Optoelectronic Applications of Tetrapyrrolic Systems

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Porphyrins and corroles are widely present in biological systems to perform various functions. Its analogues, phthalocyanines are manmade compounds and it has many optoelectronic applications. Based on optical, redox and thermal properties, both porphyrins and phthalocyanines are widely applied for various optoelectronic applications. We are particularly interested that these compounds for dye-sensitized solar cells as well as organic light emitting diodes.

Porphyrins and structurally related compounds such as phthalocyanines, corroles tetrabenzoporphyrin, expanded porphyrin, contracted porphyrins and core modified etc., are belongs to the tetrapyrrolic ring systems.[1] Of these, porphyrins and corroles are biologically important whereas phthalocyanines and tetrabenzoporphyrins are manmade compounds. Of these, we are particularly interested in optical properties of porphyrins and phthalocyanines and their applications for optoelectronic devices such as emissive layers for organic light emitting diodes, and as sensitizers for organic/polymer photovoltaics as well as dye-sensitized solar cell applications.[2] For this one has to understand its optical and electrochemical properties in detailed.

1. Porphyrins: Porphyrins and their metal complexes are involved in many biological and abiological functions including hemoglobin/myoglobin oxygenation, cytochrome activity, antenna function and charge separation reactions of both natural and artificial photosynthetic systems, catalysis of organic reactions, magnetic resonance imaging, photodynamic therapy (PDT) etc. In order to apply for optoelectronic applications, one has to understand its optical and electrochemical properties in detailed. Porphyrins are aromatic in nature[3] and they obey Hückel's rule for aromaticity, possessing $4n+2$ π electrons ($n = 4$ for the shortest cyclic path) delocalized over the macrocycle. Both porphyrins and metallo porphyrins have an intense Sore band at around 420 nm with four/two lest intense Q-bands in 500 – 650 nm region. The emission maxima of tetraphenyl porphyrin are at around 650 nm with singlet quantum yield of 0.11 (in CH_2Cl_2 solvent).[4] In contrast its phosphorescence maxima are present at 800 nm with triplet quantum yield of 0.73.[5] The triple quantum yield porphyrin is high and it suitable as emissive materials for OLED applications. The absorption emission properties are suitable for applying as sensitizers for organic/polymer photovoltaics as well as dye-sensitized solar cell. The detail optical and electrochemical properties will discuss.

