

# Institute of Chemistry Ceylon Awards

## Devanathan Memorial Award - 2008

Dr. M A V Devanathan, the doyen of physical chemistry in Sri Lanka is one the greatest and internationally renowned chemist whose name is associated with the Triple Layer Theory in Electrochemistry which is called Devanathan's Triple Layer Theory.

This award is made annually to commemorate the commendable contributions and devoted services of Dr. Devanathan to the international community, the nation and the professional body of chemists in Sri Lanka.

The award is for an exceptional research contribution of an original nature in the field of Physical Chemistry and/or related areas, such as Physical-inorganic, physical-organic and biophysical chemistry.



**Professor K M Nalin de Silva** of the Department of Chemistry, University of Colombo is the recipient of the Devanathan Memorial Award 2008.

Professor de Silva graduated with a B.Sc. Special Degree in Chemistry (First Class Honours) from the University of Colombo in 1993. After obtaining a Ph.D. degree in Physical Chemistry, related to Time-Resolved Spectroscopy and Laser Induced Fluorescence (LIF) from the University of Cambridge, UK, he undertook postdoctoral research in Supramolecular Chemistry with Professor Jeremy K M Sanders at the University of Cambridge. Later he visited Unilever Centre for Molecular Informatics at the University of Cambridge and collaborated on Computational Chemistry projects with Dr. Jonathan Goodman. Recently he visited Louisiana State University, Baton Rouge, USA where he undertook research in the fields of Photovoltaics, Nanomaterials, Metal Organic Frameworks and Theoretical Chemistry with Professors Evgueni Nesterov, Andrew Maverick and Challa Kumar. He has been focusing on research in different areas of Physical Chemistry with emphasis on inter-disciplinary research.

## Abstract of the Devanathan Memorial Award

### Molecular design and quantum chemical calculations of material properties using *ab initio* and DFT methods

**Professor K M Nalin de Silva**

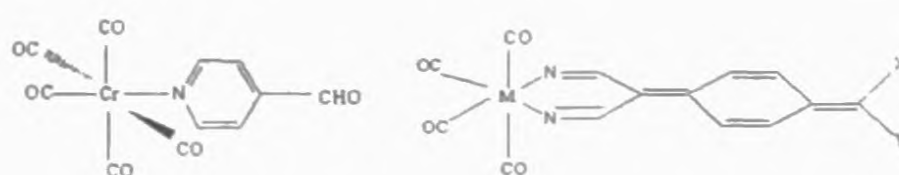
*Department of Chemistry, University of Colombo, Colombo*

The prediction of molecular properties of materials before the synthesis is becoming more important as the cost to design such materials continues to rise. A variety of theoretical methods have been used to predict molecular structure. Two of the most accurate predictions have, in general, come from *ab initio* molecular orbital theory and the Density Functional Theory (DFT). There is a real interest in discovering and designing new materials for use in non linear optical (NLO) applications such as optical switches and high-density optical recording. This abstract outlines the design of novel conjugated organic and organometallic materials and the prediction of nonlinear optical properties by using theoretical/computational methods.

Accurate *ab initio* studies of the first static hyperpolarizabilities ( $\beta$ ) of Fluorenyl derivatives were reported. The geometry optimizations, first static hyperpolarizabilities and HOMO-LUMO gaps of these molecules were calculated using Hartree-Fock level using 6-31G basis set using Gaussian 98W. (**J. Mol. Structure: THEOCHEM, 617/1-3 (2002), 169 – 175**). The basis sets incorporated in the comparison study

included STO-3G, 3-21G, 6-31G, 6-31+G, 6-31++G, 6-31G(d,p), 6-31+G(d,p), 6-311G, 6-311+G and 6-311++G. The semi empirical investigation was confined to AM1, PM3, MNDO, MNDOD and PM5 Hamiltonian. (**J. Mol. Structure: THEOCHEM, 725/1-3 (2005), 243-246.**)

