

Reductive fluorescence quenching of the photoexcited dihydroxy antimony(V) tetraphenylporphine cation in acetonitrile solution

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Abstract

At 298 K in acetonitrile solution, the dihydroxy antimony(V) tetraphenylporphine cation $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ shows an intraligand fluorescence at $\lambda_{\text{max}} = 598$ nm with $\tau_{\text{F}} = 1.46$ ns and a quantum yield of $\phi_{\text{F}} = 0.028$. While the presence of dioxygen has no significant effect on the value of ϕ_{F} , the fluorescence is very efficiently quenched by Cl^- , Br^- , I^- and SCN^- ions. At quencher concentrations below 10^{-2} M the reaction follows Stern–Volmer kinetics with high rate constants close to the diffusion-controlled limit. Based on the observation of the reduced complex $[\text{Sb}^{\text{III}}(\text{TPP})]^+$ as a permanent photoredox product, the quenching mechanism can be characterized as a bimolecular electron transfer process involving the lowest excited singlet ($\pi\pi^*$) state of the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ cation. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Luminescence quenching of metal complexes in homogeneous fluid solution has been studied extensively in the last decades [1–4]. Recently, these efforts were further stimulated by a variety of analytical and technological applications including the development of chemical and biological sensors [5,6], fluorescent probes [7,8] and novel types of imaging process [9]. Another important driving force for related research remains the crucial role of excited state quenching mechanisms for the fields of photosensitization and solar energy conversion [10]. Relevant bimolecular events in this

context are energy transfer and electron transfer reactions involving either oxidative or reductive quenching of excited dye molecules.

Porphyrins and metalloporphyrins represent the most important class of sensitizers in both natural and artificial photosynthesis, and it is well known that both the singlet and triplet excited states of closed-shell metalloporphyrins are sufficiently long-lived to participate in bimolecular quenching reactions with other species present in solution [11,12]. The fast primary electron transfer processes in the photosynthetic reaction centers proceed via the lowest singlet excited states of tetrapyrrole chromophores, and only a negligible fluorescence is observed. At the same time triplet reaction pathways are avoided in order to suppress uncontrolled release of activated oxygen intermediates. A similar approach should also be followed for the development of robust artificial photosynthetic systems

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that are able to operate under ambient conditions. With these restrictions in mind, we started to search for suitable molecular photosensitizers which in their lowest singlet excited states can lead to rapid permanent redox transformations of substrate molecules. In the present study a very efficient reductive fluorescence quenching of the ionic metalloporphyrin complex dihydroxy antimony(V) tetraphenylporphyrin tetrafluoroborate $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+\text{BF}_4^-$ by halide and thiocyanate anions is reported.

2. Experimental

The tetrabutylammonium salts $\text{N}(\text{Bu})_4\text{X}$ with $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-$ and BF_4^- were commercially available (Fluka) and used without further purification. Dihydroxy antimony(V) tetraphenylporphyrin was prepared as the bromide-containing complex $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{Br}$ according to published routes [13,14]. The Br^- counterion was quantitatively exchanged to form $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{BF}_4$ by recrystallization of the compound in the presence of an excess of tetrafluoroborate ions. Absorption and emission spectra were measured in spectrograde acetonitrile with an Uvikon 860 double-beam spectrophotometer and a Hitachi 850 spectrofluorometer using stoppered 1 cm quartz cells. Emission spectra were corrected for monochromator and photomultiplier efficiency. Time-resolved intensity decay measurements were carried out using a low-pressure hydrogen flash lamp and a multichannel analyzer for single photon counting. Quantum yields were estimated relative to EuTTA as a fluorescence standard [15]. All quenching experiments were performed with aerated samples that were thermally equilibrated to 298 K before each measurement. A constant ionic strength was maintained at different $\text{N}(\text{Bu})_4\text{X}$ quencher concentrations by using tetrabutylammonium tetrafluoroborate as an inert electrolyte.

3. Results

The electronic absorption spectrum of the compound $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{BF}_4$ in CH_3CN so-

lution (Fig. 1) shows bands in the visible spectral region at $\lambda_{\text{max}} = 419$ nm ($\epsilon = 316200$ l mol $^{-1}$ cm $^{-1}$), 482 (800), 512 (2100), 552 (11800) and 591 nm ($\epsilon = 6400$ l mol $^{-1}$ cm $^{-1}$). In acetonitrile no significant variation of the absorption spectrum occurs when the tetrafluoroborate counterion of the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ complex is exchanged against other anions. At 298 K a strong red emission occurs with maxima at 598 and 653 nm (Fig. 1). The excitation spectra for both maxima are in very good agreement with the absorption spectrum. A luminescence quantum yield of $\phi = 0.028$ and a lifetime of $\tau = 1.46$ ns are obtained.

