Account/Revue

Sacrificial electron donor reagents for solar fuel production

Les donneurs d'électron sacrificiels pour la production de combustible solaire

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A B S T R A C T

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-dihydronicotinamide (BNAH), dimethylphenylbenzimidazoline (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

reactions transforming abundant and low energy 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)):

$$2H_2O + h\nu \rightarrow O_2 + 2H_2 \qquad (1)$$

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 photoinduced 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, $E(PS^*/PS^-)$ is superior to $E(PS/PS^-)$ ($E(PS^*/PS^-) = E(PS/PS^-) + E^{00}$, 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, $E(PS^+/PS^*)$ is more negative than $E(PS^+/PS)$ and PS* is thus more prone to donate an electron to SUB (equation (3)).

$$PS^* + SD \rightarrow PS^- + SD^+ \qquad (2)$$

$$PS^* + SUB \rightarrow PS^+ + SUB^- \qquad (3)$$

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 ($E(PS^+/PS^*) < E(SUB/SUB^-)$) while the same goes for (dark) electron transfer from the SD to PS$^+$ ($E(PS^+/PS) > E(SD^+/SD)$). In the case of RQ, the photo-induced electron transfer involves PS* and SD, and therefore $E(SD^+/SD) < E(PS^*/PS^-)$

while $E(PS/PS^-) < E(SUB/SUB^-)$. RQ is considered to be a slightly preferred mechanism over OQ, because PS^- is a more potent reducer than PS^*, allowing the photo-reduction of a larger number of SUB, with more cathodic reduction potentials.

The above conditions on SDs are necessary but not sufficient. First and foremost, in order to allow SUB^- accumulation, avoiding recombination reactions (4) and (5) is mandatory

$$SUB^- + SD^+ \rightarrow SUB + SD \quad (4)$$

$$PS^- + SD^+ \rightarrow PS + SD \quad (5)$$

SDs must therefore be irreversibly oxidized into inert molecules, unable to interfere with the proper running of the photochemical cycles. This deserves further comments: in a donor-acceptor system D/A, D and A must pre-assemble in an encounter complex [D–A] to allow photo-induced charge transfer to take place within the latter.[25,58–60] As such, the photo-excitation of [D–A] yields the geminate pair [D^+–A^-]. Geminate charge recombination within this ion pair can be very fast, and competes with the dislocation of [D^+–A^-], which can be a difficult process due to possible attractive coulombic interactions between D^+ and A^-. This competition translates into the cage escape yield η_{CE}: the higher η_{CE}, the lesser the probability of charge recombination between D^+ and A^- and the larger the chance to accumulate A^-. In the case of RQ, the encounter complex after photo-electron transfer is [SD^+–PS^-]; if the kinetics of SD^+ irreversible transformations into inert entities are lesser than the kinetics of charge recombination, the TCS will fail because no accumulation of PS^- and consequently of SUB^- can take place.[25,58]

To summarize, a good SD must gather several important qualities: thermodynamic adequacy with PS ($E(SD^+/SD) < E(PS^+/PS)$ for OQ and $E(SD^+/SD) > E(PS^*/PS^-)$ for RQ), irreversible transformation upon monoelectronic oxidation into inert molecules, and – if need be – high cage escape yield or faster degradation kinetics than charge recombination. This latter condition concerns reductive quenching

mechanism; the same goes for oxidative quenching but will not be treated here since SDs are not involved in the corresponding encounter complex.

As will be shown in what follows, the reaction medium (solvent, pH), the concentration [SD], and the nature of PS can strongly control the overall efficiency of the solar fuel generation.[34,35] To review all impacts of the variations of these conditions is not the purpose of the present article, nor is to give a comprehensive view of the innumerable TCS from late 1970s until today. We rather wish to present an overview of the different sacrificial donors which have been, and are still, most commonly used in reductive TCSs. We wish to pinpoint that redox organic photochemistry,[61] despite its unquestionable interest, is irrelevant to artificial photosynthesis and will therefore be omitted in the present review.

Transition metal anions have been extensively used as sacrificial donors,[62–64] some of them like $PtCl_4^{2-}$ can however be considered as substrates SUB rather than sacrificial (waste) donors and will therefore be omitted in this review.

