

Metalloporphyrins as Photocatalysts for Driving Endergonic Reactions, Exemplified by Bromide to Bromine Conversion**

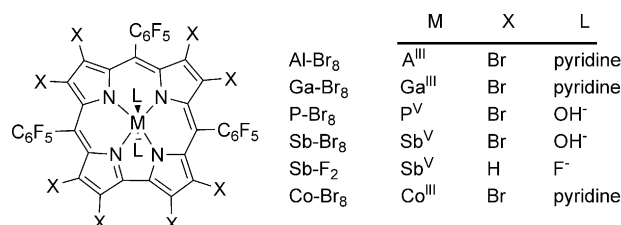
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Abstract: Photochemical oxidation of halide anions by visible light has been suggested for solar energy conversion processes. Post-transition metalloporphyrins are now disclosed as very efficient catalysts for the photoinduced transformation of bromide to bromine. The advantages of these catalysts are that they are very stable under the reaction conditions and that the energy levels of the oxidizing HOMO and the reducing LUMO are easily tuned. Insights into the mechanism of action obtained in this work is predicted to be very useful for the design of other systems that rely on photocatalysis for driving endergonic reactions.

There may be no doubt that the future of modern society depends on our ability to use affordable and clean energy for driving endergonic reactions. The best-known and also most intensively addressed example is water splitting to its elements hydrogen and oxygen, which would resolve all global energy problems if it could be initiated by sunlight as the sole energy source.^[1] Since photocatalytic water splitting is a very complicated process, simpler light-driven chemical transformations must be considered as well. One of them is the aerobic oxidation of bromide to bromine for the energy-free formation of the much more valuable product.^[2] This may be illustrated by the advantages of H₂/Br₂ fuel cells: 1) up to 90 % of the chemical energy stored in the reactants in converted to electricity, as opposed to only about 50 % for state-of-the-art hydrogen/air fuel cells; and 2) the electric-to-electric efficiency approaches 80 % compared to 40 % for hydrogen/air and 35 % for most power generators that are fired by fossil fuels.^[3] A more straightforward relevance is that the main industrial process for the production of bromine still relies on the oxidation of bromide by chlorine, which is quite obscure from the chemical (as opposed to business) point of view.^[4] Hydrogen peroxide could be used as a green oxidant, as it produces only water as side product, but that is still far from perfect.^[5] Considering photocatalysis, porphyrins come into mind since they are versatile photosensitizers and their photoexcited state is efficiently quenched by halides.^[6] Based on some very encouraging features disclosed for metalloporphyrins in completely different light-driven applications,^[7–11] we have decided to check if they may be used as photosensitizers that are able to catalyze the aerobic oxidation of bromide to bromine using only sunlight.

Corrolo complexes with post-transition elements such as aluminum,^[7] gallium,^[8] antimony,^[9] and most recently also phosphorous^[10] were lately disclosed as good photo-sensitizers of oxygen, a property that may be amplified upon bromination of the macrocycle.^[7a,11] The initial examination was performed with the 5,10,15-tris(pentafluorophenyl)corrolo difluoroantimony(V) complex, Sb-F₂ (Scheme 1), because it strongly absorbs light in the UV/visible region (Figure 1) and has a very high oxidation potential (1.47 V vs. Ag/AgCl).^[9a] This suggested to us that Sb-F₂ could be a suitable catalyst for the photoinduced transformation of bromide to bromine.

The initial experiment was performed on an aerobic acetonitrile solution composed of trifluoroacetic acid (TFA, 0.2 M), tetrabutylammonium bromide (TBABr, 0.1 M) and Sb-F₂ (25 μM), irradiated by a “sunlight” lamp (250 W, Osram) located 10 cm from the reaction mixture vessel. Bromine was clearly produced under these conditions and the amount of it was quantified by the UV/Vis absorbance of Br₃[−] (λ_{max} (ε, L mol^{−1} cm^{−1}) = 269 nm (55 000), in acetonitrile).^[6a,12] The catalytic turnover frequency (TOF) for bromine formation was determined as 35 h^{−1}. To understand why the TOF is not



Scheme 1. The chemical structures of metalloporphyrins mentioned in the text.

