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Photochemical & Photobiological Sciences

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Antimony porphyrins as red-light powered photocatalysts for solar fuel production from halide solutions in the presence of air

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Halide ions (X⁻) as cheap and abundant electron donors are oxidized with simulated sunlight in a photocatalytic reaction based on robust antimony porphyrins acting as red-light harvesting multielectron transfer sensitizers. Besides halogen formation (X_2/X_3^-) this solar energy storing process under certain conditions also accumulates hydrogen peroxide (H_2O_2) as a second energy-rich compound.

A major drawback of most systems proposed to date for photochemical energy conversion and artificial photosynthesis is the compulsory addition of a large excess of so-called "sacrificial" electron donors other than water to supply the reduction equivalents needed for solar fuel generation.[1] In terms of atom economy, this unfavourable situation, however, may significantly change if the primary electron donor itself becomes directly incorporated into a more useful reaction sequence. This strategy can open new pathways for the solar chemical production of valuable oxidation products (fine chemicals)[2] or also provide a straightforward method to form additional energy-rich compounds (fuels) instead of merely producing irreversible decomposition products (waste). As an example for such an approach, here we describe simple photocatalytic systems able to drive energetically uphill redox processes for the generation of halogen species and other energy-rich compounds such as H_2O_2 as solar fuels.

For this purpose, long-term stable main group metalloporphyrin complexes were selected as red-light harvesting chromophores.[3] Antimony porphyrins are excellent multielectron transfer sensitizers for photocatalysis and artificial photosynthesis.[3,4] Their lowest excited singlet states are characterized by an exceptionally high oxidation power (1.8-1.9 V vs. NHE) suitable for incorporating even water as an electron donor[5] which has been supported by [18]O isotope labelling experiments. In the present work, catalytic two-electron redox cycles based on the efficient reductive quenching of photoexcited antimony porphyrins by halide donors[6] are described.

Broader context

Halide salts from brine or seawater as well as O_2 from air are earth-abundant resources which can be exploited for artificial photosynthetic production of renewable fuels. In the presence of a suitable light-harvesting photocatalyst under ambient conditions the simultaneous formation of halogens and hydrogen peroxide as energy carriers is feasible upon exposure to sunlight. The chemically stored solar energy could then be converted back into electricity on demand using fuel cells or redox flow batteries. Such an approach might help to create low-cost devices for the direct photochemical conversion and storage of solar energy.

The stuctures of the photocatalysts **1-3** in their high-valent Sb(V) resting form are displayed in Figure 1. The structures and properties of the corresponding low-valent Sb(III) species carrying no axial ligands have already been described in our earlier studies on such multielectron transfer sensitizers.[7] Further details on compound synthesis, analytical data and spectroscopic features are reported in the supplementary information.[†]

1: $R_1 =$ (phenyl)
$R_2 = H$

2: $R_1 =$ (phenyl-OCH₃)
$R_2 = H$

3: $R_1 = H$
$R_2 = -CH_2CH_3$

$M = Sb$ $X = OH$
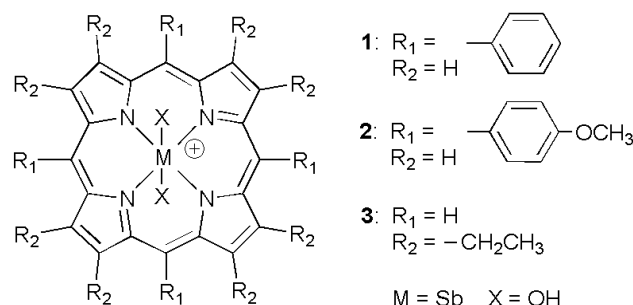
Fig. 1 Scheme showing central atom (M), axial ligands (X) and substituent pattern (R) of main group metalloporphyrins **1-3** studied as photosensitizers.

