

Chlorophyll: A Greener Catalyst in Synthetic Transformations

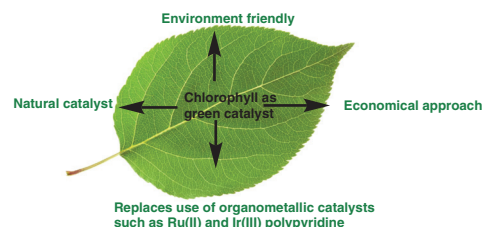
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The use of chlorophyll, a green pigment found in plants, is being recognized as an environmentally friendly method for synthesizing various heterocycles. It is located in the chloroplast, a special organelle present only in plant cells. Chlorophyll plays a crucial role in photosynthesis because of its extraordinary capacity to absorb light energy. Chlorophyll then uses this energy to photolyze water molecules in order to restore the cells' reducing power, which is necessary for the process' following stages to ingest carbon. Recently, the use of chlorophyll as a natural catalyst has been successfully reported to replace toxic organometallic catalysts such as Ru(II) and Ir(III) polypyridines for various suitable transformations. The present article aims to focus on the efficiency of chlorophyll due to its economical and eco-friendly approach.

Chlorophyll has gained attention ever since photoinduced electron transfer (PET) for the synthesis of various complex scaffolds in visible-light-driven photoredox catalyzed reactions led to an affordable, adaptable, and environmentally friendly process (Figure 1). Chlorophyll, the most common natural photocatalyst in our environment, initiates the photosynthesis process, which involves the production of carbohydrates during photosynthesis. It has been shown that there are six different varieties of chlorophyll (a–f), with chlorophyll a being the most prevalent variety in nature.^{1–6}

Ru(II) and Ir(III) polypyridines have been frequently employed as organometallic photocatalysts in organic chemical transformations, which proved to be incredibly helpful in synthetic chemistry.^{7–10} These catalysts are very efficient at promoting photoinduced electron-transfer processes for

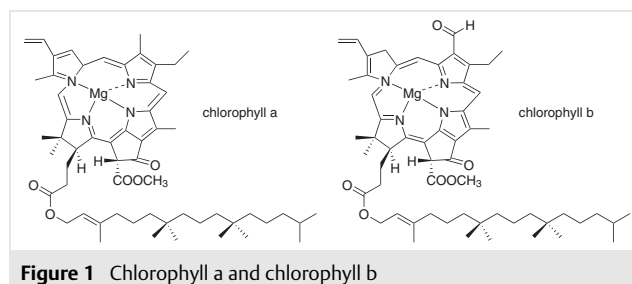


Figure 1 Chlorophyll a and chlorophyll b

organic transformations, but they have significant limitations because they contain rare earth metals like ruthenium (Ru) and iridium (Ir), which are expensive. Tiny amounts of this expensive, dangerous chemical are present in the crusts of the earth. Thus, the development of renewable photocatalysts is greatly desired.^{11–15}

Chlorophyll has occasionally been utilized to simulate photosynthesis for photosensitized organic transformations, despite its capacity to absorb solar energy and transmit it for the conversion of chemical entities into the essential products.^{16–18} Chlorophyll acts as a potent reducing agent due to its half-wave reduction potential of 1.1 V and its ability to donate an electron to an oxidant to generate a p-radical cation.^{19–22}

Plants contain chlorophyll, which can function in various chemical reactions as a typical natural photocatalyst. Despite being a widely employed, eco-friendly, and green photosensitizer, it hasn't been frequently used in photo-driven synthesis.^{23,24} As a result, chlorophyll, which is credited with having an excellent singlet dioxygen characteristic, has an excellent future and fascinates many scientists when it comes to the catalysis of organic transformations *via* PET to produce compounds that are beneficial for mankind. Consequently, it is imperative to investigate this green photosensitizer's potential for further organic transformations. Hence, chlorophyll-based photoelectron excitation could contribute significantly to the production of the desired chemicals (Table 1).

