

## SYNOPSIS

The work reported in the thesis entitled “Computational Study of Metal Complexes for Dye-Sensitized Solar Cells” includes various computational tools employed to understand the structure-property relationships in order to develop new class of efficient metal based sensitizers. The factors influencing the efficiencies of these dyes are identified and discussed in detail for each class of sensitizers. In this thesis, we have mainly dealt with three classes of metal sensitizers. The work started with tuning the structural and electronic properties of corrole macrocycle by employing push-pull substituents, thereby generating a new set of corrole sensitizers. In the second part of thesis, photophysical properties of pyridine-benzimidazole ligated ruthenium and heteroleptic phenyl carbene ligated ruthenium complexes were investigated. Good performance of these phenyl carbene ligated ruthenium complexes has prompted us to employ same ligands for earth-abundant iron complexes and to compare both ruthenium and iron based sensitizers. The final part of the thesis includes compositional engineering approaches to replace toxic lead with other suitable elements in methylammonium lead halide perovskites. The computational results obtained by varying the elemental composition of perovskite structure which in turn leads to band gap changes and structural distortions are presented.

The work done for the thesis is presented in six chapters. A chapter-wise summary of the study is given below.

### **Chapter 1: Introduction**

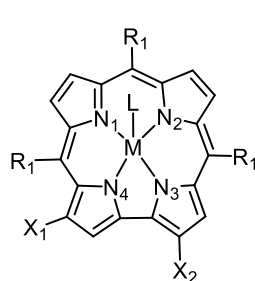
Solar energy harvesting technologies have attracted considerable attention as an alternative, renewable source of energy, particularly in view of the growing energy needs of the world and the depleting reserves of fossil fuels. This chapter outlines the importance of solar energy and reviews first, second and third generations of photovoltaic technologies available for the conversion of solar radiation into electricity. This chapter comprehends the importance of the DSSC technology in view of its cost effective and eco-friendly materials. Chapter 1 also includes the strengths and weakness of various porphyrinoid, ruthenium complexes and perovskites in harnessing the sunlight and consolidates the latest studies reported on metal complexes for DSSC applications.

## **Chapter 2: Methodology**

This chapter comprises the description of various theoretical/computational methods employed for electronic structure calculations carried out in the thesis. An overview of the quantum chemical methods (DFT and Time-Dependent DFT) and their applications to study the spectroscopic properties of dye molecules as well as interfacial electron transfer process is given in detail. It also summarizes population analysis schemes like Mulliken, Hirshfeld, natural bond orbital, and natural transition orbital analysis.

## **Chapter 3: Molecular Design of Corrole Based D- $\pi$ -A Sensitizers for DSSC Applications.**

Corrole based metal complexes were under-explored for DSSC applications compared to porphyrin sensitizers. This chapter addresses the problem of poor efficiencies of metallocorroles, in spite of having many desirable features for DSSC as compared with porphyrins. The chapter aims to improve the performance of metallocorroles (Figure 3.1) by incorporating D- $\pi$ -A architecture/push-pull, which will improve unidirectional electron flow, attaining maximum hyperpolarizabilities. The study reveals that the nature and position of substituents helps in tuning the structure and electronic properties of metallocorrole, which further (**COR1-COR4**) leads to effective and directional charge transfer towards anchoring groups, which further leads to efficient electron injection into TiO<sub>2</sub>.



#### Set-A

Where M = Al, Ga, Sn, and L = Py, Cl

**1a:** M = Al; R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; X<sub>1</sub> = X<sub>2</sub> = COOH; L = Py

**1b:** M = Al; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = X<sub>2</sub> = COOH; L = Py

**1c:** M = Al; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = COOH; X<sub>2</sub> = H; L = Py

**2a:** M = Ga; R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; X<sub>1</sub> = X<sub>2</sub> = COOH; L = Py

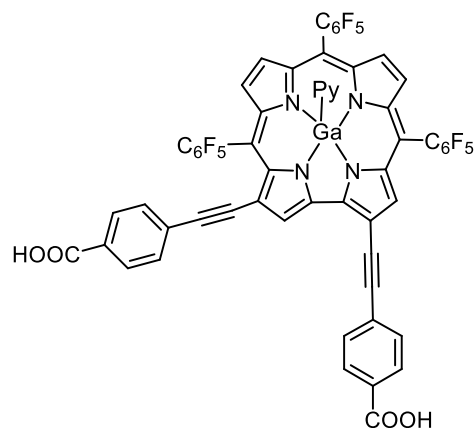
**2b:** M = Ga; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = X<sub>2</sub> = COOH; L = Py