Novel organometallic systems (Figure 1) with high  $\hat{\alpha}$  values were reported. The full geometry optimizations and calculations of the first hyperpolarizability ( $\hat{\alpha}$ ) of chromium, tungsten, iron, ruthenium and osmium carbonyls were performed using DFT method at B3LYP/LanL2DZ level of theory using GAUSSIAN 98W. (M=Cr, W, Fe, Ru and Os and X = CN, Y = NO<sub>2</sub>, These systems were designed by my collaborator Dr. Rohini M de Silva) (a) **J. Mol. Structure: THEOCHEM, 639 (2003), 195 – 201** (b) **J. Mol. Structure: THEOCHEM, 728/1-3 (2005), 141-145.**)



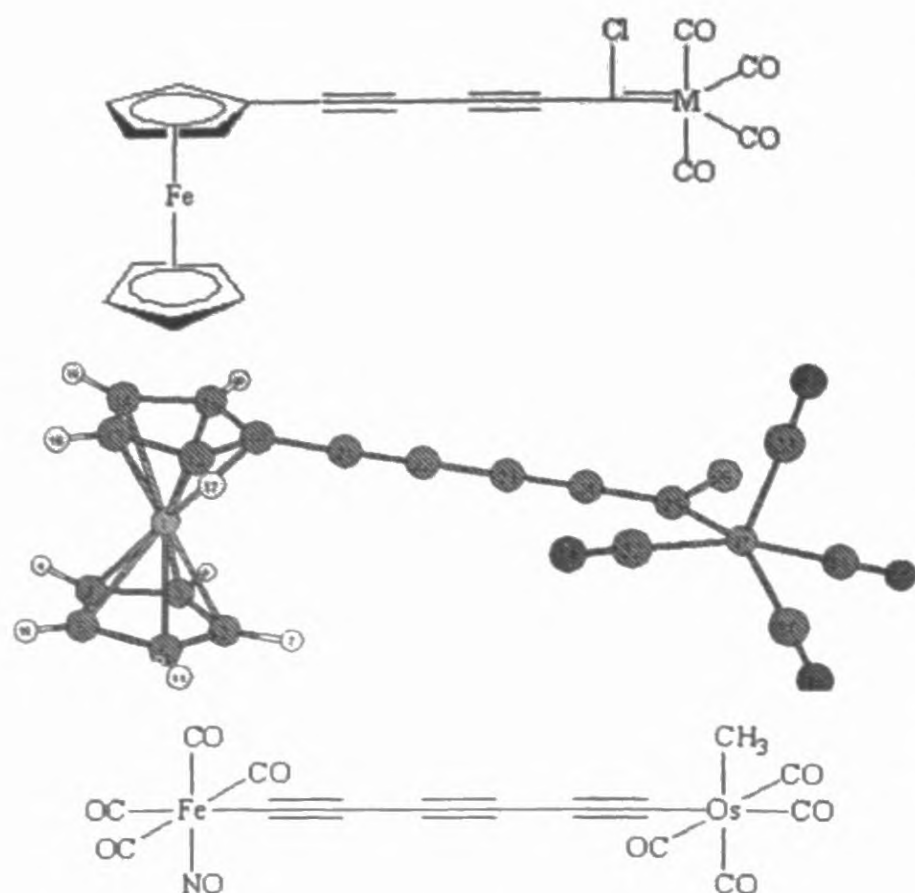


Figure 1: Some of the organometallic systems investigated by DFT method.

A comprehensive investigation of the class of compounds (Figure 2, about 15 compounds with varying X and Y) was carried out at the semi empirical level of the theory to determine their linear and non linear optical properties. (a) **J. Mol. Structure: THEOCHEM, 678/1-3 (2004), 31-38** (b) **Internet Electronic Journal of of Molecular Design, 2005, 4, 226-234.**

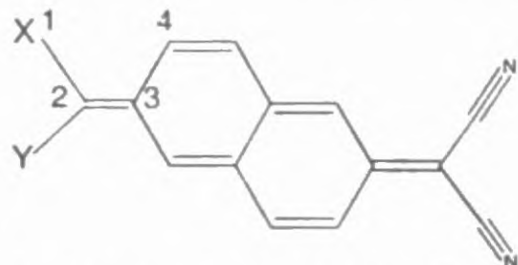


Figure 2: Conjugated  $\pi$ -system

The next contribution to the understanding of non-linear optical (NLO) properties of organic systems was concentrated on donor-acceptor aromatic systems (Figure 3). We reported the accurate *ab initio* quantum chemical calculations of the first static hyperpolarizability ( $\beta$ ) of donor-acceptor aromatic systems. (**J. Mol. Structure: THEOCHEM, 686(2004), 131-136.**)