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Results and discussion

The antimony porphyrin complexes **1**-**3** are fluorescent in solution with quantum yields between 0.01 and 0.04 and excited singlet state lifetimes in the 1.0-1.5 ns range (Table S2).[†] In frozen solvent glass matrix at 77 K an additional ligand centered phosphorescence occurs in the far-red spectral region (Table S3, Fig. S4).[†] For complex **1**, it was shown already in a previous study that the lowest excited excited singlet state is efficiently quenched by pseudohalide and halide anions including chloride.[6] In acetonitrile solution this reductive quenching process occurs in the 100 ps timescale with electron transfer rate constants reaching high values up to 10^{10} s^{-1} depending on the oxidation potential of the quencher added. Furthermore, it was found that in competition with back electron transfer permanent redox products can accumulate upon irradiation of **1** in the presence of halides (Fig. S5).[†]

We decided to further investigate these earlier observations also with other antimony porphyrin complexes and to study the capability of photocatalytic product formation under long-wavelength irradiation. It turned out that in acetonitrile solution saturated with air containing the photocatalysts **1**,**2** or **3** a photoredox reaction takes place where halide ions X$^-$ such as iodide or bromide are oxidized to the corresponding trihalide anions X$_3^-$ (Fig. 2).
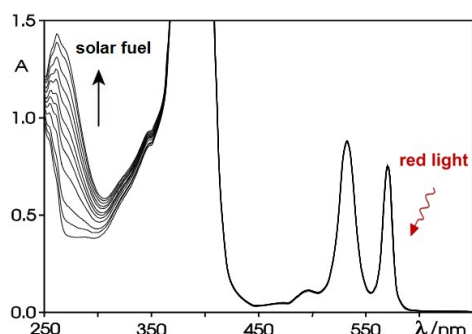
Fig. 2 Photocatalytic accumulation of tribromide (λ_{max} = 269 nm)[6] during Q-band excitation of 9.3×10^{-5} M antimony porphyrin **3** in acetonitrile solution containing 5.0×10^{-2} M Bu$_4$NBr (air, 298K).

As recently pointed out by Meyer and coworkers,[8] this type of light-driven two-electron transfer reactivity leading to the formation of covalent X-X bonds is an exceptional example for studying the direct conversion and chemical storage of solar energy. In acetonitrile solution, the photooxidation of halides mediated by compounds **1**, **2** or **3** is coupled to the intermediate formation of the corresponding low-valent Sb(III) porhyrin complexes (Fig S5).[†] These two-electron reduced forms of the photocatalysts are well-known to be readily re-oxidized in the presence of O$_2$ and visible light forming hydrogen peroxide as a second energy rich photoproduct.[7] The initial quantum yields for tribromide formation with 546 nm monochromatic light were determined as φ = 0.04 (**1**), 0.03 (**2**) and 0.10 (**3**), respectively. For these measurements, the

complex concentrations were such as to have essentially complete light absorption and the total amount of photolysis was limited to less than 5% to avoid any secondary processes. Photocatalytic product accumulation according to the overall reaction sequence shown in Figure 3, however, was found to proceed only with net quantum yields in the order of φ = 0.001, which can be attributed to the limiting quantum efficiency of the peroxide forming partial reaction in the long-wavelength visible spectral range.[7] Furthermore, product consuming cross reactions such as re-oxidation of the low-valent antimony porphyrins by bromine followed by hydrolysis and other secondary reactions between accumulated peroxide and halogens are feasible.[7,9]
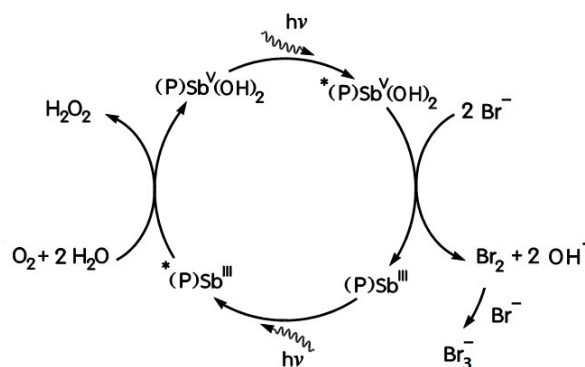
Fig. 3 Solar energy storing photoredox cycle of antimony porphyrins **1**-**3** leading to halide oxidation and dioxygen reduction.