3. Aliphatic amines as SDs

Tertiary aliphatic amines are probably the most used sacrificial donors to fuel photochemical reduction reactions. This class of molecules is epitomized by well-known triethylamine (TEA) and triethanolamine (TEOA). Both were employed in the pioneering works setting the bases for a TCS, with the general purpose of photo-producing hydrogen gas[25,35] or photo-decomposing CO_2.[48,65,66] TEA and TEOA display very similar features: they exhibit irreversible oxidation potentials around 0.7 V vs. SCE[24,67,35,65] making them thermodynamically able to be part of similar electron transfer processes. However, let us bear in mind that electrochemical irreversible processes are poorly described by a redox potential $E(SD^+/SD)$ and the anodic peak potential can only give a rough estimate of the thermodynamics lying behind the electron transfers within the SD^+/SD couple.[68] This is further demonstrated by the various reported oxidation potentials for the same species, differing sometimes by more than 100 mV.[35,53] Besides, and equally important, TEA and TEOA are used in
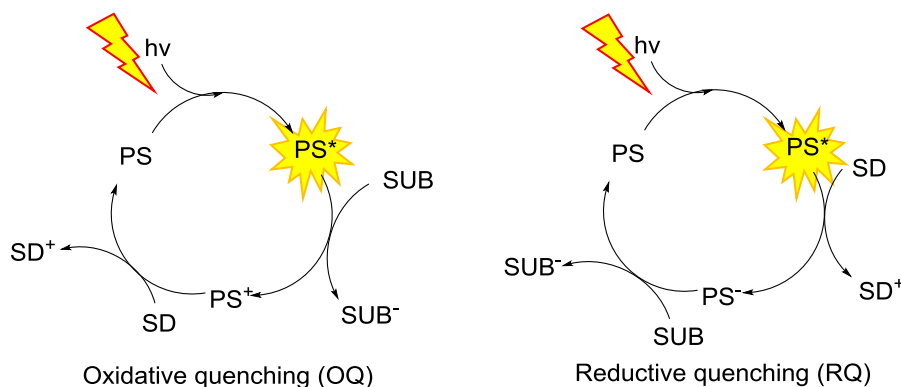

Fig. 1. Mechanisms of RQ and OQ within a TCS.

an impressive collection of various conditions (solvent, pH, concentration…) making a systematic study of the thermodynamics of OQ or RQ through the whole literature quite intricate. As such, redox potentials given in Table 1 are to be taken with great caution. Concerning the solvent, TEA or TEOA has been used in purely organic[30,65,69] or aqueous

Table 1
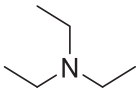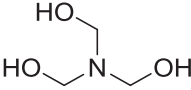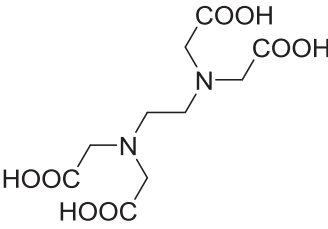Structures, names and properties of usual sacrificial donors. Redox potentials given in V vs. SCE.
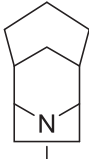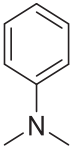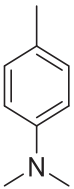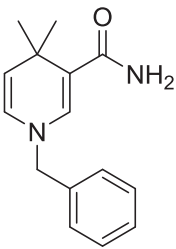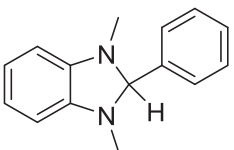
Structure	Name of general use	E_{ox}	Medium
	TEA	0.69[67]	Aqueous
	TEOA	[a]0.57[35]–0.82[53]	Aqueous
	EDTA	[b]0.57[82]–0.92[53]	Aqueous
	Amine **1**[102]	n.r.	–
	DMA	0.81[103]	MeCN
	DMT	0.71[103]	MeCN
	BNAH	0.57[115]	MeCN
	BIH	0.33[153]	MeCN

Table 1 (*continued*)

Structure	Name of general use	E_{ox}	Medium
	Ascorbic acid (H₂A)	[a]0.46[154] (HA⁻/HA•)	Aqueous
	Oxalate	–	–
	Benz-S⁻	−0.1[149]	MeCN
	Dtc⁻	0.05[54]	MeCN
	Xan⁻	0.21[54]	MeCN
	Dtb⁻	0.19[54]	MeCN
	Dtp⁻	0.71[54]	MeCN
	PPh₃	0.98[151]	MeCN

[a] Values published vs. NHE, obtained vs. SCE by removing 0.25 V.
[b] Values for EDTA are deduced from ref.[82]

media;[35,70] very often though, mixtures of water with an organic solvent (DMF, MeCN, and THF) are reported,[71–76] the reasons for this are given below.