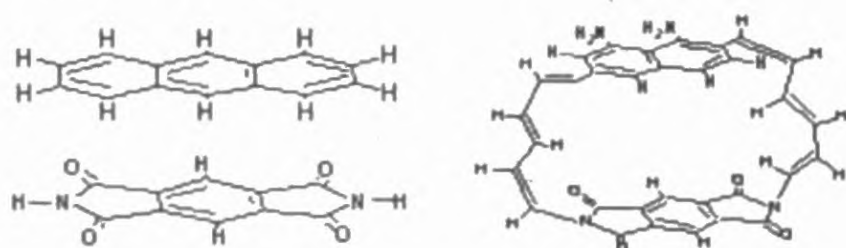


Figure 3: Donor-acceptor aromatic molecular systems

To understand the possibility of developing these systems as NLO materials we calculated the linear and nonlinear optical properties of bridged donor-acceptor systems. The study suggested that these unconnected

donor-acceptor systems equivalent to some [2]catenanes reported in the literature in general have little influence on the first static hyperpolarizability. However, the linked macro cyclic systems may have potential applications in the development of non-linear optical materials. During these calculations we have studied a 3-D potential energy surface and a contour diagram (Figure 4) of a three body recognition event using computational methods. (**J. Mol. Structure: THEOCHEM 678/1-3 (2004) 223 – 231.**)

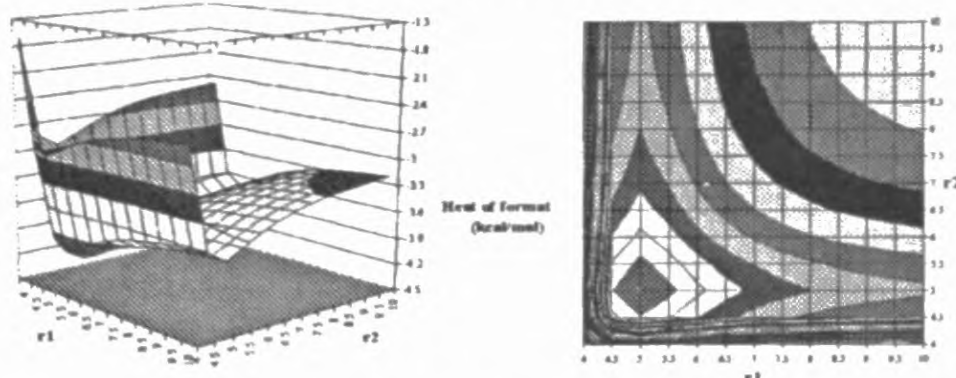


Figure 4: 3-D potential energy surface and a contour diagram of a three body donor-acceptor interaction.

The quantum chemical calculations of the non linear optical properties of meso- $\hat{a}$  doubly linked and meso-meso,  $\hat{a}$ - $\hat{a}$ ,  $\hat{a}$ - $\hat{a}$  triply linked porphyrin tapes have also been studied using PM5 Hamiltonian employing MOPAC 2002 within the BioMedCACHe 6.1. The triply linked porphyrin tapes (Figure 6) show much better enhancement of NLO properties than the doubly linked tapes (Figure 5) due to the planarity of the system. In all cases metallo porphyrin tapes show higher hyperpolarizability than the free base porphyrin tapes. (**J. Mol. Structure: THEOCHEM, 726/1-3 (2005), 39-45.**)

