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A NOVEL METHOD FOR LARGE SCALE SYNTHESIS OF PORPHYRINS USING GENETICALLY ENGINEERED *E. COLI*

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The biosynthetic method described below presents a significant improvement over the current methods of porphyrin production. It represents a sustainable, environmentally friendly, and economically viable process of making large quantities of protoporphyrin for photovoltaic and other commercial applications.

The effort in moving toward clean and renewable sources of energy has incited interest in solar energy. With the power of 120,000 terawatts, the amount of solar energy hitting the Earth's surface is more than 10,000 times the world's total energy use [1]. The sun provides more than enough energy to satisfy our energy needs, it is just a matter of harnessing it. Currently, solar energy accounts for only 1% of the total energy use. The challenges associated with increasing this fraction are: 1) increasing the efficiency of photovoltaic devices; 2) making the production and installation costs of solar panels more economically viable. **Organic photovoltaics** may offer the answer to the second problem. Organic photovoltaic materials offer the advantage of lower cost, easier processing, and desirable physical characteristics, such as light weight and flexibility, which make them an attractive alternative to traditional inorganic photovoltaic materials [2].

Some of the organic compounds that have gained interest for their potential application in photovoltaic devices are conducting polymers. Conducting polymers have overlapping pi-orbitals that allow greater electron mobility through an extended conjugates system [3]. Examples of such polymers are polyacetylene, polyaniline, polythiophenes, and polypyrroles. Another emerging field of research is **small-molecule organic solar cells**. Like polymers, small-molecule organic material can be easily processed; in addition, small molecules are easier to synthesize and purify than polymers, they are monodisperse, and have higher carrier mobilities. Polymer-fullerene materials, based on polythiophene, phthalocyanine, or oligo(p-phenylenevinylene), offer high power conversion efficiencies in the range of 5 – 10% [2]. Although their performance is lower than in some polymeric semiconductor systems, small-molecule organic photovoltaics hold a great promise for overcoming the technical and economic challenges of the field. Among the molecule classes that have a high potential for use in photovoltaic materials are porphyrins and phthalocyanines [4]. Here I will focus on porphyrins as an example of small-molecule photovoltaic material.

Chlorophyll is a molecule present in the cells of plants and algae that is involved in multiple steps of photosynthesis, including light harvesting, energy and electron transfer [4]. It is nature's solar cell in the sense that it allows conversion of solar energy into other forms. An important molecular component of chlorophyll is porphyrin, which is a cyclic tetrapyrrole derivative that gives chlorophyll its green color and is responsible for conductive its properties. Polypyrroles are a known class of conducting polymers, attractive for its high thermal stability and conductivity. Porphyrins, having extended conjugation and the ability to coordinate a metal ion, surpass polyporroles in their range of absorption [5]. Recent applications of porphyrin dyes for dye-sensitized solar cells have shown solar conversion efficiencies approaching silicon based photovoltaic devices [5], [6].

Porphyrins have many other applications. They can be used as redox catalysts, dyes, sensors, and photodynamic therapy agents [7], [8], [9]. Of particular interest is **protoporphyrin** [Fig. 1], a cyclic tetrapyrrole and an immediate metal-free precursor to heme b. Protoporphyrin can bind different metals ions, including iron, magnesium, zinc, nickel, and copper, each complex exhibiting a different UV-vis absorption, as well as fluorescence excitation-emission, profile [Fig. 2] [10]. This property presents a possibility to modify the absorption range by simple change of ligand, which could be of great utility in photovoltaic applications. Protoporphyrin has also been used for molecularly imprinted polymer (MIP) applications as a functional comonomer, along with methacrylic acid, to produce a "memory" material, which can help detect the binding of the template molecule used during polymerization based on spectroscopic changes upon complexation [11]. Based on the molecule's functional versatility, I have chosen to focus my research proposal on protoporphyrin. This molecule can be further functionalized, which expands the range of its potential applications.

The **traditional synthesis** of porphyrins involves complex chemistry carried out in solvents and under strict reaction conditions. These are exemplified by the Ruthemund sealed-tube anaerobic reaction in pyridine at 200 °C (ca. 5% yield), the Adler–Longo reaction in propionic or acetic acid under aerobic conditions (10 – 30% yield), and the MacDonald coupling of dipyrroles (10 – 20% yield) [7]. Recent proposals for green synthesis methods include a one-step synthesis of meso-Tetraarylporphyrins from pyrrole and aryl aldehydes without solvents or catalysts using air as oxidant by the Gong group [7]. However, the proposed method involves high temperature (> 200 °C) in gas phase. Another green chemistry approach for synthesis of tetraphenylporphyrin was developed by the Momenteaub group. It involves heating in microwave oven pyrrole and benzaldehyde

adsorbed on a solid acidic support [12]. This method is very quick (10 minutes), involves dry media conditions, and simple purification; however, this method is also carried out at high temperature and involves the use of chloroform, benzaldehyde, and hexane, which are hazardous to human health.