Nevertheless, the light-powered formation of Br$_3^-$ and H$_2$O$_2$ according to the reaction scheme shown in Fig. 3 can be considered as a model reaction for an endergonic solar energy storing redox process. While visible light driven hydrogen peroxide generation is an interesting observation in its own right, the potential role of H$_2$O$_2$ as a solar fuel and its back-conversion into electricity using fuel cells has recently attracted increasing attention.[10] Together with the formation of the energy-rich halogen bond,[8] the two-electron redox cycle based on bromide and oxygen (Fig. 3) is able to store $\Delta G°$ = 221.4 kJ/mol under standard conditions. Assuming the requirement of two ´red´ photons with a threshold wavelength of about 620 nm (2 × 193 kJ/mol) to drive the process with **2** as a photocatalyst, a theoretical maximum efficiency of conversion of about 57 % can be estimated, which even exceeds the corresponding values obtained for natural photosynthetic carbon fixation.[11] In combination with the moderate quantum yields reached under operating conditions, however, only a very limited solar energy conversion efficiency of no more than 0.1% remains in reality, which nevertheless is again quite similar to the average performance of natural photosynthesis creating biomass.[11]

The photocatalytic oxidation of halide anions was also studied in aqueous medium in the presence of air and simulated sunlight. Since the antimony porphyrins **1**-**3** display only a very

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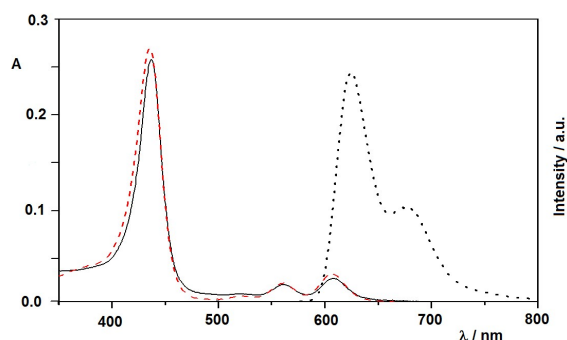
Fig. 4 Absorption (——), fluorescence ($\cdots$) and excitation spectra (– – –) of antimony tetramethoxyphenylporphyrin complex **2** in water containing the non-ionic surfactant Triton X-100 above the critical micelle concentration.[†]

limited water solubility, we started to investigate the spectroscopic and photochemical properties of these photocatalysts in microheterogeneous micellar systems. The electronic spectra of **2** in aqueous Triton X-100 medium are shown in Fig. 4. It turned out that all photophysical properties of **2** in the aqueous micellar environment essentially resemble the regular features of this compound in organic solvents such as acetonitrile or ethanol (see supporting information).[†] An intensely green coloured solution was obtained which could be readily employed for all photocatalytic experiments with aqueous halide mixtures. In the absence of added halide salts, a strong red emission signal is observed. Excitation spectra for this fluorescence from the lowest excited singlet state of **2**, which displays a lifetime of $\tau_F = 1.1$ ns, perfectly coincide with the Soret- and Q-band absorption pattern of the complex (Fig. 4). Upon addition of KBr salt to this microheterogeneous system, a partial fluorescence quenching of **2** is observed. Linear relationships of the relative luminescence quantum yields or lifetimes are obtained with increasing bromide concentrations up to 0.3 M in agreement with the Stern-Volmer kinetic model. At higher bromide concentrations, a beginning downward curvature of the Stern-Volmer plots is observed which most probably indicates the presence of exchange equilibria with the axial hydroxyl ligands of **2**. A quite similar behaviour has been reported before for the fluorescence quenching of **1** with chloride salts in organic solvents.[6] The rate constant for dynamic bimolecular quenching of **2** by bromide ions in water containing Triton X-100 was calculated as $k_q = 5 \times 10^8$ M^{-1} s^{-1}. This value is significantly smaller than typical values measured for antimony porphyrins such as **1** in acetonitrile solution,[6] but the process is still about hundred times more efficient than the quenching of benchmark photosensitizers such as [Ru(bpy)$_3$]$^{2+}$ by iodide in aqueous solution.[12]