The main appeal concerning TEA and TEOA is their degradation pathway,[24,77–79] which is described in Fig. 2 for TEOA, but is very similar for TEA. Upon mono-electronic oxidation (1), a positively charged aminyl radical is formed. The latter is a good oxidant which could in principle react with any reduced species (PS⁻ in the case of RQ, or SUB⁻ in the case of OQ), i.e. lead to counter-productive back electron transfer. However, deprotonation of the aminyl radical by TEOA itself leads to a rearrangement into a carbon centered radical displaying a significant reductive power (E(b/a) = 1 V, Fig. 2)[77]. The latter is beneficially used to reduce PS or SUB or a redox mediator shuttling between them, and therefore contributes to increase the overall yield of SUB⁻ photoproduction.[35,80] The iminium species which results from this "dark" electron transfer process is either the final product in the absence of water, or further degrades into (hydroxy) ethanal and secondary amine by hydrolysis of the iminium in aqueous media. This last step is often reported to be very important[48,77,81] to insure the buildup of reduced SUB⁻ but accumulation of reduced species upon photolysis in a purely organic medium (acetonitrile, dimethylformamide) has been reported too.[80,81] We believe this strongly
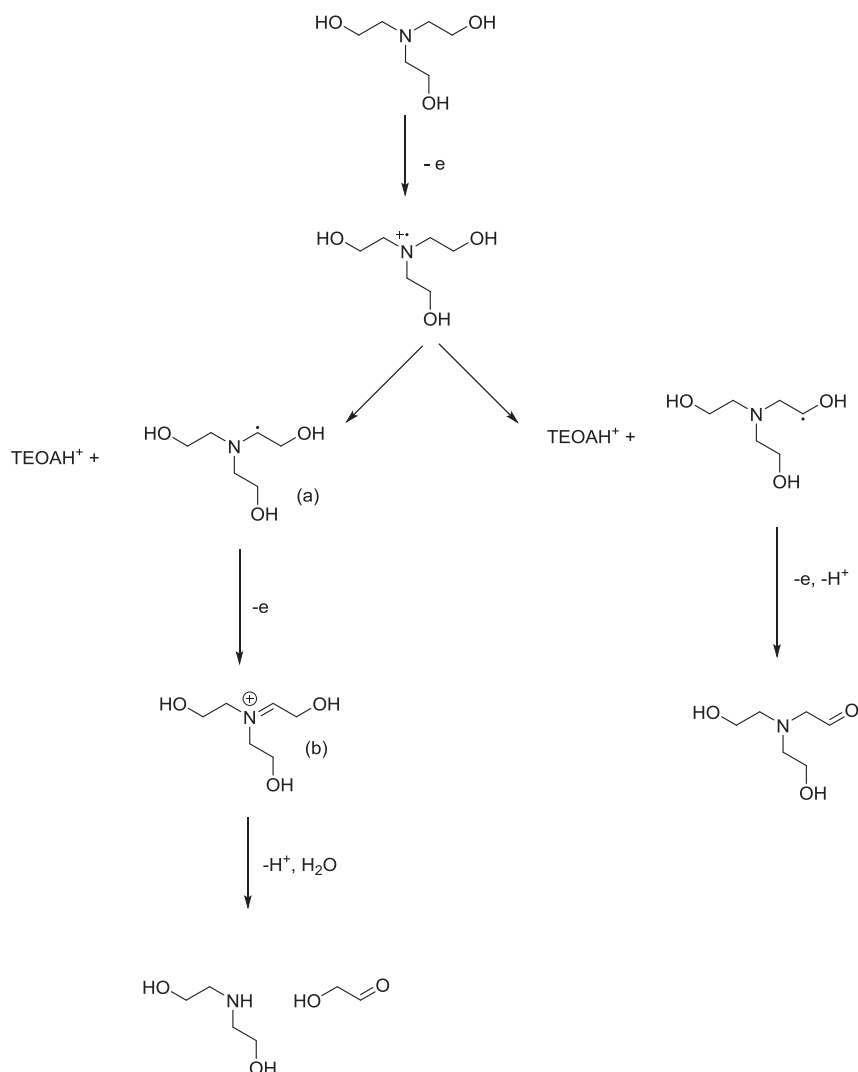
Fig. 2. Degradation pathway of TEOA upon monoelectronic oxidation.

depends on the kinetics at stake in the cage escape process. All in all, aliphatic tertiary amines are endowed with good cage escape yields,[82] but this is highly dependent on the photosensitizer and the occurrence of a reductive quenching mechanism.

When one considers the chain of reactions depicted in Fig. 2, deprotonation of the aminyl radical (or hydrogen abstraction) by a regular amine molecule is mandatory in order to form the reductive carbon centered radical, and prevent charge recombination.[35,83] Knowing that the pK_a

E(PS*/PS⁻) = 0.7 V vs. SCE   E(PS*/PS⁻) = 0.95 V vs. SCE   E(PS*/PS⁻) = 1.35 V vs. SCE   E(PS*/PS⁻) = 0.7 V vs. SCE   E(PS*/PS⁻) = 1V vs. SCE
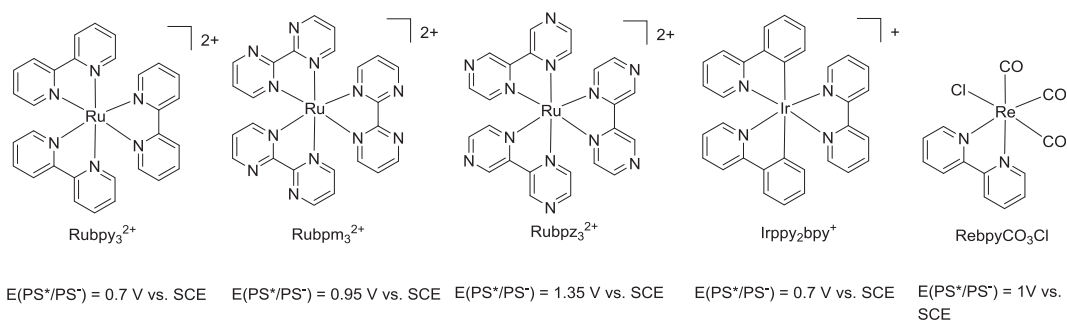
Fig. 3. Some metal based photosensitizers with various photo-oxidizing powers (Re(bpy)CO₃Cl,[65,93] Irppy₂bpy⁺ and [Ru(bpy)₃]²⁺,[87] [Ru(bpm)₃]²⁺ and [Ru(bpz)₃]²⁺)[82]

of TEOA and TEA is 7.9 and 10.7, respectively, this deprotonation step is less and less likely as pH decreases.[35,70] Consequently, most reported works implying TEOA based TCSs are performed at pH values above 8. This is particularly important to pinpoint since the optimal working conditions of catalysts in a TCS may depend on pH. Additionally, since pH is an ambiguous parameter in a purely organic medium, let us nevertheless mention that TEOA or TEA are mostly used in excess compared to SUB to insure the irreversible aminyl transformation,[25] and to improve the overall yield of the TCS.[84]

