

## ABSTRACT

Index No. 105/ 18/ Chem./ 25

### NIR Absorption with adoptive Aromaticity: the paradigmatic cases of dicarba porphyrinoids and monocarba Vinylogous porphyrinoids

Submitted by: Sumit Sahoo

Aromaticity is considered as one of the most important concepts in modern organic chemistry that determines structure, stability, and reactivity of the molecules. Aromatic compounds having absorptions and emissions in the red or near-infrared (NIR) region are capable materials for a broad range of applications such as photodynamic therapy dyes, semiconductors in light-emitting diodes, photo-sensitizers in solar cells and microscopic imaging agents. Carbaporphyrins are porphyrin analogues in which one or more of the pyrrolic nitrogens have been replaced by carbon atoms. One of the most interesting properties of such carbaporphyrinoids is model of aromaticity and stabilisation of metal in higher oxidation state.

In My thesis, I have focused on design and synthesized of NIR active aromatic carbaporphyrinoids. In my third chapter, I have synthesized of dithia/diselena aromatic core modified *trans*-doubly *N*-Confused porphyrins with strong NIR absorption. Acid catalyzed condensation of *N*-TIPS pyrrole and 2,5-bis(*p*-tolylhydroxymethyl)selenophene/2,5-bis(*p*-tolylhydroxymethyl)thiophene (1:1 molar ratio) using  $\text{BF}_3 \cdot \text{OEt}_2$  and subsequent chloranil oxidation has led to the isolation of *meso*-aryl substituted core modified *trans*-doubly *N*-Confused porphyrins **1** and **2**. The Aromaticity of these macrocycle are strongly supported by in-depth solution state spectroscopic measurements and DFT level theoretical calculations.

My fourth chapter is an attempt in arriving at Hückel aromatic/antiaromatic dithia [26]/[24] core modified expanded azuliporphyrinoids (1.3.3.1.0). Acid catalyzed condensation of azulene-1, 3-bis-acrylaldehyde and bithiophenetetrapyrane in methylene chloride using trifluoroacetic acid (TFA) as catalyst followed by oxidation with DDQ led to the exclusive isolation of Carbasapphyrins **4** and **5**. The charge separated resonance delocalized tropylium cation is surmising the aromatic nature of the this carbaporphyrinoid **3'**. Contrarily, swiping the bithiophene moiety with fused thieno [2,3, b] thiophene has anticipated anti aromatic nature of the corresponding azuliporphyrinoid (1.3.3.1.0) **5**. The spectroscopic preclusion of

aromaticity/antiaromaticity have been well supported by supported by solution state spectroscopic measurements, DFT level theoretical calculations and solid state X-ray crystal structure.

Introducing aromatic spacer linker inside the expanded macrocycles have been challenging to researcher as such porphyrinoids exhibits dual conjugated path and allowing multi-metal coordination site. My fifth chapter is an attempt in arriving at aromatic bridge expanded carbaporphyrinoids following literature known acid catalyzed condensation protocol from its easy precursors. The aromaticity of these macrocycles **6** and **7** are supported by UV-Vis-NIR and NMR spectroscopy.

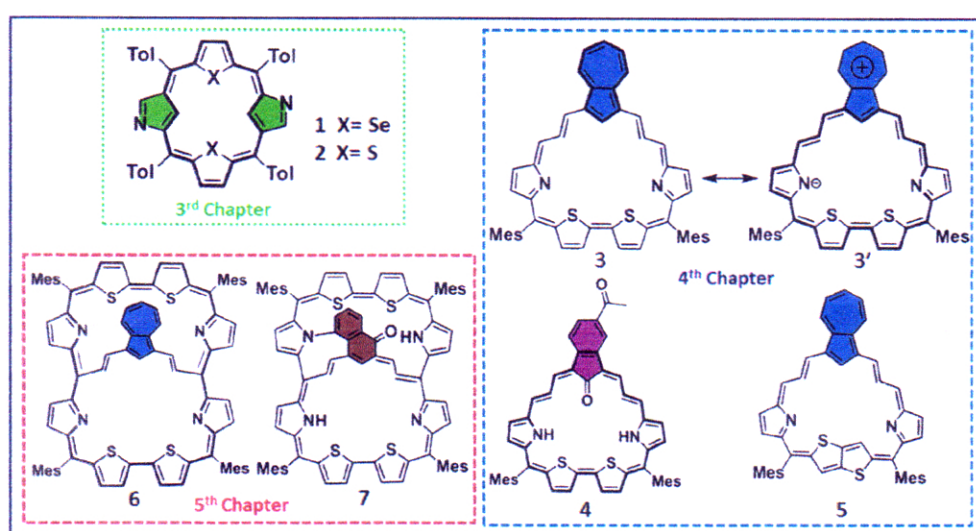


Figure 1 Dicarba porphyrinoids and monocarba Vinylogous porphyrinoids

*Harapriya Rath*  
Signature of Supervisor 09.03.2022

*Sumit Sahoo*  
Signature of Student

(Dr. Harapriya Rath)

(Sumit Sahoo)



**Dr. Harapriya Rath**  
Associate Professor  
School of Chemical Sciences  
Indian Association for the  
Cultivation of Science  
Jadavpur, Kolkata-700 032