The emission properties of the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ cation are not affected by the presence of dioxygen or by the addition of tetrabutylammonium tetrafluoroborate. However, the red luminescence is very efficiently quenched when other tetrabutylammonium salts $\text{N}(\text{Bu})_4\text{X}$ with redox-active anions $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ or SCN^- are added (Fig. 2). Linear relationships of the relative luminescence quantum yields or lifetimes are obtained at quencher concentrations below 10^{-2} M in agreement with the Stern–Volmer bimolecular kinetic model. Only at very high $\text{N}(\text{Bu})_4\text{X}$ concentrations a beginning downward curvature of the plots is observed for $\text{X}^- = \text{Cl}^-$ and SCN^- . However, in these cases spectral variations occur, which indicate the presence of exchange equilibria with the axial hydroxyl ligands of the

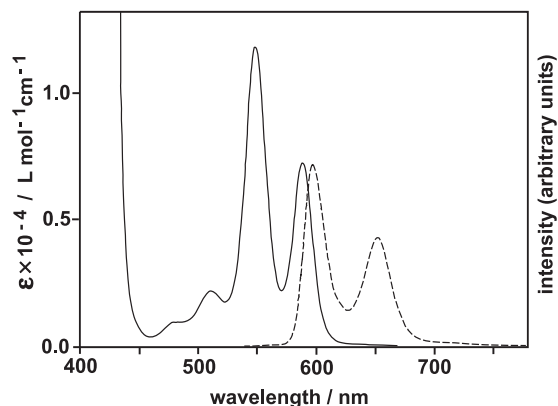


Fig. 1. Electronic absorption (—) and corrected emission spectra (---) of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{BF}_4$ at 298 K in CH_3CN . Excitation of the sample at $\lambda_{\text{exc}} = 420$ nm.

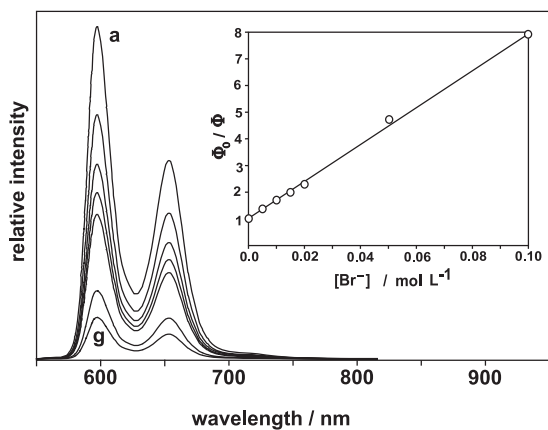


Fig. 2. Fluorescence quenching of a 1.0×10^{-5} M solution of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{BF}_4$ at 298 K in CH_3CN in the presence of increasing amounts of $\text{N}(\text{Bu})_4\text{Br}$. Inset: Stern–Volmer plot of the relative fluorescence quantum yields vs the corresponding bromide concentrations 0.0 M (a), 0.005, 0.01, 0.015, 0.02, 0.05 and 0.1 M (g).

$[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ complex. The resulting Stern–Volmer constants K_{SV} together with the associated oxidation potentials of the anions X^- are presented in Table 1. Irradiation of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ solutions in the presence of the quenching $\text{N}(\text{Bu})_4\text{X}$ salts leads to an increase of absorption at $\lambda_{\text{max}} = 465$ and 644 nm, which is characteristic for a formation of the reduced $[\text{Sb}^{\text{III}}(\text{TPP})]^+$ complex [14]. This compound reacts photochemically with dioxygen to form $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ and hydrogen peroxide. With $\text{X}^- = \text{Br}^-$ and I^- the corresponding polyhalide oxidation products Br_3^- and I_3^- are also readily identified by their absorption bands at $\lambda_{\text{max}} = 269$ nm [18] or $\lambda_{\text{max}} = 290$ and 360 nm [19], respectively.

Table 1
Stern–Volmer constants K_{SV} for the fluorescence quenching of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ by various anions X^- at 298 K in CH_3CN

Quencher X^-	Redox potential E^0 (V vs NHE)	Slope K_{SV} (l mol^{-1})
Cl^-	1.6 [16]	41 ± 5
Br^-	1.2 [16]	68 ± 2
I^-	0.7 [16]	107 ± 1
SCN^-	1.6 [17]	42 ± 2