The concentration of amine in the medium varies a lot (from less than 10 mM to more than 1 M) from a TCS to another. The higher the concentration of SDs, the higher the probability to observe RQ vs OQ.[75,77,85] Although RQ was reported with common $[Ru(bpy)_3]^{2+}$,[81] OQ is more often observed with this milder photo-oxidant.[30,86–88] Alterations of the structures of bpy (bipyrazine bpz, bipyrimidine bpm,[58] or carboxyester-tethered bpy[78]) allowed to increase the photo-oxidizing power of ruthenium polypyridine complexes and RQ was thus monitored (Fig. 3).

RQ with TEA or TEOA is often reported with iridium complexes as PS, even though its thermodynamics are not often very different from those of ruthenium systems,[24,69,70,85,89–92] underlying the importance of kinetics and bringing further evidence that even a careful study of redox potentials for SDs and PS* is not enough to discard an SD over another. Admittedly though, strongly photo-oxidizing PS (like rhenium complexes, Fig. 3) tends to allow RQ.[50,80]

Let us lay stress on the fact that the effect of changing the ratio MeCN/H_2O within the frame of H_2 photogeneration with TEA[74] and TEOA[84] as SDs was investigated and it was proven that the TCS worked better when the ratio MeCN/H_2O was increased. The improved solubility of TEA in the solvent mixture, modifications of the redox potentials and changes of dielectric constant of the medium were invoked to explain these observations. The action of SDs on the catalyst is not excluded but is irrelevant to the objectives of this review. All in all, those

experimental observations are very difficult to support the given complexity of a TCS.

TEA and TEOA are clearly able to provide two reductive equivalents for each photon absorbed by PS.[34,80] Importantly, quenching efficiencies are therefore theoretically equal to 2, but are more or less comprised between 0.1 and 0.5 at best. Loss in the overall efficiency is thought to be grounded in back electron transfer occurring within the geminate pair ([PS–SD] for RQ, [PS–SUB] for OQ).[35] This highlights again the importance of having TCSs with significant cage escape yields. Importantly, in the case of H_2 photogeneration from H^+, protons stemming from TEOA degradation are reported to be implied in H_2 evolution.[80]

The use of TEA vs. TEOA is difficult to rationalize. For instance, Bernhard et al. described the superiority of TEA over TEOA for their photocatalytic system for stability reasons.[71,94] Chang et al. observed an improved efficiency with TEA rather than TEOA,[69] whereas Zou et al. reported the improved reductive quenching rates with TEOA vs. TEA.[70] The conditions are nevertheless rather different from one experiment to another, depending on the requisites of each property (solubility, activity of the catalysts…) in the considered TCS. There is therefore no clear-cut consensus, TEA and TEOA having very similar properties. Let us mention nevertheless that alcohol groups in TEOA necessarily improve miscibility in water, and that a lower pK_a for TEOA than TEA allows working at lower pH.

Additionally, the amines are Lewis bases too, likely to play a role in some other steps of the intricate TCS's operation, and may for instance take part in the catalysis itself (coordination of the metal centers in a molecular catalyst, or participation in the overall mechanism[69,95]) or even poison nanoparticulate catalysts.[94]

Other aliphatic tertiary amines have been used: increasing the carbon atom number of the alkyl chain from ethyl to pentyl, passing from symmetrical NR_3 to unsymmetrical NR_2R', and altering the steric bulk was studied.[48,66] Like TEA and TEOA, irreversible oxidation of the amines leads to dealkylation (secondary amine) and aldehydes if water is present.[79] It is not the purpose of the present article to review the various results obtained with those SDs. Nevertheless, in the particular case of CO_2 photoreduction in CO and H_2 by $[Ru(bpy)_3]^{2+}$ and Co^{II} ions, NPr_3 (where Pr means *n*-propyl) was reported to be a better SD than TEA[66] and yet the great majority of nowadays TCSs are based on TEA rather than NPr_3.

At low pH, protonated amines cannot behave anymore as sacrificial donors. Some of them however with lower pK_a, can be used in a relatively acidic medium, for instance *N*-ethyl morpholine ($pK_a = 6.8$) or famous ethylenediaminetetraacetic acid (EDTA).[57,96,97] EDTA is a tertiary diamine with four carboxylic functions, and logically displays a series of 6 pK_a (0, 1.5, 2.0, 2.7, 6.1, 10.2).[55] Usually employed between pH 5 and pH 7, the so called "EDTA" is as a matter of fact utilized as its disodium salt. It is a two-electron donating sacrificial donor like TEA or TEOA[98,99] mostly utilized in an aqueous medium, and degradation of EDTA upon monoelectronic oxidation is well described.[99]