Encouraged by these results, we decided to study the luminescence behaviour and the photoreactivity of antimony porphyrin **2** also in a heterogeneous system where the light-harvesting catalyst is immobilized on a support surface and combined with a supernatant of the substrate solution. Such

an approach not only allows to work with **2** in neat water as a solvent, but also facilitates the possibility of catalyst recycling and simplifies detection and separation of all photoproducts formed.[13] For this purpose, the metalloporphyrin complex was covalently attached to the surface of silica gel, which resulted in a bright green solid material containing 0.1wt% of **2** (see supporting information).[†] Spectroscopic experiments carried out at 298K and 77K confirm that an intact and almost unperturbed photocatalyst is present on the SiO$_2$ surface (Fig S7, S8).[†] It could also be demonstrated that the immobilized antimony porphyrin **2** is able to oxidize halide ions when exposed to simulated sunlight, red light or diffuse daylight. As a first example of such a reaction, the accumulation of potassium triiodide in water is shown in Fig. 5 and Fig. 6 below. Product formation was quantitatively followed by UV-Vis detection at 352 nm ($\varepsilon = 24600$ M^{-1} cm^{-1}) and 400 nm ($\varepsilon = 6196$ M^{-1} cm^{-1}).[14] Additional control experiments were carried out to ensure that product formation with visible light ($\lambda_{irr} > 590$ nm) only occurs in the presence of the photocatalyst (Fig. S10).[†]
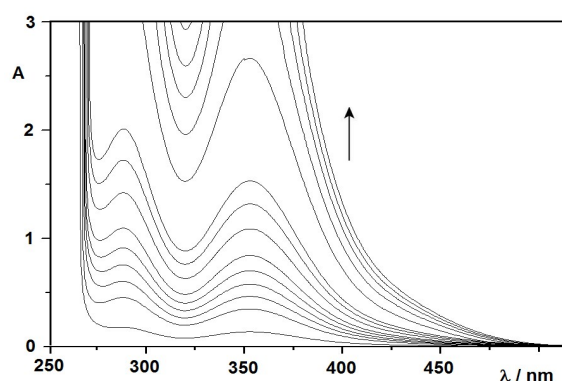
Fig. 5 Photocatalytic oxidation of an aerobic aqueous solution of KI (1M) sensitized by 30 mg of SiO$_2$ carrying 0.1 wt% **2** (simulated sunlight, AM 1.5, one sun).[†] Irradiation times shown in the plot are t = 5, 10, 15, 20, 25, 30, 40, 50, 60, 120, 180, 240, 300 and 360 min.
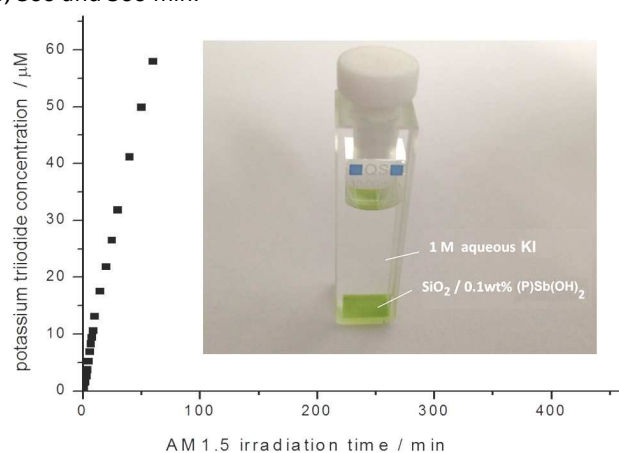
Fig. 6 Initial rate of solar photocatalytic triiodide formation and picture of a freshly prepared sample cuvette before exposure to simulated sunlight with t = 0 - 60 min irradiation times under AM 1.5 conditions. All concentrations are such as those reported in Fig. 5.

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After several hours of irradtiation in the solar simulator the rate of iodide oxidation gradually diminishes (Fig S11).[†] Exchanging the triiodide solution formed within the first 6 h of sunlight exposure against a fresh substrate solution containing 1M KI, however, results in recurrent product accumulation without any detectable loss of activity (80 ± 2 μM h^{-1} initial rate under these conditions). This simple procedure of photocatalyst recycling allows a convenient harvesting of the halogen products formed and could thus be easily coupled to fuel cell applications based on the reversible two-electron redox couple I$^-$/I$_3^-$ in aqueous solution ($E°$ = +0.54 V vs. NHE).[8] Assuming that all active sites in the silica gel supported catalyst containing 0.1 wt% of **2** are accessible and lead to photoproduct formation, an initial turnover frequency of TOF = 6.7 h^{-1} and a turnover number of TON = 19 for the first 6 hours of irradiation under AM 1.5 conditions can be calculated.