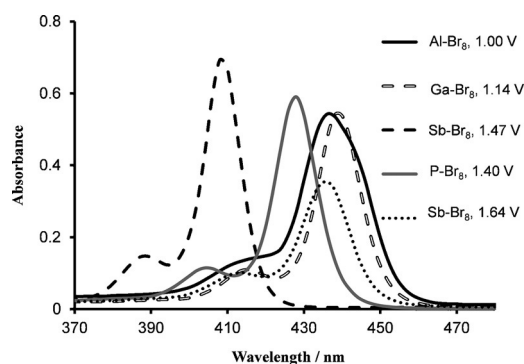


Figure 1. The electronic spectra of all examined catalysts in acetonitrile (2.5 μM each) and their redox potentials (V vs. Ag/AgCl, in 0.1 M TBAP/CH₃CN).

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larger, both the intensity and the spectrum of the applied lamp were examined. This revealed that while the total light intensity reaching the reaction vessel is very high (150 mW cm^{-2}), it is very low at 400–450 nm where the absorbance of the catalyst is maximal. We thus turned our attention to the use of a blue-light-emitting diode (LED, $\lambda_{\text{max(emit)}} = 450 \text{ nm}$, power = 150 mW cm^{-2}) which has the advantage of emitting more relevant wavelengths, not emitting warm radiation that heats the solution, and also of consuming much less energy. Figure 2 shows the evolution of bromine during LED irradiation, revealing a TOF of 72 h^{-1} , that is, twice as large as with the sunlight lamp. Aiming towards further improvement, we decided to prepare the brominated antimony corrole, Sb-Br₈. The rationale was that bromination would induce shifts of the Soret band of the catalyst to longer wavelengths, where the LED lamp emits most, and also of the redox process to more positive potential.^[13] Direct bromination of Sb-F₂ by molecular bromine provided a mixture of products, but metalation of the already brominated corrole ($\text{H}_3(\text{tpfc-Br}_8)$, 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris-pentafluorophenylcorrole) by SbCl₃ afforded Sb^{III}-Br₈. This complex suffered from demetalation during attempted column chromatography purifications, which was resolved by oxidation of non-purified Sb^{III}-Br₈ by iodosylbenzene to the stable enough for purification Sb^V-Br₈. The differences between Sb^{III}-Br₈ and Sb^V-Br₈ in terms of stability regarding demetalation is a consequence of the larger ionic radius of Sb^{III}, which is not well accommodated by the N4 coordination core of the corrole.^[14] The abovementioned hypothesis was fully fulfilled: the Soret band maximum shifted from 408 nm in Sb-F₂ to 436 nm in Sb-Br₈ (Figure 1), and the oxidation potential of the latter was determined to be very positive (1.64 V). Sb-Br₈ could how-

ever not be used as catalyst for the photooxidation of bromide since it was demetalated by hydrobromic acid.

Based on the above, the attention was driven to the previously synthesized Al-Br₈^[7a] and Ga-Br₈^[11] and to the analogous phosphorous corrole. The latter was expected to have photophysical properties that are similar to Sb-Br₈, but of higher stability regarding demetalation. Treatment of $\text{H}_3(\text{tpfc-Br}_8)$ by PCl₃ at RT and subsequent column chromatography allowed the isolation of the bis-hydroxophosphorus(V) corrole P-Br₈ in high yield. The ionic radius of P^V is small and apparently fits perfectly into the corrole cavity, which is the reason for its stability to acid, the reaction conditions, and the absence of any indications for phosphorous(III) corrole.^[10c,d] The electronic spectra and the redox potentials of all complexes were determined for evaluating their suitability as photosensitizers for work with the blue LED lamp and for acquiring information about the energies of their HOMO and LUMO orbitals. The λ_{max} (Soret band) of Sb-F₂, P-Br₈, Al-Br₈, and Ga-Br₈ are 408, 428, 437, and 438 nm, respectively (Figure 1), suggesting that Ga-Br₈ would be best suited for the applied LED lamp. The redox potentials were determined to be in the order of Sb-F₂ (1.47 V) > P-Br₈ (1.40 V) > Ga-Br₈ (1.14 V) > Al-Br₈ (1.0 V), implying that the photoexcited state of all of them are high enough to oxidize bromide. The results obtained under the same conditions used for the antimony corrole Sb-F₂ produced Br₂ with TOFs of 93 h^{-1} , 290 h^{-1} , and 341 h^{-1} with P-Br₈, Al-Br₈, and Ga-Br₈ as catalysts, respectively (Figure 2a).

