Journal of Photochemistry & Photobiology A: Chemistry 364 (2018) 140–144

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Short note

Approach for the electrochemical analysis of hydrophobic compounds included in photo-responsive liposomes

Silvia Soto Espinoza[b], Irene Rezzano[a,b,1], Santiago Sobral[b], Romina Carballo[a,b,*,1]

[a] Universidad de Buenos Aires, Facultad de Farmacia y Bioquímica, Buenos Aires, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas, Instituto de Química y Fisicoquímica Biológica (IQUIFIB), Buenos Aires, Argentina

ARTICLE INFO

Keywords:
Photo-response
Liposomes
Porphyrins
Optical materials and properties
Biomimetic

ABSTRACT

A highly hydrophobic porphyrin: di-octadecyl-amide deuteroporphyrin (D-ODA) was synthesized and incorporated into liposomes (Lipo-D-ODA) through self-assembling of the aliphatic chains. From the fluorescence spectra, it was concluded that the long alkyl carboxylate chains accommodate the sensitizer into the lipid bilayer, is less exposed to quenching induced by aggregation.

The light excited liposome Lipo-D*-ODA activated the ground state molecular oxygen to produce oxygen singlet or superoxide anion.

The electrochemical responses of two structurally different redox-active analytes were studied. Quercetin oxidation at 200 mV was only observed after irradiation on the Lipo-D-ODA/Quercetin, indicating that it is embedded in the liposome and requires membrane rupture. On the contrary, the signal of Ferrocene-ODA was independent of irradiation because the redox polar moieties (Ferrocene) were oriented in aqueous space.

1. Introduction

There has been intense research on lipid vesicles since the 60's due to their capacity for embedding and encapsulating materials, imitating the biological membranes. In this sense, liposomes and micelles of different lipidic composition have been applied in chemical, and biochemical analytics, drug delivery, cosmetics, food technology, and proteomics [1,2].

The liposomes can accommodate hydrophobic molecules inserted into the bilayer by self-assembly during membrane formation and hold entrapped the hydrophilic compounds in the aqueous centre [3]. Most of the studies were carried out in the field of drug delivery, provided that the efficient liberation in a controlled and selective manner is the crucial point of its applicability. The release of molecules embedded in liposomes was triggered by a wide range of physical stimuli, including magnetic or electric fields [4], temperature [5], light [6] and acoustic waves [7]. Electromagnetic irradiation is an attractive stimulus because it is easy to apply and can be localized in time and space. Moreover, the irradiation parameters can be modulated to the system requirements [8].

Efficient solute release from liposomes by electromagnetic irradiation was achieved when they included photoactive molecules, capable of inducing membrane destabilisation and permeabilisation. These physicochemical changes are highly dependent on the intrinsic polarity of the chromophore which affects the localisation in the liposome [9]. One of the most common mechanisms for disruption of membranes is light-induced oxidation by reactive oxygen species (ROS).

Porphyrinic compounds are excellent photosensitizer, in their excited state (Psen*) can interact with molecular oxygen ($^3O_2$) to produce ROS, including singlet oxygen ($^1O_2$), hydroxyl radicals (OH·), and superoxide (O^{2-}) anions which are highly oxidant species capable of deteriorating the phospholipid membrane [10].

The present work reports the preparation and characterisation of a new type of photoactivable liposome, containing a hydrophobic porphyrin. This new material was explored as nanocarrier of electrochemically active molecules of different polarity to be delivered by light stimuli in aqueous solution for their analysis.

2. Experimental details

Soybean phosphatidylcholine (PC) was purchased from Lipoid (Ludwigshafen, Germany). Deuteroporphyrin IX dimethyl ester (D) was from Frontier Scientific. Cholesterol (99%), octadecylamine (97%), quercetin (≥95%), ferrocene carboxaldehyde (98%), 4-aminoantipyrine and phenol were provided by Sigma-Aldrich. 6, 7dioctadecylamide deuteroporphyrin (D-ODA) was obtained by saponification and

* Corresponding author at: Universidad de Buenos Aires, Facultad de Farmacia y Bioquímica, Buenos Aires, Argentina.
E-mail address: rocar@ffyb.uba.ar (R. Carballo).
[1] CONICET permanent staff.

