Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 29 Oct 2010

To cite this article: Don Keun Lee & Young Soo Kang (2002): Molecular Devices of Artificial Photosynthesis with Chlorophyll, Molecular Crystals and Liquid Crystals, 377:1, 261-264

To link to this article: http://dx.doi.org/10.1080/713738559

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 261-264

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290089031

Molecular Devices of Artificial Photosynthesis with Chlorophyll

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The artificial photosynthetic systems which simulated the natural photosynthetic system, were built by incorporating chlorophylls into lipid bilayer vesicles such as dihexadecylphysphate (DHP), dipalmitoylphosphatidylcholine (DPPC) and dioctadecyldimethyl-ammonium chloride (DODAC). The formation of vesicles were identified by measuring λ_{max} value change from chloroform solution to vesicles solutions indirectly, and observed directly with SEM and TEM images. The efficiency of photosynthesis in model system was determined by measuring the amount of chlorophyll radical yields which were obtained from integration of ESR spectra. This can be used as a nano molecular devices for the light energy conversion into chemical energy.

Keywords: artificial photosynthesis; photoinduced charge separation

INTRODUCTION

Molecular assemblies such as micelles and vesicles may be used as model systems for the storage of light energy.[1],[2] These self-forming molecular assemblies compartmentalize the electron donors and acceptors relative to the solvent, typically water. The objective of this research is to manipulate the vesicle structure to optimize the charge separation to store light energy. We have studied systematically the

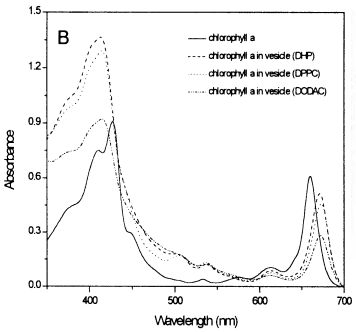

FIGURE 2. Optical absorption spectra of chlorophyll a in diethyl ether, DHP vesicles, DPPC vesicles and DODAC vesicles containing chlorophyll a.

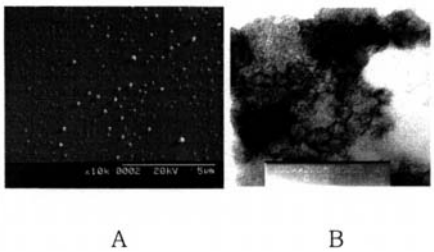

FIGURE 3. Scanning electron micrographs of DHP vesicles (A, ×10,000) and transmission electron micrographs of DHP vesicles (B, ×100,000) containing chlorophyll a. The size of vesicles is 80 – 180 nm.

photoionization of chlorophyll a in vesicles with different interface charge of the lipid headgroup without an electron acceptor or scavenger.

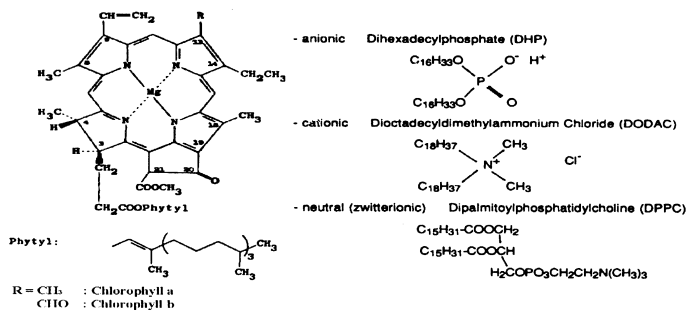

FIGURE 1. The molecular structures of chlorophylls (a and b) and lipids (DHP, DODAC and DPPC)

EXPERIMENT

Chlorophyll a was extracted form fresh spinach leaves by the conventional method. [3] Its purity was determined to be 96% from its

extinction coefficient 8.6×10^{-4} M^{-1} cm^{-1} in diethyl eter at 660 nm.[3] DHP and DPPC were purchased form Sigma Chemical Co. and were used without further purification. DODAC was prepared as described previously.[4] The molecular structures of chlorophylls and lipids (DHP, DODAC, DPPC) are shown in FIGURE 1. All of vesicle solutions of chlorophyll a were prepared by the method developed by Huang[5] and modified by Norris et al.[6] Photoirradiation at 77 K was performed with 300-W Cermax Xenon lamp with a power supply form ILC Technology. The light was passed through a 10-cm water filter and a Corning 5030 band pass filter for blue light irradiation ($300 \text{ nm} < \lambda_{irr} < 558$). ESR spectra were recorded at X-band on JEOL JEX-FX 2000-300. Mn^{2+} in MgO was used as a magnetic field marker. Optical absorption spectra were measured in 1 cm path length quartz cell with a Varian CARY 1C UV-vis spectrophotometer at room temperature.