All complexes remained stable during the irradiation, that is, there were no bleaching or structural changes (see below). Thus, the catalytic efficiency for photooxidation of bromide by the post-transition metalcorroles is Ga-Br₈ > Al-Br₈ > P-Br₈ > Sb-F₂, which led to the following conclusions: 1) the metalcorroles whose absorption is better matched with the wavelength emitted by the LED light perform better; and 2) the complexes that have more positive redox potentials are more efficient catalysts. The latter variable comes in effect in the comparison between Ga-Br₈ and Al-Br₈. Their electronic spectra are practically identical, but the performance of Ga-Br₈ is better because its oxidation potential is higher than that of Al-Br₈. Control experiments showed that the catalytic reaction requires light, oxygen, acid, and a photosensitizing catalyst. No significant amounts of tribromide were formed when the latter was replaced by the transition-metal analogue Co-Br₈^[15] or when the reactions were performed under nitrogen. Irradiation of a nitrogen-purged TBABr/TFA/Sb-F₂ solution led to an about 50% catalyst bleaching and partial conversion into the antimony(III) corrole.

Taken together, the plausible mechanism for catalysis is as follows: visible light irradiation of the photosensitizer creates a hole in its HOMO that oxidizes the bromide, while the electron in the half-filled LUMO is donated to oxygen (Scheme 2). The redox potential of the catalysts provides information about the oxidizing and reducing powers, since the electrochemical HOMO–LUMO gap of corroles is quite constant (about 2.1 V).^[16] A more positive redox potential of the photosensitizer leads to a more oxidizing HOMO and a less reducing LUMO, features that are tunable by changing

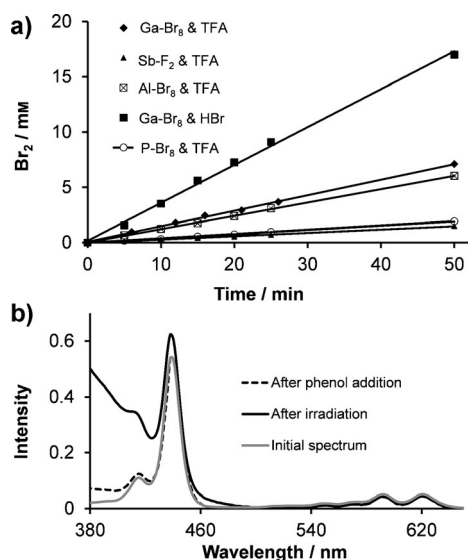
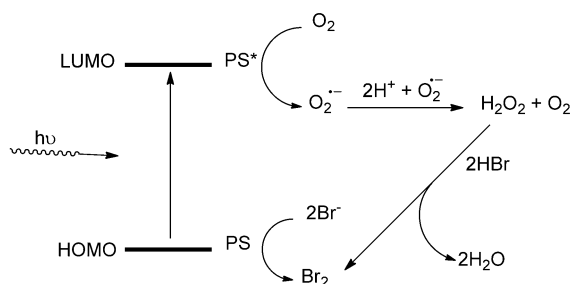


Figure 2. a) Time-dependent production of bromine during visible-light irradiation of acetonitrile solutions containing 25 μL metalcorrole and either 0.1 M TBABr and 0.2 M TFA or 0.1 M HBr and 11 % water. b) UV/Vis spectra of the reaction mixture of Ga-Br₈, TFA, and TBABr in acetonitrile before irradiation, after irradiation, and after irradiation followed by addition of excess phenol.