**2c:** M = Ga; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = COOH; X<sub>2</sub> = H; L = Py

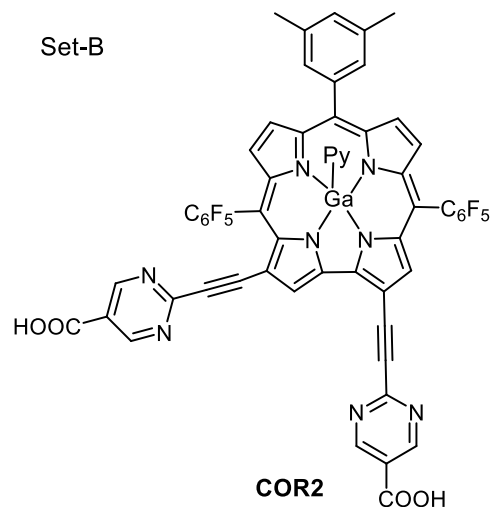
**2d:** M = Ga; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = X<sub>2</sub> = SO<sub>3</sub>H; L = Py

**2e:** M = Ga; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = -CH=C(CN)COOH; X<sub>2</sub> = H; L = Py

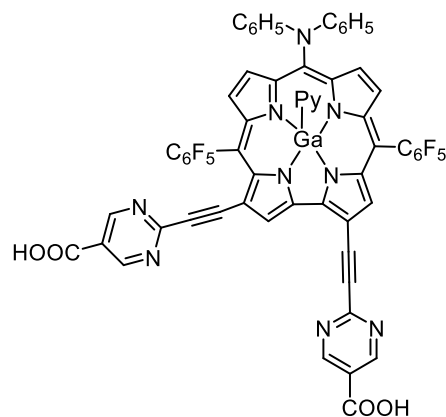
**3d:** M = Sn; R<sub>1</sub> = C<sub>6</sub>F<sub>5</sub>; X<sub>1</sub> = X<sub>2</sub> = SO<sub>3</sub>H; L = Cl



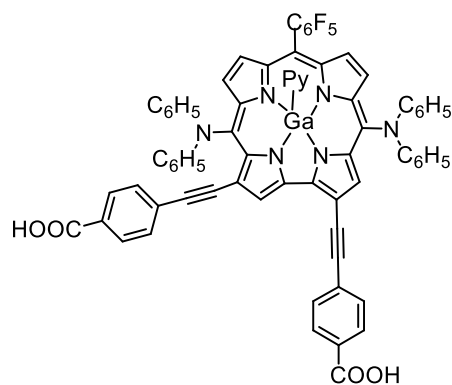
**COR1**



**COR2**



**COR3**

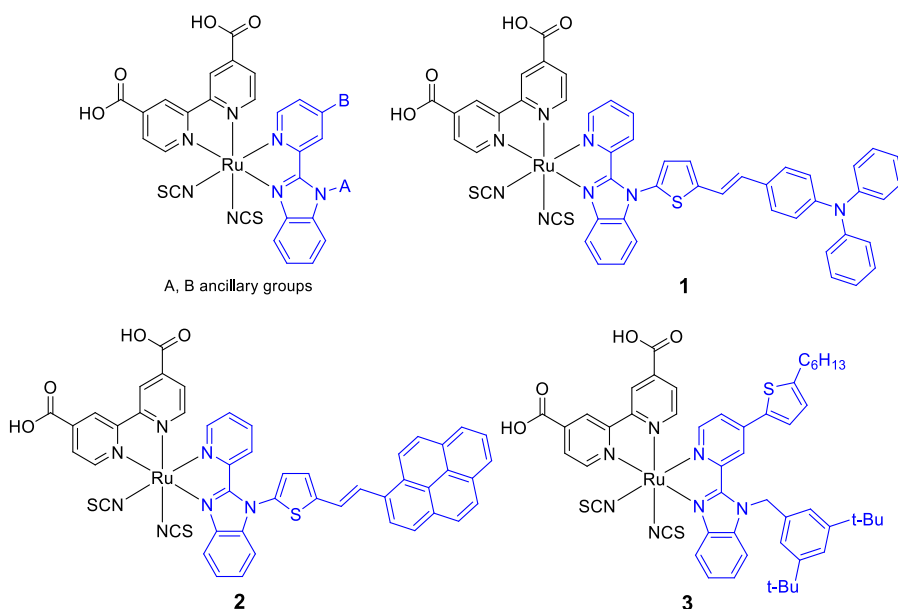


**COR4**

**Figure 3.1** Structures of non-ethynylmetallocorrroles systems (Set-A) and ethynylmetallocorrrole systems (Set-B) considered in this study.