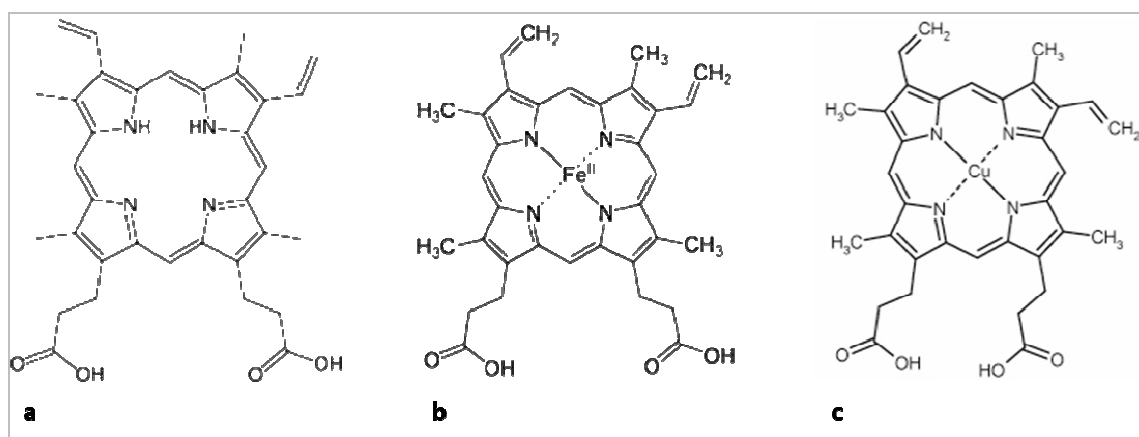


Fig. 1. Structures of *a* – protoporphyrin; *b* – heme b; *c* – protoporphyrincomplexed with copper ion

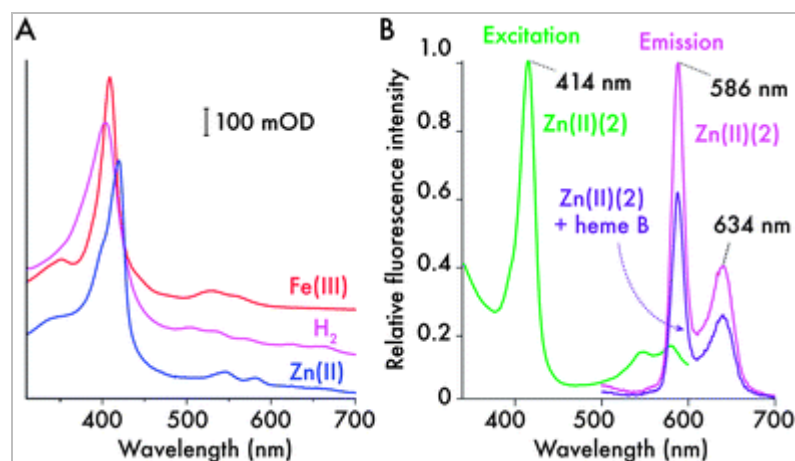


Fig. 2. *a* – UV-vis and *b* – fluorescence spectra of free; Zn- and Fe-bound protoporphyrin

Biosynthesis of porphyrins is an attractive **green alternative** to synthetic methods. Enzymatic reactions have extremely high efficiency, excellent substrate specificity, and regioselectivity, allowing precise control over spatial orientation of functional groups. In addition, most enzymes can function in mild conditions (ambient temperature, physiological pH), limiting the need to use of expensive metal-based catalysts, hazardous chemicals and solvents. Pathways for synthesis of porphyrin derivatives are present in major classes of organisms. In non-photosynthetic eukaryotes such as animals, insects, fungi, and protozoa, the pathway begins with the reaction of the amino acid glycine with succinyl-CoA from the citric acid cycle. In plants, algae, bacteria (except for the α -proteobacteria group) and archaea, it is produced from glutamic acid [13]. Normally, however, the production of porphyrins is limited by the cell's physiological needs. In order to overcome this limitation and be able to produce porphyrins in industrial quantities, the biological pathway needs to be modified using synthetic biology tools.

I propose a **novel method for large scale synthesis of porphyrins** using genetically engineered *E. coli*. This method offers the advantage of using renewable feedstocks, environmentally benign chemicals, and low-energy production requirements. These improvements are in accordance with the principles of green chemistry defined by the ACS [15]. In addition to being sustainable and clean, the described biotechnology approach offers a promise of bringing down the cost of these materials, especially in the light of the long-term prospect of petroleum shortage. I hypothesize that large-scale production of protoporphyrin for commercial applications can be carried out using recombinant *E. coli*. The strategy for this project is to utilize molecular biology and genetic engineering tools for *E. coli* genome manipulation in order to increase the amounts of compound produced.

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**LABOUR PROTECTION. GENERAL INFORMATION ABOUT FIRES.
FIRE SAFETY AT ENTERPRISES****EGOR TIHONENKO, ALEXANDR TANKOVID
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Labour protection is a system of preservation of life and health during labour activity. Labour protection must not be identified with safety engineering, industrial hygiene, occupational health, because they are elements of labour protection, its constituent parts.

The tasks of labour protection are:

- 1) Establishing of a system of laws and normative legal acts in the field of labour protection;
- 2) Control over law compliance and normative legal acts;
- 3) Evaluation and analysis of conditions and safety of labour;
- 4) Analysis of injuries and illnesses, investigation and registration of accidents at work;
- 5) Training and instructing employees in rules and safety requirements;
- 6) Creation of measures for improving working conditions and performing of norms and rules of labour safety.

An important question in the field of labour protection is to provide safe work at enterprises, and in particular to ensure fire safety.

Fire is the uncontrolled process of burning, which is accompanied by the destruction of material values and it poses a danger to people's lives. The causes of fires at industrial facilities can be divided into two groups. The first is a violation of fire safety conditions or careless handling of fire, the second one is a violation of fire safety in the design and in the construction of buildings.

Fire is a chemical reaction between combustible substances and oxygen (or other kind of oxidizing environment). There are three components necessary for the occurring of fire. They are combustible material, oxygen, and the initial heat source with sufficient energy to start the combustion reaction.

Fire may cause several different hazards. The first one is increased temperature in the combustion zone. It can cause thermal burns of humans' skin and internal organs as well as loss of bearing capacity of buildings and