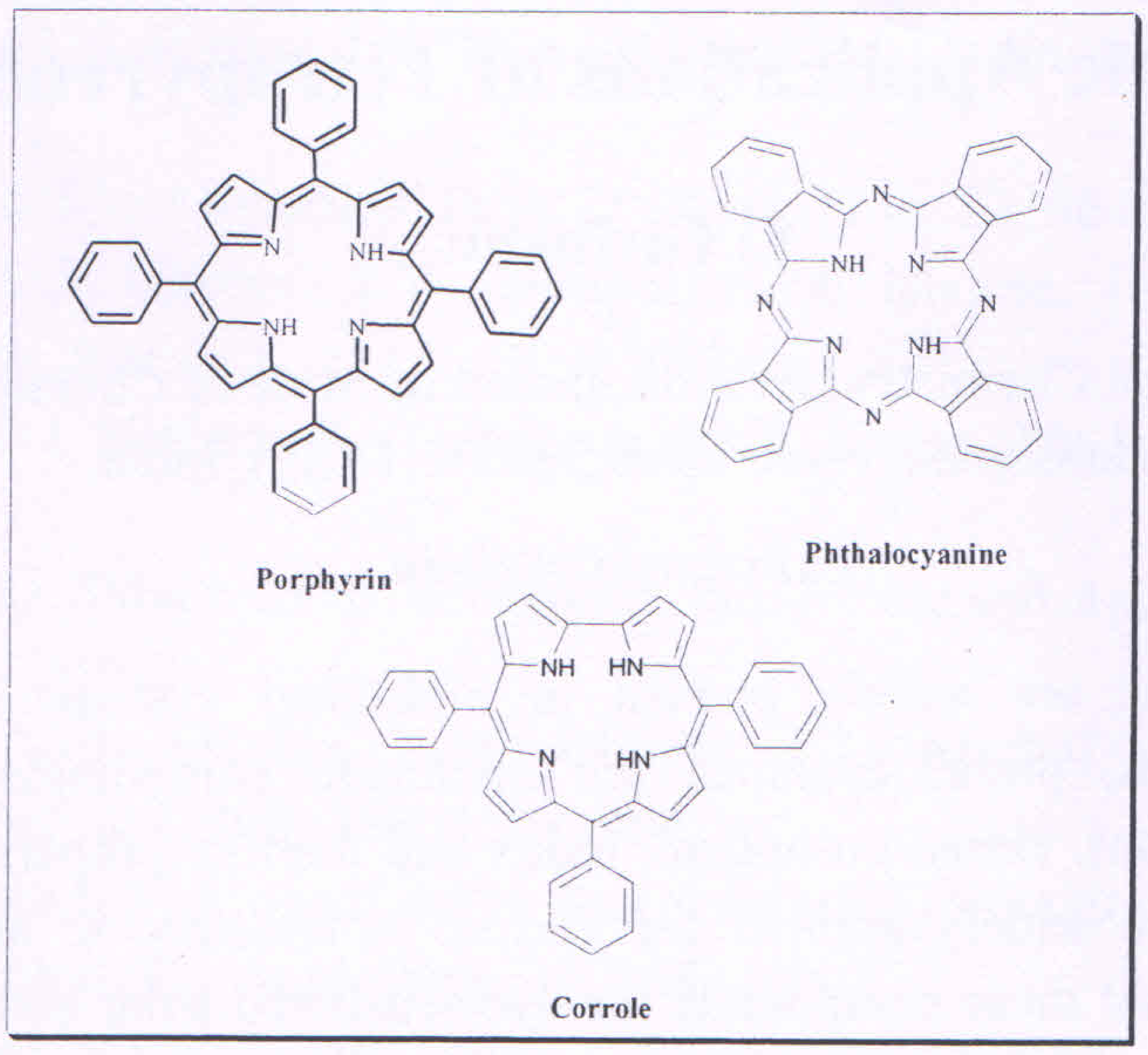

Figure 1: Structure of tetrapyrrolic compounds.

2. Phthalocyanines:

Unlike porphyrins, phthalocyanines are not present in biological systems. Phthalocyanine is an intensely blue-green coloured aromatic macrocyclic compound that is widely used in dyeing[31] Phthalocyanines form coordination complexes with most elements of the periodic table.

Based on electronic, thermal and redox properties, phthalocyanines are found to be alternative sensitizers to Ru(II) polypyridyl complexes for DSSC applications and as red emissive materials for OLED applications. Phthalocyanines are tetra pyrrolic cyclic organic molecules, which can find applications in several fields.[6] They are 18-π electron aromatic systems and possess an intense Soret-band at 350 nm and Q-bands at 650-700 nm regions. Thus providing good absorption in the red/near-IR-region of the solar spectrum, phthalocyanines can be tuned to be transparent over a large region of the visible spectrum, thereby enabling the possibility of using them as "photovoltaic windows": a red/near-IR absorbing photovoltaic cell, in place of a window, will allow visible light to enter a building whilst harvesting the solar power from the red/near-IR part of the spectrum. In addition to directly generating power, this also reduces the solar heating of buildings, thereby reducing the demand for, and power consumption of, air-conditioning units.[7]

3. Corroles:

A **corrole** is an aromatic organic chemical, the structure of which is in the form of the corrin ring, which is also present in cobalamin (vitamin B_{12}). The ring consists of nineteen carbon atoms, with four nitrogen atoms in the core of the molecule. Unlike the porphyrins and phthalocyanines, corroles are very less explored due to lack of proper synthetic methods.[8,9]