## Chapter 4: Theoretical Study of Heteroleptic Ruthenium Complexes for DSSC Applications

Due to its favorable photochemical properties, ruthenium complexes have been sought as potential sensitizers in manifold studies of DSSC. However, most of these studies were done on homoleptic dyes, because of which invariably display poor stability and durability. In this chapter, efforts to improve these factors by using heteroleptic ligands for ruthenium complex are included. The results demonstrate that a subtle change in the peripheral ancillary groups on benzimidazole heteroleptic ligand exerts a substantial effect on the excited states and dye regeneration in heteroleptic ruthenium sensitizers (Figure 4.1). The influence of these factors on the efficiencies of these dyes has also been explained.

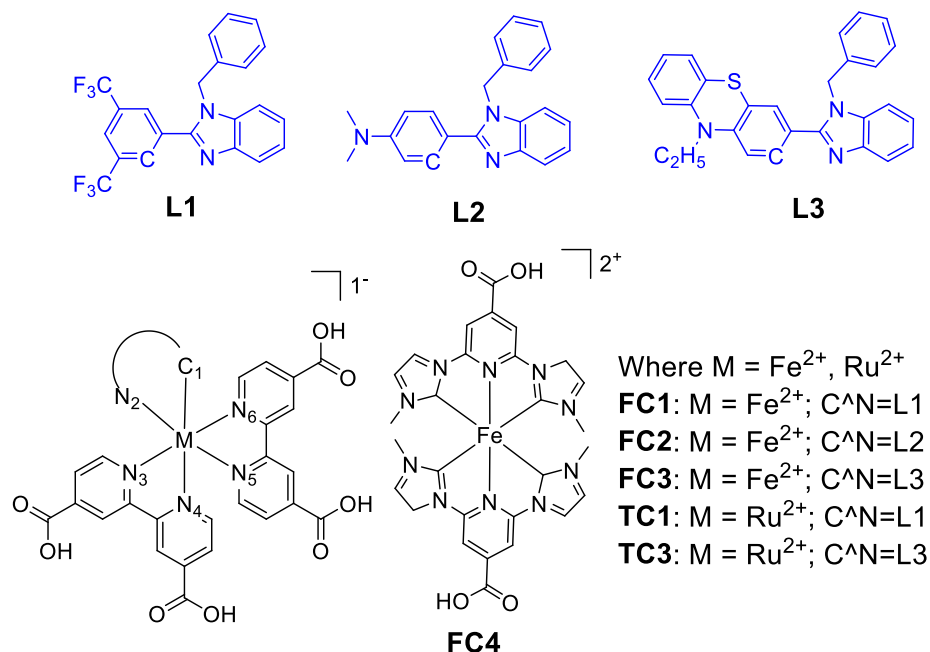


**Figure 4.1** Ru-complexes containing the heteroleptic pyridine-BI ligand appended with ancillary ligands represented in blue color (triphenylamine) **1**, (pyrene) **2** and (*t*-butylbenzyl) **3** that are investigated in this study. (Ancillary ligands given in blue color)

## Chapter 5: Towards the Development of Iron Photosensitizers with Bis-coordinated C<sup>^</sup>N Ligands for DSSC Applications

In continuation of studies reported in Chapter 4, strategies adopted to bring down the cost involved in tedious synthetic protocols of traditional ruthenium dyes are included in Chapter 5. A rational approach is included in this chapter towards the design of efficient iron sensitizers based on heteroleptic phenyl carbene ligands, which involves simple

synthetic protocols and inexpensive starting precursors. Here heteroleptic phenyl carbene ligands have been substituted with electron-withdrawing  $\text{CF}_3$ , donating  $-\text{N}(\text{CH}_3)_2$  and benzothiazine annulation of carbene ring (Figure 5.1). The substitution effects on the electronic structure and optical properties of Fe- and Ru-complexes have been investigated using DFT, TD-DFT, energy decomposition analysis and spin density distribution analysis.