Scheme 2. Proposed mechanism for photocatalytic oxidation of bromide to bromine, with metallocorroles as photosensitizers (PS).

the identity of the corrole-chelated element and by bromination of the macrocycle. The acid is required for assisting the O_2 reduction which becomes much more feasible when the one-electron product superoxide anion radical is protonated.^[17] The thus-formed $HO_2^\bullet$ undergoes very efficient disproportionation to oxygen and hydrogen peroxide, the latter which may also react with bromide to produce bromine and water. An alternative mechanism that relies on the photocatalyzed formation of singlet oxygen may also be considered, but is disfavored because it is known that bromide does not react with the short-lived singlet oxygen.^[18] On the other hand, prior coordination of bromide to the catalyst (which was confirmed for the Ga complex in the dark) may safely be predicted to contribute to the fast redox process that leads to bromine.

As Ga-Br₈ was identified as the best catalyst among the investigated metallocorroles, it was further utilized in a much more practical fashion by using aqueous hydrobromic acid instead of the TFA/TBABr combination. Irradiation of a CH₃CN/H₂O solution (9:1) that contained 0.1 M HBr and 25 μM of Ga-Br₈ led to the formation of bromine, with a turnover frequency (TOF) of 816 h⁻¹, which is more than twice than under the previously described conditions (Figure 2a). The stability of the photosensitizer was very large, which was deduced from the spectral measurements shown in Figure 2b: the UV/Vis spectra of the reaction mixture solution before irradiation, after irradiation, and after the addition of phenol. The absorbance of bromine produced due to irradiation (in the form of Br₃⁻) shields the absorbance of the catalyst. When phenol is added to the reaction mixture it consumes all bromine (to produce bromophenol, which was also confirmed by GC and NMR) and clears the solution from species that adsorb above 300 nm, thus allowing for examination of the catalyst concentration. The comparison between the initial and final spectrum of the solution proves that the catalyst is very stable and may be used for a long time to accumulate bromine just by irradiation. The ability to brominate organic molecules during the photooxidation of bromide was also examined. Irradiation of a CH₃CN solution composed of Ga-Br₈, TFA, TBABr, and phenol produced a 1:1 ratio of *ortho*- and *para*-bromophenol with a TOF of 296 h⁻¹. When toluene was added instead of phenol, benzyl bromide, benzaldehyde, and bromine were formed with TOFs of 50, 129, and 200 h⁻¹, respectively. The production of the two organic products is not only fully consistent with the

above described proposed reaction mechanism (Scheme 2), but also suggests that the system described in this work may be adjusted for photocatalyzed organic reactions. Another practical aspect was addressed by exposing a vial containing a CH₃CN/H₂O solution (9:1) with 0.1 M HBr and 25 μM of Ga-Br₈ to direct sunlight: bromine was formed with a TOF of 30 h⁻¹ under these conditions (the average power of the sunlight during the experiment was 50 mW cm⁻²). No bromine was detected in the absence of Ga-Br₈.

In conclusion, we have introduced very efficient catalysts for the photocatalyzed transformation of bromide to bromine. The advantages of metallocorroles are that they are very stable under the reaction conditions and that the energy levels of the oxidizing HOMO and the reducing LUMO are easily tuned. The mechanism of action insight obtained in this work is predicted to be very useful for the design of other systems that rely on photocatalysis for driving endergonic reactions.

Experimental Section

The photooxidation of bromide to bromine was performed in acetonitrile solutions containing either: a) tetrabutylammonium bromide (TBABr, 0.1 M), trifluoroacetic acid (TFA, 0.2 M), and catalyst (25 μM); or b) HBr (0.1 M), catalyst (25 μM), and 11 % water. The Pyrex glass vial containing the reaction mixture was placed 10 cm from the LED 450 nm lamp with an intensity of 150 mW cm⁻², as determined by using an OPHIR model NOVA II power meter.