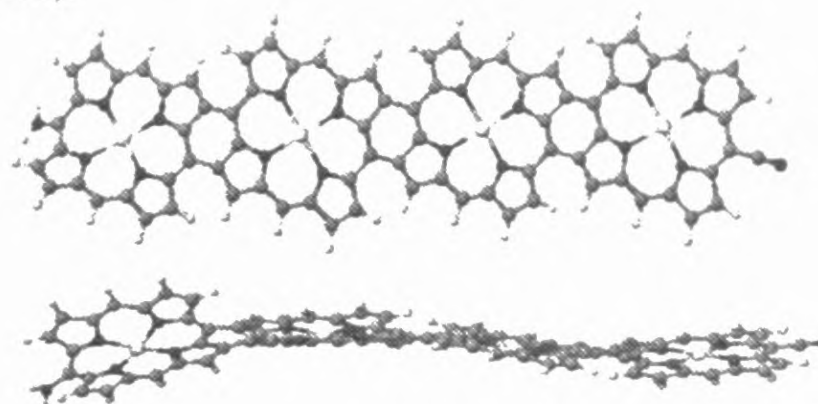


Figure 5: Optimized structures of meso- $\hat{a}$  doubly linked porphyrin tetramer molecular tape; Zn-tetramer – top view and Zn-tetramer – side view

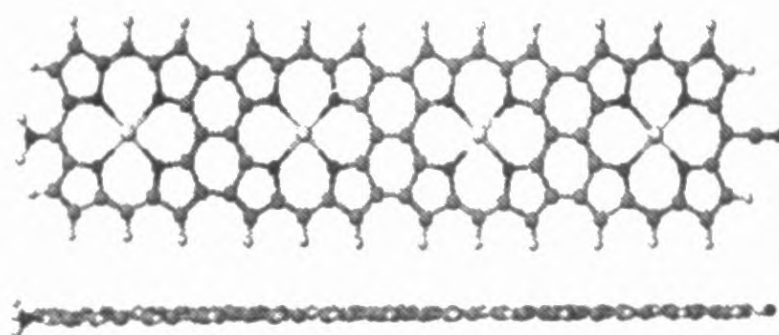


Figure 6: Optimized structures of meso-meso,  $\hat{a}$ - $\hat{a}$ ,  $\hat{a}$ - $\hat{a}$  triply linked porphyrin tetramer molecular tapes; tetramer-Zn – top view and tetramer-Zn – side view