Like the previously reported amines, EDTA can be involved in reductive and oxidative quenching, depending on the oxidative power of PS*. We could consider that the
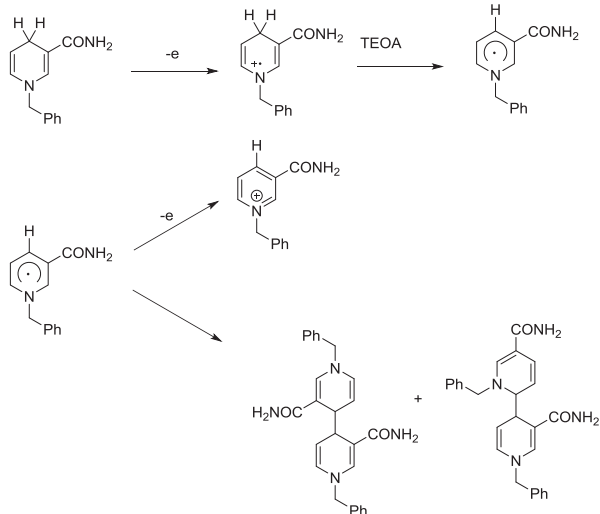

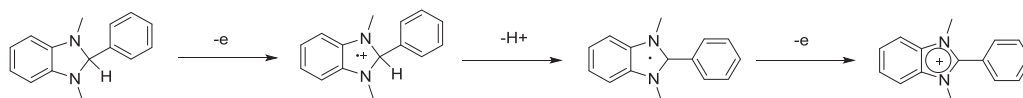**Fig. 4.** Mechanism of BNAH degradation upon monoelectronic oxidation.

Fig. 5. Mechanism of BIH degradation upon monoelectronic oxidation.

reaction of SDs with traditional $[Ru(bpy)_3]^{2+*}$ may serve as a diagnostic for the efficiency of reductive quenching in a TCS (this makes sense since $[Ru(bpy)_3]^{2+}$ is by far the most used chromophore in artificial photosynthesis). In that case, EDTA displays very high oxidation potentials for $[Ru(bpy)_3]^{2+*}$ to photo-oxidize it. Incidentally, chemical engineering of the ligands coordinating ruthenium (from bpy to bipyrazine or bipyrimidine, Fig. 3) allowed to increase the photo-oxidizing power of corresponding ruthenium complexes and reductive quenching was monitored. Like in the case of TEA or TEOA, transformation of monoreduced EDTA into a carbon centered reductive radical is very rapid and competes efficiently with charge recombination.[100]

Regarding the influence of pH, EDTA may operate at lower pH than TEA or TEOA as mentioned above. Efficient reductive quenching at pH as low as 5 can be found in the literature[34] or lower.[101] However, slower kinetics for reductive quenching are reported at lower pH (see for instance, PS = $[Ru(bpz)_3]^{2+}$, pH = 4.7).[98,99] Importantly, EDTA has excellent coordinating ability and has exhibited deleterious interactions with methylviologen, which are pH-dependent.[99]

Defying the usual, fair comments about the polluting and "useless" nature of most SDs, amine **1** (see Table 1) was reported as a renewable SD: after photo-induced oxidation and further degradation (implying photoproduced reduced carbon dioxide), the amine can be regenerated in its initial state by mere catalyzed hydrogenation, and can therefore be used again.[102]

Conclusively, picking an amine SD over another depends on many parameters. With the exception of pH considerations (which favor EDTA over TEA and TEOA for lower pH *vide supra*), the choice of a suitable SD among all amines presented in Table 1 is mostly empirical, depending on each property of the TCS and the overall reaction medium.

4. Aromatic amines as SDs

The latter point is clearly exemplified by the case of N,N-dimethylaniline (DMA, $E \approx 0.8$ V vs. SCE). Although well-known as a potent SD in the early literature,[62,103,104] DMA performed poorly in a H_2 photoproduction TCS by Bernhard et al. Fast charge recombination, energy transfer and

unfavorable interactions with the catalyst were invoked to rationalize this result.[24] On the other hand, Brewer et al. demonstrated the efficient photoproduction of H_2 from a heterotrinuclear triad ruthenium–rhenium photocatalyst with DMA as a sacrificial donor.[32,105,106] Different photocatalytic systems and different conditions (concentrations and composition of the solvent mixture) can easily account for those discrepancies, and underline again the importance of serendipitous experimental work in those intricate, multi-component artificial photosystems. Noteworthily, Brewer's system used highly concentrated DMA (between 1 and 3 M) in a water/DMF or water/MeCN mixture. High [SD] as mentioned above tends to favor RQ.

A number of other aromatic amines have been studied as potential sacrificial donors.[103,107–109] It was concluded that tertiary aromatic amines were superior to secondary and primary amines to achieve reductive quenching of the excited state of $[Ru(bpy)_3]^{2+}$ in MeCN. However, in the event of an RQ mechanism, the charge recombination within the geminate pair $[PS^-–SD^+]$ was often observed.[103,107,108,110] Hence dimethyl paratoluidine (DMT) displays very similar properties to DMA, with a 100 mV less anodic oxidation potential and was successfully used as the SD.[103,111] Advantageously, the irreversible transformation of DMT upon oxidation is well documented[112] (the $DMT^{•+}$ radical loses a proton to DMT resulting in a carbon centered radical which dimerizes) and leaves little room for counterproductive interactions (equations (4) and (5)).