Preparation of Sb-Br₈: A flask loaded with a pyridine solution (10 mL) of H₃(tpfc)Br₈ (30 mg, 21 μmol) and SbCl₃ (200 mg, 880 μmol) was heated to reflux and monitored by UV/Vis absorption measurements in dichloromethane as solvent. After 30 min of reflux, the solvent was evaporated and the reaction residue was re-dissolved in dichloromethane (100 mL) and filtered. The dichloromethane solution was carefully titrated with iodobenzene and monitored by UV/Vis absorption measurements in dichloromethane as solvent, to confirm the oxidation of Sb^{III}-Br₈ (two (split) Soret bands at 466 and 478 nm) to Sb^V-Br₈ (one Soret band at 438 nm). After complete oxidation, the solution was filtrated and evaporated to dryness. Column chromatography on silica (eluent: CH₂Cl₂/hexanes 2:1, which was gradually changed to CH₂Cl₂) afforded Sb^V-Br₈ (28 mg, 18 μmol, 86 % yield). HR(APPI)-MS in positive ion mode (M⁺) (M = C₃₇H₂Br₈N₄O₂F₁₅Sb): calcd for *m/z*-OH = 1562.2255, obs. 1562.2327. UV/Vis (acetonitrile): λ_{max}, nm (log ε) 436 (5.20), 590 (4.23), 616 (4.25). ¹H NMR (CDCl₃, 200.13 MHz): δ_H = -4.64 ppm (2H, br s, OH). ¹⁹F NMR (CDCl₃, 188.31 MHz): δ_F = -135.6 (dd, 2F, ³J(F,F) = 24.6 Hz, ⁴J(F,F) = 7.1 Hz, *ortho*-F), -136.1 (dd, 4F, ³J(F,F) = 24.6 Hz, ⁴J(F,F) = 7.1 Hz, *ortho*-F), -149.6 (t, 2F, ³J(F,F) = 21.2 Hz, *para*-F), -149.8 (t, 1F, ³J(F,F) = 20.9 Hz, *para*-F), -161.5 (m, 4F, *meta*-F), -161.8 ppm (m, 2F, *meta*-F).

Preparation of P-Br₈: A flask loaded with a pyridine solution (15 mL) of H₃(tpfc)Br₈ (20 mg, 14 μmol) and PCl₃ (100 μL, 1.15 mmol) was stirred at RT. After 5 min, two other portions of 100 μL of PCl₃ were added in 5 min intervals. The reaction was monitored by UV/Vis absorption measurements in dichloromethane as solvent. The solvent was evaporated after 15 min and the product was re-dissolved in 100 mL dichloromethane and washed with three portions of water. The dichloromethane was evaporated and 18 mg of P-Br₈ (12 μmol, 86 % yield) were isolated after column chromatography on silica gel with dichloromethane as eluent. HR(APPI)-MS in negative-ion mode (M⁻) (M = C₃₇H₂Br₈N₄O₂F₁₅P): calcd for *m/z*-H = 1488.2983, obs. 1488.2883. UV/Vis (acetonitrile) λ_{max}, nm (log ε) 428 (5.45), 584 (4.53), 600 (4.51). ¹⁹F NMR (CD₃CN, 188 MHz): δ_F = -138.5 (d, 2F, ³J(F,F) = 22.00, *ortho*-F), -139.4 (d, 4F, ³J(F,F) = 22.0 Hz, *ortho*-F), -125.5 (t, 2F, ³J(F,F) = 18.2 Hz, *para*-

F), -152.6 (t, $1F$, $^3J(F,F) = 18.2$ Hz, *para*-F), -164.5 (m, $4F$, *meta*-F), -165.0 ppm (m, $2F$, *meta*-F). ^{31}P NMR (CD_3CN): $\delta = -182.1$ ppm.

Keywords: bromide · bromine · corroles · oxidation · photocatalysis

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