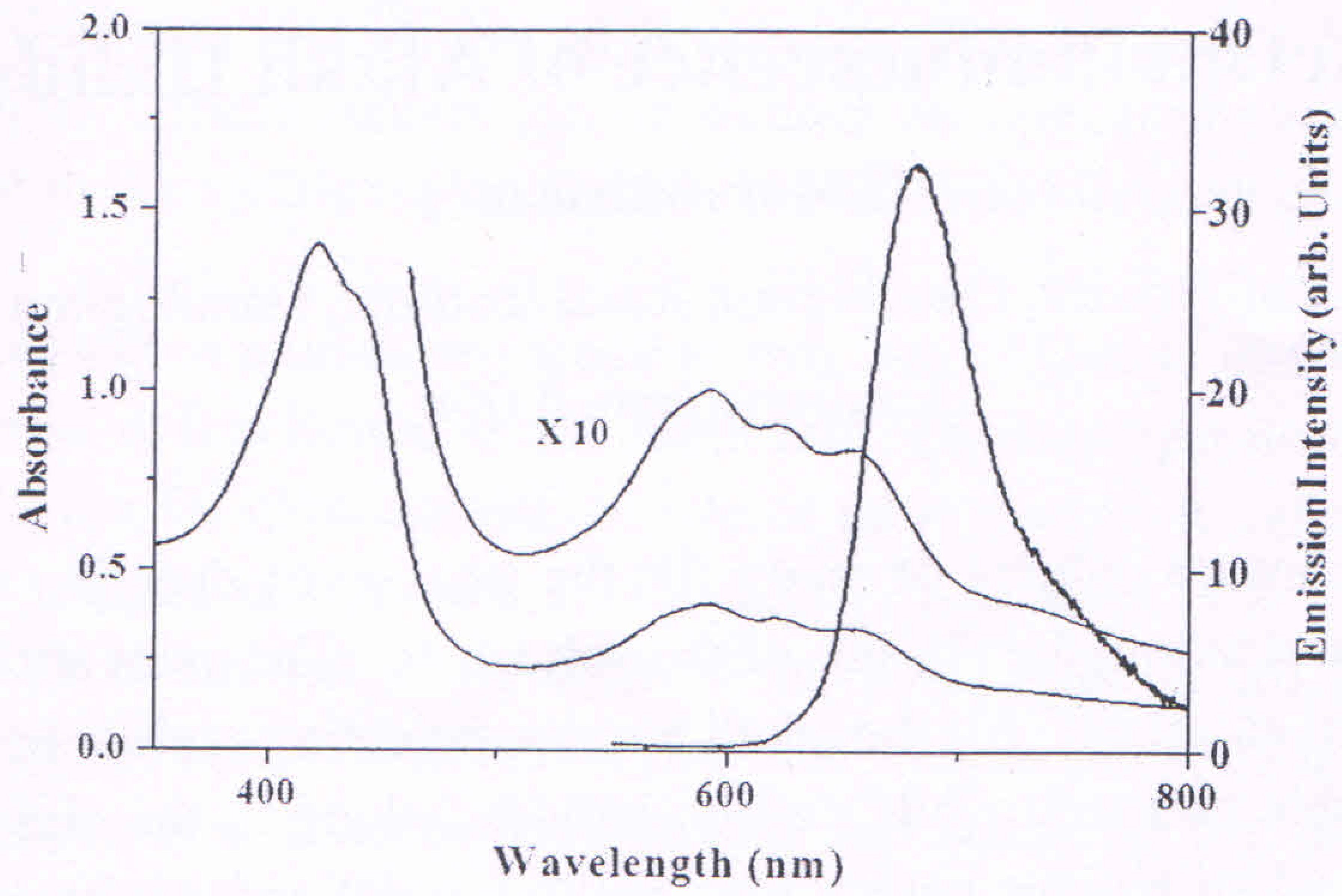

Figure 2: Absorption and emission spectra of corrole

However, after the discovery of easy synthetic routes for *meso*-substituted corroles by Gross et al. and Paoless et al. in 1999, investigations of corroles have been increased significantly. Based on absorption, thermal, and electrochemical properties, they are also potentials candidates as emissive layer for OLED applications as well as sensitizers for DSSC and OPV applications.[10] The advantage of corroles over porphyrins and phthalocyanines that it can stabilizes higher oxidation states of metals such as Cu(III), Fe(IV), P(V) etc.

The details of optical and electrochemical properties of porphyrins, phthalocyanines and corroles will be presented.

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