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Sacrificial electron donor reagents for solar fuel production

*Les donneurs d'électron sacrificiels pour la production de combustible solaire*Yann Pellegrin^{*}, Fabrice Odobel

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ABSTRACT

Although justly considered as a cumbersome component in artificial photosystems, these simple molecules are a “necessary evil” to drive photo-induced reactions aiming at producing high added value molecules by photo-induced reduction of low energy value substrates. This review first presents the specifications of sacrificial electron donors. Then the various families of sacrificial donors used from the early 1970s to nowadays are reviewed, such as aliphatic and aromatic amines, benzyl-dihydropyridinamide (BNAH), dimethylphenylbenzimidazole (BIH), ascorbic acid, oxalate and finally thiols. Experimental conditions (pH, solvent) are immensely versatile but important trends are given for adequate operation of a three-component system. Although literature abounds with various, very different artificial photosystems, we will realize that virtually the same sacrificial donors are used over and over again.

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R É S U M É

Dans le domaine de la photosynthèse artificielle, les donneurs d'électron sacrificiels sont un mal nécessaire, permettant de produire des molécules à haute valeur ajoutée à partir de molécules à faible contenu énergétique, en alimentant les photosystèmes artificiels en électrons. Cet article passe en revue les différents donneurs sacrificiels utilisés par la communauté scientifique depuis les années 1970 jusqu'à nos jours. Les amines, les thiols, les modèles du NADH sont ainsi, entre autres, répertoriés ainsi que leurs conditions d'utilisation optimales.

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1. Introduction

Converting solar light into a usable form of energy is a very worthy challenge, since sunlight is relatively equally

distributed on the planet, very abundant, strictly nonpolluting, virtually inexhaustible and free. Taking inspiration from photosynthesis, scientists have early tried to develop artificial photosystems, capable of harvesting and converting light into chemical potential, storing the immaterial electromagnetic energy in the shape of chemical bonds.^{1–5} In other words, using light to drive highly endothermic

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reactions transforming abundant and low energy raw materials into high added value molecules is the ambitious purpose of a significant part of the scientific community.^{6–8} This is epitomized by the well-known and much desired water splitting reaction (equation (1)):



This would provide humanity with an inexhaustible source of H_2 , which is a clean, energy rich solar fuel.^{9–11}

In natural photosynthesis, H_2O is first oxidized to O_2 and the electrons resulting from this redox process are used to generate the biological reductant NAD(P)H from NAD(P)^+ .^{12,13} Ultimately, NADH is implied in CO_2 reduction into biomass. In a way, biomass, growth of the photosynthetic organisms, results from the reduction of CO_2 by the electrons photo-extracted from water and O_2 is nothing but a waste product. Therefore, photosynthesis promotes CO_2 reduction into biomass by water, the energy necessary to drive this very endothermic reaction being provided by solar light. In a way, H_2O can be seen as a sacrificial electron donor, fueling the natural photosystem with electrons.

Ideally, the same goal is envisioned for artificial photosynthesis but extracting electrons from water, low added value molecule *par excellence*, is particularly difficult and requires several processes (light harvesting,¹⁴ charge photoaccumulation,^{15,16} and catalysis^{17–19}) which are at the very core of artificial photosynthesis research field. Crudely, the great ordeal to mimic a full photosystem lead scientists to study half photosystems separately, oxidative ones on one hand (models of PSII)^{7,20–23} and reductive ones on the other (models of PSI).^{3,24–40} Despite the obvious interest of oxidative artificial photosystems, we will in this review focus exclusively on the reductive ones. For the latter, simpler electron donors than H_2O were used, to meticulously focus on the reductive processes. By “simple”, we mean that these electron donors can readily fuel a photosystem with electrons. The latter are the subject of this review, namely “waste” molecules, sacrificed in the course of the photochemical reactions, and used essentially for the practical study of the artificial reductive photosystems. These molecules are most often referred to as *sacrificial donors* (SDs) and are playing a pivotal role in peculiar artificial photosystems called “three-component system” (TCS).⁴¹