5. 1-Benzyl-1,4-dihydronicotinamide BNAH as a SD

The biological reductant NADH is formed –for instance-during the photosynthetic process, *en route* towards CO_2 reduction into biomass. Reports of NADH employed as a SD in artificial photosystems can be found in the literature.[113,114] However, the manipulation of biological materials can be difficult. Inspired by the original NAD^+/NADH couple, an efficient model has been developed: BNA^+/BNAH (Table 1 and Fig. 4). Similar to NADH, BNAH stores 2 electrons which are released in the presence of a (photo)oxidant ($E(BNA^+$/BNAH) is often reported to be equal to = 0.57 V/SCE in acetonitrile,[115] but the irreversibility of

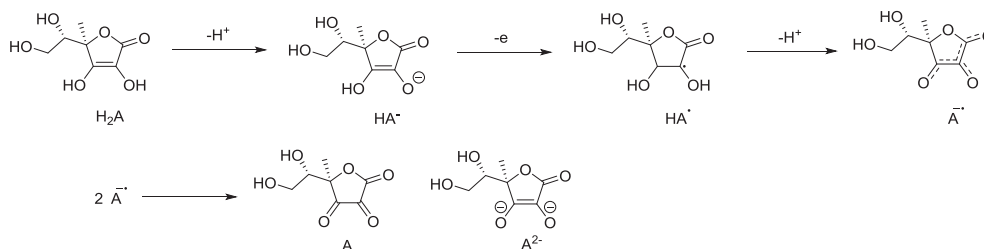**Fig. 6.** Mechanism of ascorbic acid degradation upon monoelectronic oxidation.

$$Ph_3P \xrightarrow{-e} Ph_3\overset{+\bullet}{P} \xrightarrow{H_2O} Ph_3\overset{\bullet}{P}\overset{\oplus}{-}OH_2 \xrightarrow[-H^+]{-e} Ph_3\overset{\oplus}{P}-OH \xrightarrow{-H^+} Ph_3P=O$$
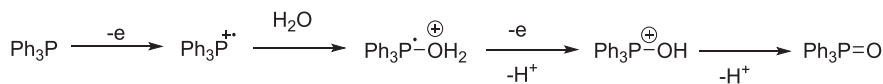
Fig. 7. Mechanism of degradation of PPh$_3$ upon monoelectronic oxidation.

the process makes it difficult to give such a precise value and it seems fairer to assign a 0.6–0.8 V vs. SCE range).[68] Importantly, a proton is released upon oxidation of BNAH into BNA$^+$, a feature that earned BNAH the reputation of a hydride donor.[115–117]

BNAH is an efficient SD which is particularly famous for achieving the reductive quenching of [Ru(bpy)$_3$]$^{2+*}$,[118] although the driving force for this process is rather weak, underlining the paramount importance of kinetics. This is a very significant appeal for BNAH as a SD because reduced [Ru(bpy)$_3$]$^{2+}$ is more reductive than excited [Ru(bpy)$_3$]$^{2+*}$ by more than 500 mV.[108] This strong reductive power and hydride donating character were used to reduce substrates such as olefins[118,119] and aromatic ketones.[120] Activation of CO$_2$ reduction catalysts (which are known to display quite negative onset reduction potentials)[121–123] is reported as well.[124–128] In this case, a typical TCS designed for CO$_2$ reduction with BNAH as the SD is set in a mixture of organic solvents such as DMF or MeCN with a base, typically TEOA. The mechanism is represented in Fig. 4. As mentioned above, BNAH can be a one- or two-electron donor.[56,120] The first electron transfer is photo-induced in nature, and yields BNAH$^{+\bullet}$ and PS$^-$ within the frame of a reductive quenching process. BNAH$^{+\bullet}$ being very acidic (pK$_a$ below 1)[56] can donate a proton, hence the importance of the base in the mixture. The absence of the latter (or any proton acceptor) entails a patent weakening of the quantum yield of the photochemical reaction.[127] A neutral radical BNA$^\bullet$ is then capable of providing another electron to the photosystem (in a dark process) resulting in the formation of a stable pyridinium species; or, it merely dimerizes into BNA$_2$,[127] which happens to be a potentially good SD too.[129] However, when the kinetics of the formation of BNA$_2$ are more favorable than the electron transfer from BNA$^\bullet$ to PS or SUB, the photo-induced cycle reaches the end and BNAH behaves as a one-electron donor.[126,129,130]

Mild variations of the molecular structure of BNAH were performed in order to shift the oxidation potential to less positive values[115,129] (electron donating groups on the benzyl moiety, such as methoxy) and consequently increase its reactivity with PS*, yielding improved photochemical yields.

6. 1,3-Dimethyl-2-phenylbenzimidazoline BIH

BIH (Fig. 5) shares common features with BNAH. Originally used to reduce organic compounds,[131] it was recently applied in a TCS for CO$_2$ photoreduction.[130] Like BNAH, BIH is a two electron, one proton source (hydride donor)[132] which can react as well with the excited state of [Ru(bpy)$_3$]$^{2+}$ as PS in a reductive quenching process, yielding PS$^-$ and oxidized BIH$^{+\bullet}$. BIH$^{+\bullet}$ is very acidic and loses a proton to a base in the medium. This step is important to limit back electron transfer between reduced PS$^-$ and BIH$^{+\bullet}$.[130] It is relevant to

note that deprotonation of BIH$^{•+}$ is 100 times faster than deprotonation of BNAH$^{•+}$ (data in DMF). Thus, besides knowing that E(BIH$^{•+}$/BIH) is more than 200 mV less anodic than E(BNAH$^{•+}$/BNAH), this suggests that BIH is a more potent SD than BNAH, at least in DMF. BI$^\bullet$ is besides a strong reductant (E(BI$^+$/BI$^\bullet$) = −1.5 V/SCE)[130,132] and can transfer a second electron (dark process) either to PS or SUB. BIH is thus a two-electron, one-proton releasing system, which requires BNAH in the presence of a base (such as TEOA).