Table 1 Chlorophyll-Catalyzed Organic Transformations

<p>(A) In 2019, Harsh et al. employed a chlorophyll-sensitized method for the synthesis of 3,4-dihydropyrimidin-2(1<i>H</i>)-ones using multicomponent click chemistry. The method involves irradiating the thoroughly stirred mixture of aromatic aldehyde, alkyl acetoacetate, and urea in equimolar concentration under concentrated solar radiation (CSR) till the completion of the reaction. The same reaction, when performed without the use of chlorophyll and in the presence of the radical scavenger TEMPO, resulted in a trace amount of product, thereby justifying the important role played by chlorophyll in the reaction as well as supporting the radical mechanism involved in the reaction. The method holds several advantages, such as excellent product yield, energy efficiency, simplicity of methodology, sustainability, affordability, and ecology, for the synthesis of functionalized dihydropyrimidinones, which have immense applications. Therefore, photoelectron excitation by the use of chlorophyll led to the desired product in excellent yield.²⁵</p>	
<p>(B) Another category of reactions involving the use of chlorophyll as a biocatalyst via visible light involved the cross-coupling of the C3-position of coumarin with a variety of diazonium salts to prepare 3-aryl coumarin derivatives. The approach involved the use of chlorophyll as a photosensitizer as well as an economical and environmentally friendly biocatalyst. The straightforward procedure involved the reaction of coumarin and substituted diazonium salts in the presence of chlorophyll under white LED light in the presence of chlorophyll until the completion of the reaction. The method holds good versatility as the arylation supports tolerance with various electron-donating as well as electron-withdrawing substituents, with the exception of coumarin bearing an electron-withdrawing nitro group. The radical mechanism of the method was supported by the complete suppression of the product of the reaction between coumarin and phenyldiazonium salt in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO).²⁶</p>	<p>Ar² = H, 2-CH₃, 4-CH₃, 4-OCH₃, 4-F, 4-Br, 4-COOH, 4-OH, 3-F, 3,4-(CH₃)₂ Ar¹ = H, 6-CH₃, 7-OH, 7-OCH₃, 7-OBn, 6-Br, 6-NO₂</p>
<p>(C) The drive for the exploitation of visible light as a sustainable source of energy encouraged Heidari and team to work on the synthesis of novel tetrahydroquinoline derivatives. The approach involved the extraction of chlorophyll b from fresh spinach leaves and immobilising them on the surface of TiO₂ using 3-aminopropyltriethoxysilane (APTES) as a coupling reagent. The immobilisation of chlorophyll b on the surface of TiO₂ extended the absorption ability from the ultraviolet a region to the visible region and also enhanced its photocatalytic properties. The method involved irradiating the glass vial containing <i>N,N</i>-dimethylaniline, 1-phenyl-1<i>H</i>-pyrrole-2,5-dione dissolved in DMF, and a pinch of synthesized chlorophyll b modified TiO₂ nanoparticles under a 23 W fluorescent lamp at room temperature for 24 h. The developed method resulted in a highly efficient, economical, and eco-friendly approach for the synthesis of tetrahydroquinoline derivatives.²⁷</p>	
<p>(D) A series of pyrrolo[2,1-<i>q</i>]isoquinoline derivatives were synthesized by Koohgard et al. in 2021 by using chlorophyll a as photocatalyst extracted from fresh leaves of spinach. The reaction involved irradiating the mixture of dihydroisoquinoline ester (1.2 mmol), maleimide (1 mmol), and a pinch of chlorophyll a in toluene as solvent under 15 W LED light at room temperature. The reaction was reported to proceed well in the presence of various electron-withdrawing as well as electron-donating groups. The plausible mechanism involved the excitation of chlorophyll a as chlorophyll a*, which eventually transfers its energy to ground-state molecular oxygen, which subsequently gets converted into singlet oxygen. The singlet oxygen then oxidizes <i>N</i>-substituted tetrahydroisoquinoline via single-electron transfer (SET), which leads to the formation of radical cations and azomethine ylides. Lastly, the generated azomethine ylide undergoes a [3+2]-cycloaddition reaction with a suitable dipolarophile, which gets converted into a pyrrolidine adduct, followed by an aromatization reaction to finally produce the corresponding pyrrolo-isoquinoline derivative.²⁸</p>	

The immense importance of chlorophyll in the synthesis of various heterocyclic rings has fascinated organic and synthetic chemists. Chlorophyll as a natural catalyst not only speeds up the chemical reaction but also replaces the use of organometallic catalysts such as Ru(II) and Ir(III) polypyridine for various suitable transformations. The use of chlorophyll as a catalyst in chemical synthesis is an efficient green chemistry method due to its advantages, including its high efficiency, environmental friendliness, and economical approach.

Conflict of Interest

The authors declare no conflict of interest.

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