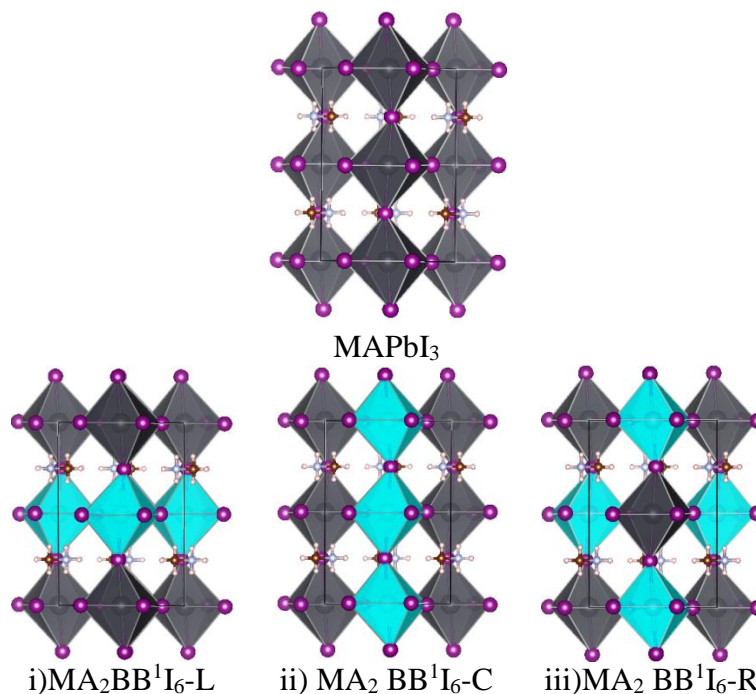


**Figure 5.1** Heteroleptic phenyl carbene ligands represented in blue color ( $\text{C}^{\wedge}\text{N}$ ) containing iron (**FC**) and ruthenium (**TC**) complexes.

## Chapter 6: Exploring Earth-abundant Elements to Replace Toxic Lead in Perovskite Solar Cells

Perovskite solar cell technology (PSC) which stem from DSSC has been selected as one of the biggest scientific breakthroughs of recent times. Perovskite solar cells (PSCs) which integrate DSSC technology have recently achieved the efficiencies greater than 20%. However lead toxicity and long-term stability are major concerns for large scale fabrication. The most commonly studied perovskite absorber is methylammonium lead trihalide ( $\text{CH}_3\text{NH}_3\text{PbX}_3$ , where X is a halogen ion such as  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ). Hybrid organic lead halide perovskite with multi valley and multi band gap material as a reference and Sn atomic layered compounds are studied and compared with experimental band gaps (Figure 6.1) in this chapter. Electronic properties reveal that iodine 5p electrons can be photo-excited to Sn 5p and Pb 6p empty states. Pure lead halide perovskites having inverse band

structure is transformed to normal band structure by doping with  $\text{Ba}^{2+}$  ( $5s^2 5p^6 4d^{10} s^0$ ). Barium layered perovskites with other divalent cations (lead, tin, germanium, zinc, cadmium, mercury) found to exhibit direct band gaps. Moreover, the band gaps for these barium intercalated perovskites structure found to be direct band gaps and are in the range of 2-3 eV.



**Figure 6.1** Perovskite compound with three types of ordering of  $\text{BI}_6$  (grey) and  $\text{B}^1\text{I}_6$  (blue) octahedral in i) horizontal (010), ii) columnar (100) and iii) rock salt layering type (111).

### Publications included in the thesis

- 1 Molecular design of corrole-based D- $\pi$ -A Sensitizers for dye-sensitized solar cell applications. Srikanth, M.; Sastry, G. N.; Soujanya, Y. *Int. J. Quantum Chem.* **2015**, *115*, 745–752.
- 2 Benzimidazole-functionalized ancillary ligands for heteroleptic Ru(II) complexes: synthesis, characterization and dye-sensitized solar cell applications. Jella, T.; Srikanth, M.; Bolligarla, R.; Soujanya, Y.; Singh, S. P.; Giribabu, L. *Dalton Trans.* **2015**, *44*, 14697–14706.
- 3 Heteroleptic Ru(II) cyclometalated complexes derived from benzimidazole-phenyl carbene ligands for dye-sensitized solar cells: an experimental and theoretical approach. Jella, T.; Srikanth, M.; Soujanya, Y.; Singh, S. P.; Giribabu, L.; Islam, A.;

- Han, L.; Bedja, I.; Gupta, R. K. *Mater. Chem. Front.* **2017**, *1*, 947–957.
- 4 Towards the Development of Iron Photosensitizers with Bis-coordinated C<sup>N</sup> Ligands for DSSC Applications. Srikanth, M.; Soujanya, Y. (submitted to *Phys. Chem. Chem. Phys.*).
- 5 Exploring Earth-abundant Elements to Replace Toxic Lead in Perovskite Solar Cells. Srikanth, M.; Soujanya, Y. (*Manuscript underpreparation*).