7. Ascorbic acid

L-Ascorbic acid and related ascorbate ions are famous anti-oxidant natural preservative agents. As such, they are likely candidates for SDs and were successfully used in the 80s.[49,51,133] One particular appeal of ascorbic acid and related anions is its water solubility, and the possibility to work in a neutral and acidic medium, compared to traditional TEA and TEOA which require basic conditions. By ascorbate, one mostly means monodeprotonated ascorbic acid. If H$_2$A designates plain ascorbic acid, HA$^-$ is indeed the predominant form within the usual pH window for TCSs (between 5 and 9, pK$_a$s 4.0 and 11.3)[134]. HA$^-$ is reported to be implied in both reductive and oxidative quenching processes.

Mechanistically speaking, HA$^-$ is first oxidized to HA$^\bullet$ (E ≈ 0.5 V/SCE),[134] which is a much stronger acid than HA$^{-51,135}$ and then quickly dissociates into A$^{•-}$ and H$^+$.[136] A$^{•-}$ disproportionates into dehydroascorbic acid A and ascorbate A^{2-} (Fig. 6).[27,50–52,137] The couple A/A$^{•-}$ exhibits a potential of roughly −0.3 V/SCE[134] and it is therefore very unlikely that A$^{•-}$ may further reduce any species in the medium (PS or SUB). Besides, E(A/HA$^-$) lies around 0.28 V, in other words A is a mild oxidant thermodynamically able to oxidize PS$^-$ or reduced SUB (charge recombination, equations (4) and (5)), thus counter-productively interfering within the photochemical cycle.[50,134,138] Moreover, HA$^\bullet$ was reported to merely recombine with PS$^-$ where PS stands for the classic [Ru(bpy)$_3$]$^{2+}$ chromophore and therefore was considered as non-sacrificial, albeit being an efficient quencher of PS*.[82] As a matter of fact, the chemical reversibility of the couple A/H$_2$A was mentioned by Creutz,[134] and that justifies the use of ascorbate HA$^-$ rather than ascorbic acid H$_2$A for a TCS.

8. Carboxylic acids

Lactic acid is intensively used as a sacrificial donor in TCSs involving particularly quantum dots as PS and H$_2$ photoproduction or organic substrates reduction, in the presence of water.[139–141]

The redox properties of oxalate naturally lead to attempts to use it as a sacrificial donor. The one-electron reduction of oxalate entails the formation of gaseous CO$_2$

leaving the medium and very reductive radical $CO_2^{\bullet-}$. The double advantage of oxalate oxidation is the evolution of CO_2 setting at naught the risks of charge recombination,[82] and the highly reductive power of $CO_2^{\bullet-}$ ($E(CO_2/CO_2^{\bullet-}) < -2$ V) which is capable of further reducing substrates (PS, SUB…) in a dark process.[142]

$$C_2O_4{}^{2-} \xrightarrow{-e} {}^{-\bullet}CO_2 + CO_2$$
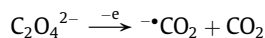
Oxalates (pK_a 1.2 and 4.2)[82] can be employed in water, over a wide range of pH from acidic pH (3) to basic (11).[58,82,101] Nevertheless, its rather high oxidation potential imposes conditions on the reductive power of PS* (high $E(PS^*/PS^-)$ for reductive quenching). No quenching of the excited state of PS* was monitored for instance in the case of classic $[Ru(bpy)_3]^{2+}$;[143] more photo-oxidizing $[Ru(bpz)_3]^{2+}$ (Fig. 3) was necessary.[58] Additionally, the anionic nature of oxalates came in very handy to form ionic pairs with cationic acceptors such as methylviologen, and photolysis of the latter system in UV efficiently leading to charge separation.[142]

9. Thiols

Thiols and thiolates are very relevant monoelectronic sacrificial donors because of their low oxidation potential and the irreversibility of the oxidation process yielding inert disulfide bridged dimers.[144,145] Reports of chromophore emission quenching by cysteine (and other amino acids) date back to late 1970s.[146]

$$RSH \underset{-H^+}{\overset{-e}{\rightarrow}} RS^\bullet$$

$$2RS^\bullet \rightarrow RSSR$$
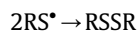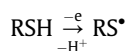
Cysteine was for instance utilized in a number of TCSs,[35,82,147,148] formation of the radical $Cys^\bullet$ (and concomitant deprotonation) occurred first, followed by dimerization. In another contribution,[82] cysteine and various alkylthiols were involved in reductive quenching of $[Ru(bpy)_3]^{2+}$ excited state in water. Those SDs singled out among other donors, thanks to their reducing ability which was maintained even at lower pH. At higher pH (12), RS^- is predominant over RSH (e.g., pK_a (benz-SH/benz-S$^-$ = 9.4) and it was reported that oxidized thiolates displayed very low cage escape yields yielding to cumbersome charge recombination within the geminate pair PS^-/SD^+. This fact was justified by electrostatic attractive interactions between $[Ru(bpy)_3]^{2+}$ and $RSSR^{\bullet-}$, formed by the reaction of RS^- and photoproduced $RS^\bullet$. $RSSR^{\bullet-}$ is furthermore a rather good reductant ($E = 0.65$ V vs. ENH)[145] which can easily react with PS^-. Importantly, R–S$^-$ can play the role of ligands, or nucleophiles which could interfere with the smooth operation of a TCS.

