

Porphyryns: Important Materials with Diverse Functionalities

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Porphyryns are a large class of organic and metal-organic molecular compounds, the structural units of which all include at least one macrocycle, comprised of four five-membered heterocyclic pyrrole rings (C₄H₄NH), bound together by four methine (=CH-) bridges, with the pyrrole nitrogens facing inward. The parent compound, porphine, C₂₀H₁₄N₄, is a stable solid at room temperature. Numerous sidearm substitutions are possible on the outward-facing four *meso* (methine) and eight *beta* (pyrrole) positions. Fully substituted examples include tetraphenyl porphyrin (C₄₄H₃₀N₄) and octaethyl porphyrin (C₃₆H₄₆N₄). More complicated substituents and linkages lead to a large variety of structures, compositions, and properties. Additionally, the nitrogens of the macrocycle core may be deprotonated and axially bonded to any of more than 50 metals, with the distance from the macrocycle plane and the coordination being determined by the metallic radii and valences. Porphyryns and related compounds are important in nature, and macrocycles form a central part of such well-known molecules as hemoglobin, chlorophyll, and vitamin B-12. Due to their optical absorption properties, they have been termed the “colors of life.” It is thought that porphyrin molecules were present in the primordial seas in which life originated. The stability of the porphyrin macrocycle is further attested to by the occurrence of the naturally-occurring mineral abelsonite (C₃₁H₃₂N₄Ni) in the 49-54 m.y. Eocene sediments of the Green River Formation, Utah.

The variety of structures, compositions, and related properties possible makes synthetic porphyryns of interest for many materials applications, including: artificial photosynthesis, solar cells, redox and catalysis reactions, molecular electronics, non-linear optics, displays, sensors, and gas storage. The semiconducting nature of porphyryns originates in their aromaticity. Structural details such as the crystal packing, type of substituents, covalent intermolecular linkages, metalation, and macrocycle planarity have a large effect on the π - π interactions and conjugations which determine the optical and electronic properties, and ideally can be tuned to achieve the desired results.

More than 4000 porphyrin X-ray crystal structures are known to date, yet fewer than 200 powder patterns have been published, highlighting the need for more work in this area. The experimental challenges include difficulties in synthesis of sufficient quantities for powder XRD, presence of solvates (most are grown from solution), sample preparation, and low-intensity of diffraction peaks. Some of these issues can be mitigated by the use of synchrotron methods. The anticipated use of laboratory machines for the majority of R & D investigations requires in-house phase identification and the availability of standard reference X-ray powder patterns. In view of the rising number of porphyrynic materials applications, efforts directed toward increasing the available data are needed.