RESULTS AND DISCUSSION

Optical absorption spectra of chlorophyll a in diethyl ether, DHP vesicles, DPPC vesicles and DODAC vesicles containing chlorophyll a is shown in FIGURE 2. Chlorophyll a solubilized into a phospholipid vesicles, causes a 10 nm shift to the red region compared to diethyl ethyl solution in which $\lambda_{max} = 662$ nm. This red shift is still persisted in DPPC vesicle solutions with $\lambda_{max} = 672$ nm.[7] This red shift indicates the chlorin ring being located in a polar environment near the surfactant headgroup region and possibly exposed to the aqueous environment. Scanning electron micrographs of DHP vesicles (A, ×10,000) and transmission electron micrographs of DHP vesicles (B, ×100,000) containing chlorophyll a were shown in FIGURE 3. The size of vesicles is 80 – 180 nm. The photosynthesis of chlorophylls in vesicles was studied with ESR. The photoproduced cation radical of chlorophyll was identified as g = 2.0026 and broad singlet in frozen state at 77K. Dependence of the normalized photoyield of chlorophyll a upon the kind of lipids was shown in FIGURE 4. The efficiency of photosynthesis in model system was determined by measuring the amount of chlorophyll radical yields which were obtained from integration of spectra. This was comparatively studied on the effect of vesicle structure and interface

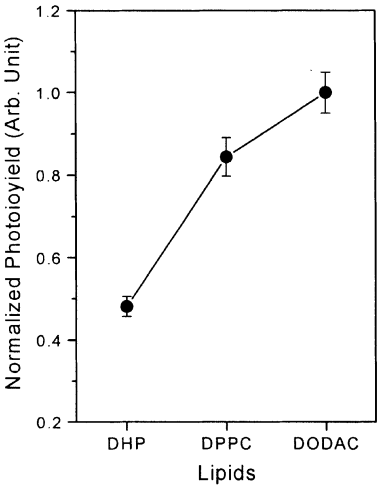

FIGURE 4. Dependence of the normalized photoyield of chlorophyll a upon the kind of lipids at 77 K after 90 min blue-light irradiation.

charge of vesicles. The bulkier head group structure and lower energy barrier for the electron transfer of vesicles resulted in the higher radical yields. This is shown as increasing photoyields as DHP < DPPC < DODAC. DODAC vesicles enhanced the photoionization yield compared to DHP and DPPC vesicles. This is interpreted as to cross DHP vesicle interface the electron has to overcome a negative electric field, which decreases the probability of electron transfer. But the trans-interface electron transfer is promoted by a positive electric field as in DODAC vesicle interface. This system can be used as a nano molecular devices for the utilization of light energy conversion into chemical energy.

Acknowledgments

This project was supported by Ministry of Science and Technology (MOST) as a part of the Nuclear R&D Program.

References

[1] J.H. Fendler Acc. Chem. Res. **13**, p. 7 (1980)
[2] J.K. Hurley and G. Tollin Sol. Energy **28**, p. 197 (1982)
[3] H.H. Strain and W.A. Svec In The Chlorophylls Academic Press: New York, p. 21 (1966)
[4] T. Hiff and L. Kevan J. Phys. Chem. **93**, p. 2069 (1989)
[5] G.H. Huang Biochemistry **8**, p.344 (1969)
[6] W. Oettmeier, J.R. Norris and J.J. Katz Naturforsch **31**, p. 163 (1976)
[7] T. Trosper, D. Raveed and B. Ke Biochem. Biophys. Acta **223**, p. 463 (1970)