of present study demonstrate that “pacman” porphyrin- C₆₀ compounds are real candidates for study of photo-induced charge transfer processes.

4. Acknowledgements

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[1] M.E El-Khouly, Y. Araki, O. Ito, S.Gadde, A.L. McCarty, P.A. Karr, M.E. Zandler, F. D’Souza. *Phy. Chem. Chem. Phys.*, Vol. 7, 3163-3171, 2005