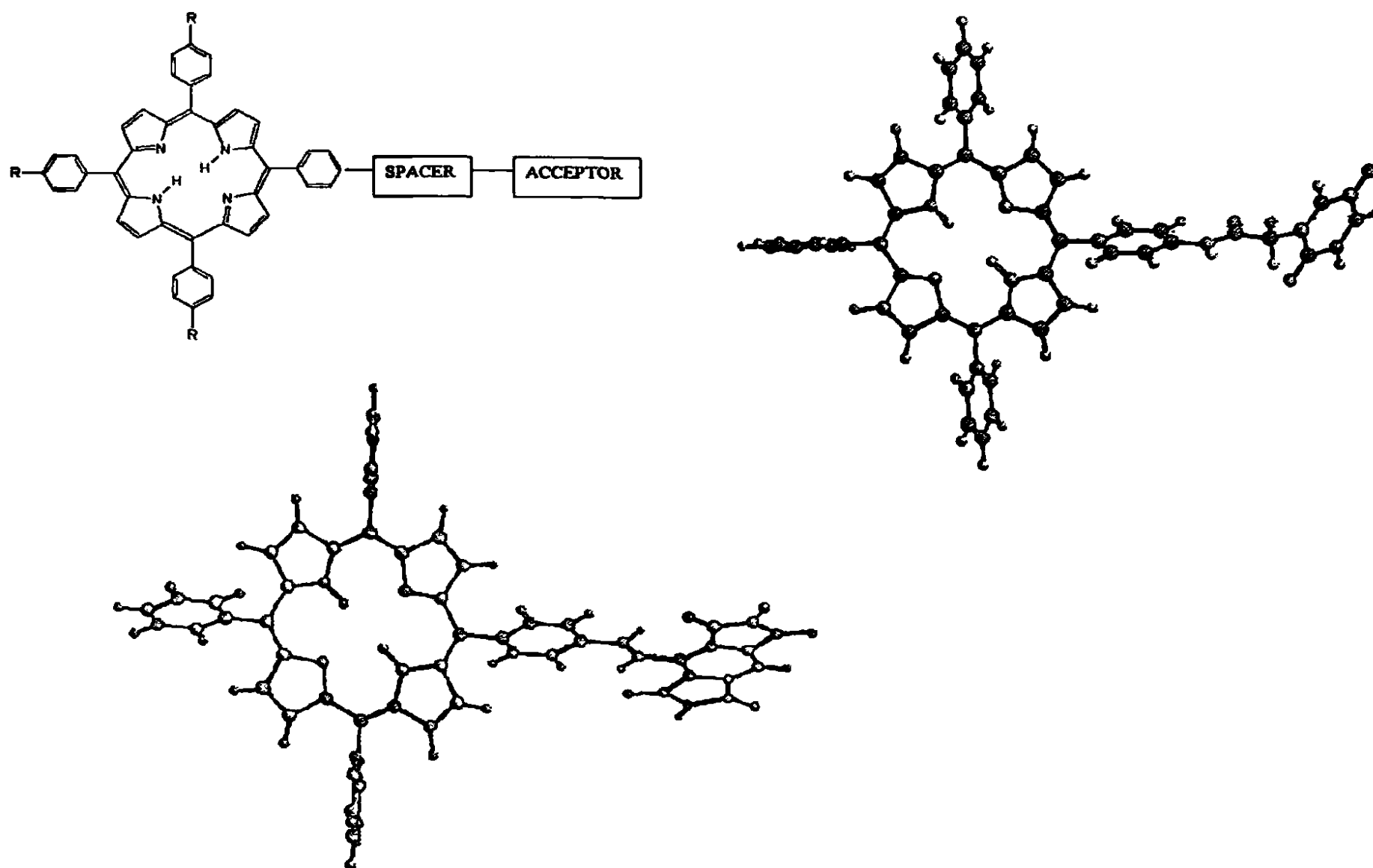


Figure 7: Porphyrin molecular systems

We have also reported accurate *ab initio* quantum chemical calculations of the first static hyperpolarizability ( $\beta$ ) of porphyrin systems (Figure 7) containing porphyrin moiety as the electron donor and quinone and pyromilliticdiimide as the electron acceptors separated by a spacer which influence the electronic communication between donor and acceptor. Geometries of all porphyrin molecules were optimised at the Hartree-Fock level with STO-3G minimal basis set and with the 3-21G split valence basis set using GAUSSIAN98W. (*J. Mol. Structure: THEOCHEM*,

638 (2003), 169 – 176).

These investigations have produced a tremendous amount of data and 12 full papers have been published in international journals during 2002 - 2005. By looking at the citations received for this work, exclusively carried out by the final year undergraduates of the Department of Chemistry, University of Colombo it is evident that some of the research groups have already started the synthesis of the reported organic and organometallic systems which show enhanced non linear optical properties.

### Kandiah Memorial Awards - 2008

Three Kandiah Memorial Awards are made annually to commemorate Prof. A Kandiah, the first President of the Chemical Society of Ceylon. Professor Kandiah served in the University of Ceylon from 1933 and was the Professor of Chemistry at the University of Ceylon from 1934 until his death in 1951.

The Kandiah Memorial Awards for Basic Chemistry and Applied Chemistry are awarded for the best research contribution in Chemistry carried out by a postgraduate student registered at a Higher Education Institute and for work carried out in Sri Lanka with the exception of special analysis (less than 20% of findings) that cannot be done in the country.

The Kandiah Award for Basic Chemistry is made for research predominantly in Basic Chemistry (Organic, Inorganic, Physical & Analytical).

The Kandiah Award for Applied Chemistry is made annually for research in related areas such as polymer, food, biochemistry, biotechnology etc. where interdisciplinary research is involved, provided that chemistry has a central role & comprises at least 50% of the content.

The Kandiah Memorial Graduateship Award is awarded to the best piece of research in the chemical sciences carried out by a Graduate Chemist of the Institute of Chemistry Ceylon registered with a Higher Educational Institute for a postgraduate degree.