Chlorophyll a Molecular Organization and Photoreactivity

P. COSMA§, A. AGOSTIANO, L. CATUCCI§, A. CEGLIE, G. COLAFEMMINA, A. MALLARDI§, G. PALAZZO, M. TROTTA§ and M. DELLA MONICA.
Dipartimento di Chimica-Università degli Studi di Bari
§ CNR-Centro Studi Chimico-Fisici sull'Interazione Luce-Materia 4, Traversa Re David 200, 70126 Bari (Italy)

1. Introduction

The Chlorophyll a (Chl a) is the main pigment in plant photosynthesis, whose relevance resides in its functional duality. The Chl a, indeed, acts as antenna, collecting and funneling light, and as photoreactive center, where the energy transduction takes place. The different roles played by this molecule are closely related to its molecular organization due to stereospecific interactions involving the Mg atom and the C=O group of the Chl a with water or side chains (N-H, S-H, O-H) of natural aminoacids [1]. For this reason, the problem of pigment aggregation and interaction with water is of great interest in the in vitro studies of photosynthesis, whose important focus is the characterization of the photoreactive form of the Chlorophyll a [2, 3]. Currently the work on Chl a aggregation and photochemistry is focussed on its aqueous solutions with organic solvents [4-11]. Chl a aggregation, in a wide range of composition of the water/polar solvent mixtures, has been the subject of investigation in our laboratories [12-15].

The first part of this paper summarizes the results of our researches on the different factors affecting the Chl a aggregation. The influence of the different functional groups of the solvents, the role played by the water content of the solution, the relevance of the hydrophobic effect and the correlation with the excess properties of the medium will be discussed.

Although the existence of an efficient energy transfer between different Chl a aggregates in water/polar solvent mixtures has been demonstrated [16], the study of Chl a photochemistry is not an easy task because of the lack of compartmentalization, which is essential for the stabilization of the charge separated state and vectorial electron transfer in in vivo photosynthesis.

The second part of the paper reports the attempts to immobilize the photoreactive Chl a at the interface between different phases. Reverse micelles were chosen as microreactors in which the trapping of the Chlorophyll could supposedly be possible by the use of water/organic solvent binary mixtures [17, 18].

The results of NMR studies on this system, indicating the impossibility of Chl a to be
trapped inside the reverse micelles [19], shifted our attention on a new family of water-in-oil microemulsions formed by lecithin in n-heptane. Upon water addition the microemulsion is transformed into transparent gel [20].
The last part of this note reports the results obtained by introducing a photoreactive form of Chl α at the interface between the water and the lipidic phase. The photoinduced electron transfer catalyzed by the Chlorophyll was verified in presence of suitable electron donors and acceptors solubilized in the different phases of the microemulsion [21].

2. Binary Mixtures

The behavior of the Chl α in solution is governed by the inter and intra molecular interactions of its functional groups. Namely, the Mg atom of the porphyrin ring provides the site of binding for the nucleophylic moiety of solvents, such as the oxygen of water, ketones or alcohols. The carbonyl groups in C-131, C-133, C-173 act in addition as a nucleophil in the hydrogen bonding to the solvents or to a second Chl α molecule. Finally, the hydrophobic phytic chain allows the Chl α solubilization in the hydrocarbon constituent of the medium (Fig. 1). In other words in the binary mixtures the polar component favors the aggregation of porphirinic rings of Chl α, while the hydrophobic component tends to keep the phytologic chains far apart. The formation of various solvated and aggregated species is a multistep

Figure 1. Chlorophyll α molecule.