

Comprehensive Series in Photochemical  
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# Singlet Oxygen

Applications in Biosciences and Nanosciences  
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## Chapter 12

# Endogenous Singlet Oxygen Photosensitizers in Plants<sup>†</sup>

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<sup>†</sup>This chapter is dedicated to the memory of María Cabeza Arellano (1964–2015), a dedicated and well-beloved teacher of biology.

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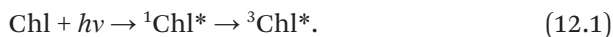
## 12.1. Introduction

Since all preliminary matters concerning the reactivity and photophysical properties of singlet oxygen ( $^1\text{O}_2$ ) have already been dealt with in the preceding chapters, we need not dwell on these issues here, apart from reminding the reader that  $^1\text{O}_2$  formation through photoexcitation of a ground-state oxygen molecule ( $\text{O}_2$ ) has a negligibly small probability because the corresponding radiative transition is doubly forbidden, as it violates the selection rule for spin as well as that for electric-dipole radiation. This leaves photosensitization as the main feasible means of generating  $^1\text{O}_2$ . We proceed therefore to discuss the sensitization mechanisms through which  $^1\text{O}_2$  is formed in plants. Additionally, we briefly introduce the formation and decomposition of some derivatives of lipid hydroperoxides as a possible source of chemical  $^1\text{O}_2$  production in plants. The chapter also deals with photoprotection processes by which  $^1\text{O}_2$  formation is prevented or  $^1\text{O}_2$  is efficiently deactivated after its formation. Finally, the distance over which  $^1\text{O}_2$  can diffuse in a viscous cellular medium, such as that found inside chloroplasts, is analyzed.

## 12.2. Mechanisms of Singlet Oxygen Production in Plants

### 12.2.1. Photosensitization by Chlorophyll

A molecule with a singlet ground state can act as a photosensitizer (PS) when it is in its lowest triplet excited state ( $^3\text{PS}^*$ ) or in its lowest singlet excited state ( $^1\text{PS}^*$ ). The latter case will not be discussed here, because the singlet-state lifetime ( $\tau_s^0$ ) of the relevant PSs is too short, and the energy gap between  $^1\text{PS}^*$  and  $^3\text{PS}^*$  too small, to warrant contemplation in the present context. In order to be an efficient PS, a molecule must have a large molar absorption coefficient in at least one region of the visible spectrum, a large quantum yield for intersystem crossing (ISC) denoted as  $\Phi_{\text{IS}}$ , and a long triplet lifetime,  $\tau_T^0$ . Among photosynthetic pigments, chlorophyll (Chl) molecules are by far the most important PSs in plants, although their derivatives, such as pheophytin (Phe), also meet all the above requirements. Photoexcitation of a Chl molecule to a high-lying level in the singlet manifold (Soret or  $\text{Q}_x$  band) is followed by a rapid (within a few ps or even faster) internal conversion to the lowest singlet excited state ( $\text{Q}_y$ ,  $^1\text{Chl}^*$ ), characterized by a lifetime ( $\tau_s^0$ ) of a few ns. In the absence of a fast competing event, which may be singlet excitation energy transfer (EET) to another Chl molecule or transfer of an electron to a neighboring molecule, the  $\text{Q}_y$  state of Chl makes a transition either to the ground state (through internal conversion or fluorescence emission), or to the first triplet excited state through ISC, leading to the formation of  $^3\text{Chl}^*$  (eqn (12.1)).



In photosynthetic antenna complexes of plants, ISC is the only route for the formation of  $^3\text{Chl}^*$ , but in the reaction center (RC) of photosystem II (PSII),