Transformation of lipid bilayers under photo-induced oxidation: bummer or crackerjack?

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Oxidation can intimately influence and structurally compromise the levels of biological self-assembly embodied by intracellular and plasma membranes. Lipid peroxidation, a natural metabolic outcome of life with oxygen under light, is also a salient oxidation reaction in photomedecine treatments. However, the effect of peroxidation on the fate of lipid membranes remains elusive. Here we use a new photosensitizer that anchors and disperses in the membrane to achieve spatial control of the oxidizing species. We find, surprisingly, that the integrity of unsaturated giant unilamellar vesicles is preserved even for fully oxidized membranes. Membrane survival allows for the quantification of the transformations of the peroxidized bilayers, providing key physical and chemical information to understand the effect of lipid oxidation on protein insertion and on other mechanisms of cell function.

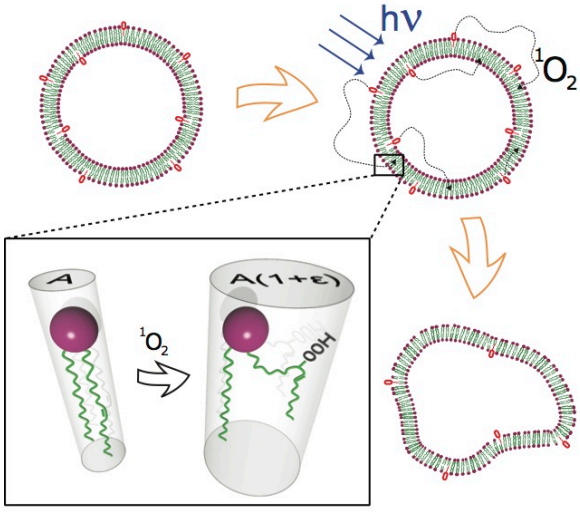

Figure Lipid and membrane transformations induced by hydroperoxidation. Irradiation of a vesicle decorated with the anchored photosensitizer generates singlet oxygen species that induce, under a constant irradiation, an increasing amount of oxidized lipids. Following a reaction with the singlet oxygen moiety, the double bond in the unsaturated lipid tail of each lipid is converted into the organic hydroperoxide group -OOH. Its migration to the bilayer surface leads to a relative increase of the average molecular area of the oxidized lipid. As the total area of the GUV bilayer expands, the membrane displays phenomena characteristic of membrane area increase, such as enhanced fluctuations followed by bud and tube formation.

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