https://doi.org/10.1016/j.jphotochem.2018.06.010
Received 17 February 2018; Received in revised form 30 May 2018; Accepted 2 June 2018
Available online 05 June 2018
1010-6030/

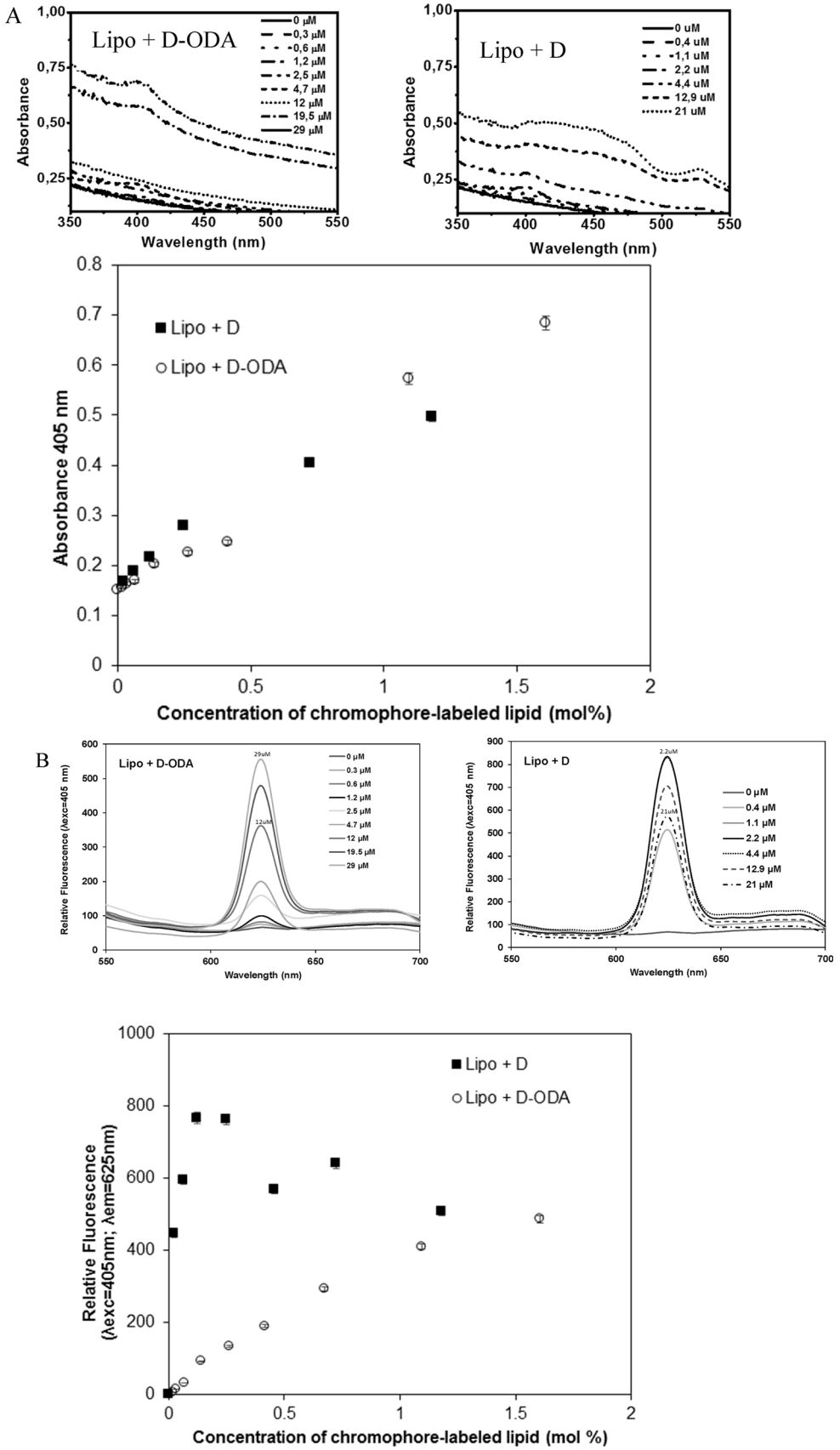

Fig. 1. Changes of (A) absorbance and (B) fluorescence emission spectra as a function of the concentration of deuteroporphyrin (■) and D-ODA (○) in liposomes (mol %).