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Phototoxicity of chlorophylls: a major photobiochemical constraint on the energy flux from photosyntheis

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The “entrance of energy flux” driving biological systems in Earth’s biosphere had shifted largely to solar radiation since the invention of the mechanism of photosynthesis. Chlorophylls as photosensitizers serve as central and indispensable factors in photosynthesis, which enables conversion of photon energy to chemical potential that is conserved in organic matters. Particularly, the emergence of oxygenic photosynthesis, recruiting water molecules ubiquitous in Earth’s environments as the terminal electron donor, is regarded as a major innovation of Earth’s biosphere by accelerating photosynthetic primary production, that is, drastically increasing the flux from solar energy. Yet, generated molecular oxygen in compensation for this innovation is rather incompatible with chlorophylls, for chlorophylls photosensitizing normal molecular oxygen (triplet oxygen) to generate highly toxic reactive species called “singlet oxygen” (*i.e.*, phototoxicity of chlorophylls). Modern plants (*i.e.*, all oxygenic phototrophs including cyanobacteria and eukaryotic phototrophs) have developed elaborated mechanisms that protect against phototoxicity of chlorophylls[1]. Paradoxically, the first oxygenic phototrophs must have already invented any mechanism against the phototoxicity in prior to oxygenation of Earth’s atmosphere. Moreover, in order to draw energy flux from photosynthesis to the subordinated ecosystem, which is presumably conducted by heterotrophs, it requires intake of organic matters deriving in phototrophs into the cells. Heterotrophic, particularly phycophagic protists (*i.e.*, unicellular eukaryotes), plays important roles in the modern aquatic ecosystem through phagocytosis of algal cells, which perhaps was a much more important process in early ages before emergence of metazoan planktons. Although the process taking chlorophyll-containing matters into the cell inevitably accompanies the risk of the phototoxicity, yet any such a problem is generally observed in the environment in practice. We recently discovered a metabolic process converting phototoxic chlorophylls to non-phototoxic derivatives, 13^2,17^3-cyclopheophorbide enols (CPEs), associated with phagocytosis of algae by protists[2,3]. This metabolism is found to be shared by a very wide range of heterotrophic protists that virtually distribute among almost all major supergroups of Eukarya. In fact, CPEs are turned to be highly abundant pigments in any aquatic environment, suggesting importance of the phycophagic process by protists in the energy flux. Furthermore, production of CPEs is also reported from phototropic protists[4,5]; we observed that the “CPE metabolism” functions in some secondary algae such as Euglenophyceae during self-degradation processes of own plastids. We infer the CPE metabolism of the algae must be inherited from the ancestral phycophagic protists. In summary, although plesiomorphy of the CPE metabolism in Eukarya must carefully be examined after accumulations of studies through various approaches, we argue possible importance of metabolism(s) for detoxification of chlorophylls among eukaryotes both in early radiation enabling ingestion of oxygenic phototrophs and in evolution of eukaryotic phototrophs enabling retention of chlorophyll-containing organelle by controlling its phototoxicity, hence being a major factor allowing expansion and sophistication of the flux originating from solar energy.

References:
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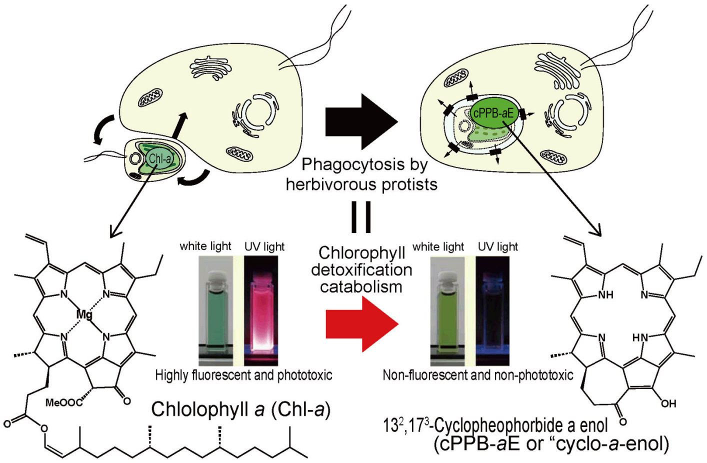
Keywords: chlorophyll, oxygen, phototoxicity, protist, microalgae, cyclopheophorbide enol


Chl-a
cPPB-aE
Phagocytosis by herbivorous protists
white light
UV light
Chlorophyll detoxification catabolism
white light
UV light
Mg
N
MeOOC
O
NH
HN
OH
Highly fluorescent and phototoxic
Non-fluorescent and non-phototoxic
Chlolophyll *a* (Chl-*a*)
$13^2,17^3$-Cyclopheophorbide a enol
(cPPB-*a*E or “cyclo-*a*-enol)