In contrast to the photoreactions of antimony porphyrins observed in halide salt containing acetonitrile solution (Fig. 2), the corresponding reactions of **2** in aqueous medium did not lead to a stoichiometric accumulation of hydrogen peroxide (Fig. 3). Several reasons may account for this observation. While decomposition by direct photolysis[15] of the aqueous peroxide solution can be excluded for all of our experiments, a catalytic disproportionation of H_2O_2 into water and dioxygen in the presence of halide halogen mixtures has to be considered. For example it is well-known that H_2O_2 can oxidize iodide ions to iodine in acid solution, reduce iodine to iodide ion in alkaline solution and is catalytically decomposed under intermediate conditions.[16] Moreover, a completely different possibility explaining the lack of peroxide accumulation in aqueous solution should also be discussed here. Peroxide formation as shown in Fig. 3 requires metal-centered photoreduction of the catalyst with an intermediate formation of low-valent Sb(III) species[7] (Fig. S5).[†]. Since the photoreduction pathways of antimony porphyrins such as **1** have been found to be switched in different solvents,[5] in case of the reactions studied with complex **2** in water a ligand-centered reduction process of the photocatalyst may result from reductive quenching by halide anions. The corresponding ring reduced metalloporphyrins formed are known to be powerful reductants for the catalytic evolution of dihydrogen.[17] Indeed, no spectroscopic evidence for the peroxide generating Sb(III) species was found in all experiments carried out with complex **2** in water. Thus, the electrons extracted from the halide substrate and intermediately stored in the porphyrin ligand could lead to the formation of H_2 instead of H_2O_2 upon irradiation with simulated sunlight to close the two-electron redox cycle for further halide oxidation. Photocatalytic solar energy conversion by HX splitting[18] into H_2 and halogens X_2 is an attractive alternative to artificial photosynthetic water splitting. At the current stage, further more detailed investigations, however, are required to confirm such an additional possibility of solar fuel generation for the antimony porphyrin systems **1**-**3** described here using halides as cheap and abundant electron donors.

Conclusions

Antimony porphyrins are robust photocatalysts acting as strongly oxidizing reagents under red-light or sunlight exposure. Their lowest excited singlet states are efficiently quenched by halide anions (iodide, bromide and chloride). The compounds can be employed as light-harvesting sensitizers in organic solvents, in aqueous micellar medium and also when immobilized on the surface of porous silica gel. Halide photooxidation products are readily formed and accumulated with these non-precious metal catalysts under ambient conditions. Different types of net two-electron photoredox cycles for solar energy conversion and storage are feasible.

Acknowledgements

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Graphical Abstract
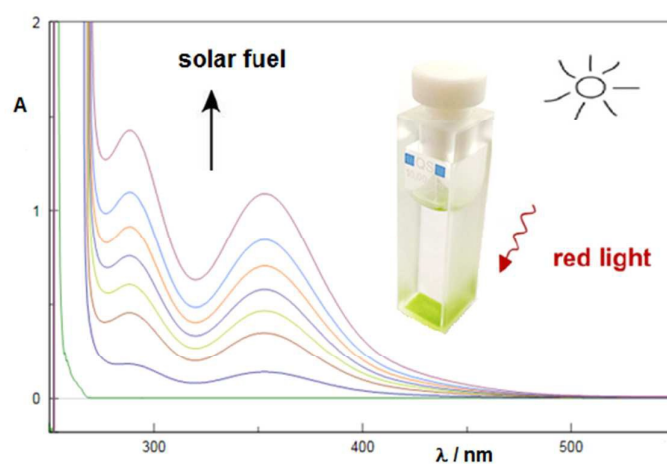
Stable light-harvesting sensitizers for the two-electron oxidation of halide ions are reported. Photocatalysis is studied in solution, in aqueous micellar medium and with surface immobilized samples for convenient photocatalyst recycling.