Using thiols and thiolates as SD in organic medium is possible too. Reductive quenching of the excited state of $[Ru(bpy)_3]^{2+}$ and subsequent accumulation of $[Ru(bpy)_3]^{2+}$ was observed in acetonitrile in presence of benzylthiolate (Table 1, benz-S$^-$).[149] The anodic peak potential for benzylthiolate $E(benz-S^-/bens-S^\bullet)$ is -0.1 V vs. SCE, therefore

even low photo-oxidizing systems (i.e. $E(PS^*/PS^-)$ weakly positive) are susceptible to react with benz-S$^-$, making the latter a candidate of choice for reductive quenching. Once again, premium was put on the inertness of dimer (benz-S)$_2$, which reduction potential was below -2 V vs SCE.

Within the same frame, diethyldithiocarbamate (Table 1, dtc$^-$, $E_{ox} = 0.05$ V vs. SCE), ethylxanthate (xan$^-$, $E_{ox} = 0.21$ V vs. SCE) and p-methoxydithiobenzoate (dtb$^-$, $E_{ox} = 0.19$ V vs. SCE) were studied for reductive quenching with $[Ru(bpy)_3]^{2+*}$.[54] Those deprotonated carbodithioic acids tend to dimerize like thiolates when oxidized. It was proven that the reaction of photoproduced $[Ru(bpy)]^+$ with a reducible substrate (such as anthraquinone) was quicker than the charge recombination involving dtc$_2$ dimers.

A number of quenching experiments have been performed with other sacrificial donors, such as triphenylphosphine in an aqueous organic medium.[150] The monoelectronic oxidation of PPh$_3$ ($E_{ox} = 0.98$ V vs. SCE)[151] generates a radical which decomposes in the well-known inert triphenylphosphine oxide. The mechanism is represented in Fig. 7.

One notices that PPh$_3$, like tertiary amines above, is a two-electron donor triggered by monoelectronic photo-induced transfer. One PPh$_3$ molecule can therefore theoretically participate in two reduction processes sparked off by one photon.[152]

10. Miscellaneous

Other sacrificial donors can be found in the literature. For example amino acids,[155] and phenols[156] which are hazardous pollutants whose photo-induced degradation is considered a positive boon. Besides, this is somehow reminiscent of the famous action of Tyr$_Z$ in photosystem II,[13] although the latter is a redox relay and not a sacrificial reagent. The use of sugars (such as glucose or fructose) in basic or acid aqueous media[144,157,158] is reported too. An impressive list of organic molecules as potential SDs is available in the articles of Krasna et al.,[144,157] where hydrogen production from water using solar light is attempted in a TCS. Only few SDs could assist H$_2$ photogeneration.

11. Conclusion

Apart from the redox potential considerations presented in part 1, knowing though the difficulties related to accurately defining a potential for an irreversible step, the choice of an SD over another is not easy to rationalize. Accordingly, aliphatic and aromatic amines are well ahead of all other sacrificial donors in the field of artificial photosynthesis, from the sheer experimental point of view. As mentioned above, the properties of SD candidates may depend on the pH and nature of the medium, and in three-component systems the mixture can quickly become painfully complex (because in particular changing one parameter such as the solvent will have drastic effects on PS, SUB and SD altogether). To develop a working TCS and to optimize are therefore largely an empirical work. Nevertheless, trends can be observed. In particular, hydrophobic amines seem to necessitate the presence of an organic solvent, without nonetheless excluding the

presence of water which is necessary to achieve irreversible degradation of the photo-produced radicals. The choice of an SD is likewise conditioned by pH and environment. Oxalates or ascorbates are more adapted to an aqueous, possibly acidic medium. The ambivalence of TEA and TEOA may precisely be the reason why they are so popular sacrificial donors.

However, the era of SD will reach an end, since a typical TCS is admittedly not a viable approach for large scale and economical production of solar fuels. Such TCSs are accordingly only proofs of concept and can be seen as experimental laboratory-scale tools, not futuristic solar fuel generators. Using water as the SD, just like photosynthetic organisms, would lead to the proverbial water splitting: generating hydrogen and oxygen gas with nothing else but water and light would put an end to the energy crisis and pollution. But the efficient oxidation of water (into molecular oxygen) and the control of all the side reactions is a very difficult task. An interesting alternative is the elaboration of photoelectrochemical devices (PEC), where sacrificial donors or acceptors are replaced by biased electrodes.[7,37,159,160,22,36,38,161] Even more relevant are the tandem devices where the bias is no more necessary.[162–164] As mentioned before though, TCSs with artificial SDs will be necessary to design the efficient PS and catalysts which will be implemented in a PEC, justifying why SDs still have a comfortable few decades ahead.

Acknowledgments

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