2. General operating mechanism of sacrificial reagents and thermodynamic considerations

Artificial photosystems other than TCSs are currently developed,^{22,42–47} but the latter is historically the first artificial photosystem.^{3,34,35} There are both oxidative^{21–23} and reductive TCSs,^{4,34,48} with SDs intervening in the latter one. Those three components are 1) the photosensitizer (PS) which must harvest solar light and convert it into chemical potential, i.e. into reductive or oxidative potential; 2) the sacrificial donor SD, providing electrons on photo-induced command by PS; 3) the reduction catalyst, accumulating electrons. A fully operational TCS is very often designed to photo-produce high added value molecules

such as H_2 from H^+ or CO_2 reduction compounds (CO , HCHO ...)⁴¹ and this naturally requires appropriate catalysts (a molecular entity^{27,28,30,49–52} or an insoluble material).^{3,34,35,53} Redox relays shuttling electrons between PS and the catalyst are often required in a TCS.^{3,34,35} Thus, TCSs where there is no catalyst but only a redox shuttle have been extensively studied in order to comprehend the photo-induced redox mechanisms at stake, independently from catalysis requirements.^{54,55–57} In the rest of the text, TCSs with catalysts and TCSs without will not be differentiated because SDs are not primarily involved in corresponding steps. We will call SUB, like “SUBstrate”, the ensemble of molecules and materials which are the ultimate electron acceptors in a TCS, the photo-produced electrons' final destination, accumulating during photolysis.

The *modus operandi* of a TCS is the following: upon light absorption, PS is promoted to its excited state and acquires at the same time enhanced oxidative and/or reductive power(s). Thermodynamically speaking, $E(\text{PS}^*/\text{PS}^-)$ is superior to $E(\text{PS}/\text{PS}^-)$ ($E(\text{PS}^*/\text{PS}^-) = E(\text{PS}/\text{PS}^-) + E^{00}$, where E^{00} is the lowest excited state energy) and PS^* is therefore more prone to harvest an electron from the nearby donor SD (equation (2)). Similarly, $E(\text{PS}^+/\text{PS}^*)$ is more negative than $E(\text{PS}^+/\text{PS})$ and PS^* is thus more prone to donate an electron to SUB (equation (3)).



In equation (2), PS ends up in a reduced state, which is why quenching of PS^* by an electron donor is referred to as “reductive quenching” (RQ). On the other hand, PS^* endures an “oxidative quenching” (OQ) in equation (3). Whether PS^* will be implied in a reductive or an oxidative quenching depends on the nature of PS, SUB, and SDs and the external medium can play a major role too (pH, solvent ...); all is governed by the thermodynamic and kinetic parameters at stake.

In a working TCS, both oxidative and reductive quenching pathways can be used: for OQ based TCSs, a photo-induced electron transfer from PS^* to SUB entails the reduction of the latter, and the oxidation of the former. PS^+ is then regenerated by the SD, while SUB accumulates upon repeating such cycles (Fig. 1, right). Conversely, PS^* can abstract an electron from the SD first, and resulting PS^- is regenerated by transferring an electron to SUB (Fig. 1, left). In the end, regardless of the mechanism, SUB was reduced by the SD using light as the sole source of energy to perform this otherwise endothermic reaction, and the reaction may theoretically proceed until all SDs have been oxidized.

From the mechanisms above, a few constraints can be deduced: in the case of OQ, photo-induced electron transfer from PS^* to SUB must be thermodynamically allowed ($E(\text{PS}^+/\text{PS}^*) < E(\text{SUB}/\text{SUB}^-)$) while the same goes for (dark) electron transfer from the SD to PS^+ ($E(\text{PS}^+/\text{PS}) > E(\text{SD}^+/\text{SD})$). In the case of RQ, the photo-induced electron transfer involves PS^* and SD, and therefore $E(\text{SD}^+/\text{SD}) < E(\text{PS}^*/\text{PS}^-)$

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