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Stabilization of Cu-Chlorophyllin by Incorporation into Hydrotalcite Interlayer

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Abstract

The stability of copper chlorophyllin dye, a derivative of the naturally occurring chlorophyll, was improved by the intercalation into the interlayer space of a layered inorganic host material. As the layered inorganic compounds, hydrotalcite was used. The copper chlorophyllin could be inserted between the layers either by the reconstruction method or by the ion exchange method. We found the preparation condition for the composite materials that successfully included the dye molecules between the layers. The obtained composite samples showed high durability under visible light irradiation. The intercalation of the copper chlorophyllin into the hydrotalcite layers effectively suppressed the elution of the dye molecules by water or ethanol. We proposed the potential application of these highly stable composite materials as environmentally friendly natural dye-based colorants.

Key-words: *Copper chlorophyllin, Hydrotalcite, Complexation, Stabilization, Intercalation*

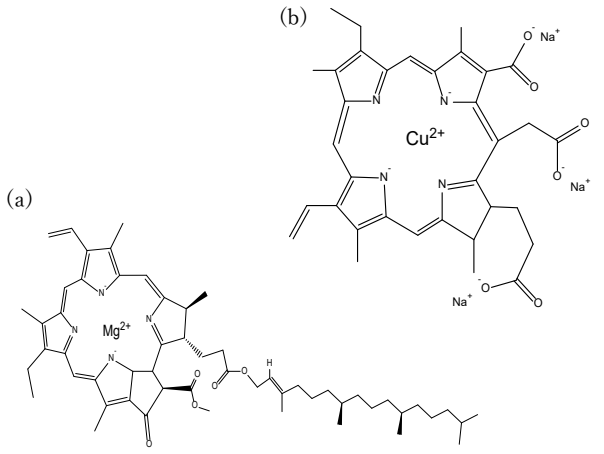
1. Introduction

Naturally occurring dyes are more environmentally friendly and suitable for the human body, compared with synthetic ones. Natural dyes are used as colorants for cosmetics and foods due to their safe properties. Chlorophyll is one of the most abundant natural dyes, which generally exists in the leaves of plants[1]. Chlorophyll exhibits green color, and in addition, it has a functionality of deodorant effect. However, chlorophyll cannot be easily used as a practical colorant, because of its quite low stability.

The structure of chlorophyll *a* is shown in **Scheme 1** (a). It has a porphyrin ring with magnesium ion as a coordination center. The porphyrin ring has several carboxylate substituents, one of which is esterified with a long alkyl chain. Therefore, chlorophyll molecules often exhibit rather hydrophobic nature.

Scheme 1 (b) shows the structure of copper chlorophyllin (CuChl), which is a derivative of natural chlorophyll. In CuChl, the coordination center is substituted from magnesium to copper ion, and the long alkyl chains are removed by hydrolysis. The remaining carboxyl groups are made sodium salts. Therefore, CuChl shows hydrophilic property and is highly soluble in water. More importantly, the stability of CuChl is enhanced compared to the original chlorophyll[2]. CuChl is also nontoxic and has the functionality of deodorant, so that it is used as a functional food additive[3]. However, even though the stability is enhanced, the durability of CuChl is still not enough for wide practical use.

Making a composite with an inorganic host is known as a method of improving the stability of natural or synthetic dyes. Itoh *et al*. reported that natural chlorophyll could be stabilized by incorporation in mesoporous silica[4]. Besides, there are many studies that have reported the stability enhancement of the dye by complexing with an inorganic host such as clays[5], mesoporous silica[6] or zeolite[7]. We have also investigated the stability enhancement



Scheme 1　Molecular structure of chlorophyll derivative pigment (a) chlorophyll *a*, (b) sodium copper chlorophyllin.