4. Discussion

The spectroscopic features of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{BF}_4$ (Fig. 1) are consistent with the properties of a regular diamagnetic metalloporphyrin complex which shows a normal type absorption and a strong emission at room temperature [20]. In polar solvents at the rather low concentrations applied, the compound is expected to be completely dissociated into ions. This assumption is supported by the lack of counterion dependency of the optical spectra observed in acetonitrile. The presence of a sharp *B* (Soret) band at 419 nm and a less intense *Q*-band pattern between 480 and 600 nm with vibronic progressions of 1200 cm^{-1} clearly indicates that the electronic absorption spectrum is dominated by intraligand $\pi\pi^*$ transitions of the porphyrin macrocycle. The luminescence spectrum is characterized by a small Stokes-shift of approximately 200 cm^{-1} and a vibronic structure corresponding to a prominent group vibration around 1400 cm^{-1} present in the ground state IR spectra of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{BF}_4$ and free base tetraphenylporphyrin. In accordance with other metalloporphyrin complexes this luminescence is unambiguously assigned as intraligand fluorescence from the lowest excited singlet state of the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ cation with $E_{0-0}(S_1) = 2.09 \text{ eV}$. The experimental fluorescence quantum yield and lifetime values of $\phi_{\text{F}} = 0.028$ and $\tau_{\text{F}} = 1.46 \text{ ns}$ are in good agreement with the theoretical values of $\tau_{\text{F,calc}} = 1.39 \text{ ns}$ and the radiative lifetime of $\tau_{\text{rad}}^0 = 49.6 \text{ ns}$ calculated according to the method of Strickler and Berg [15]. At 77 K in ethanol matrix the corresponding intraligand phosphorescence is observed at $\lambda_{\text{max}} = 760 \text{ nm}$ with $E_{0-0}(T_1) = 1.64 \text{ eV}$, a lifetime in the ms range and a $S_1 - T_1$ gap of 3700 cm^{-1} typical for the TPP ligand.

As indicated by the observation of linear Stern–Volmer plots (Fig. 2), the effect of increasing concentrations of Cl^- , Br^- , I^- and SCN^- ions on the fluorescence intensity of the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ cation can be interpreted as a dynamic bimolecular quenching process. The K_{SV} values obtained for the various quencher molecules $\text{N}(\text{Bu})_4\text{X}$ (Table 1) reflect the electron donor strength of the anions X^- , although the redox potential for thiocyanate is tainted with some uncertainty [17,21]. In general,

the quenching efficiencies reported in Table 1 are considerably larger than those observed for the neutral quencher molecule PPh₃, which yields a slope of $K_{SV} = 11.8 \text{ l mol}^{-1}$ [22]. The corresponding fluorescence quenching rate constants k_q (Table 2) calculated according to the relationship $K_{SV} = k_q \cdot \tau_F$ are rather high. In order to estimate the diffusion-limited rate constants k_d relevant for the bimolecular quenching reactions (Table 2), the following assumptions were made. The diffusion coefficients D of the reactants were calculated according to the Stokes–Einstein equation, where k is the Boltzmann constant and $\eta = 0.341 \text{ cp}$ is the kinematic viscosity of acetonitrile at $T = 298 \text{ K}$ [23]:

$$D = \frac{kT}{6\pi\eta R}. \quad (1)$$

The radii $R = 1.21, 1.18, 1.20$ and 1.39 \AA of the anions Cl^- , Br^- , I^- and SCN^- were extracted from the literature [24]. A radius of $R = 5.7 \text{ \AA}$ for the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ cation approximated as a spherical molecule was obtained from an estimate of its van der Waals volume. Since the metalloporphyrin cation displays a rather short fluorescence lifetime, a significant contribution of transient diffusion effects to the quenching rate coefficients had to be considered [25]. Instead of the well-known time-independent Smoluchowski equation [23], a more general expression [26,27] was applied to evaluate the diffusion-controlled rates k_d for the reaction of the oppositely charged particles A and B (MKS units):

$$k_d(\tau_F) = \frac{4\pi z_A z_B e^2 N D_{AB} \cdot 1000}{4\pi\epsilon\epsilon_0 kT [\exp(z_A z_B e^2 / 4\pi\epsilon\epsilon_0 kTR_{AB}) - 1]} + \frac{4\pi R_{AB} N D_{AB} \cdot 1000}{\exp(z_A z_B e^2 / 4\pi\epsilon\epsilon_0 kTR_{AB})} \frac{2R_{AB}}{\sqrt{D_{AB}\tau_F}}. \quad (2)$$

In this term, z_A and z_B are the charges of the ions, e the elementary charge, N Avogadro's number, ϵ the dielectric constant of the solvent, ϵ_0 the permittivity of free space, D_{AB} is the sum of the diffusion coefficients of the two species, and R_{AB} denotes the contact radius which is taken as a sum of the individual R values. The time-dependency of the rate process is expressed by a factor that depends on the average lifetime τ_F of the excited molecules with no quencher present. It should be mentioned that this approximation is only valid, if the quenching is not too large ($< 50\%$), [27]. A comparison of the estimated k_d values with the experimental rates k_q (Table 2) suggests that the bimolecular quenching process of the $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ cation with various $\text{N}(\text{Bu})_4\text{X}$ salts, although very efficient, does not yet approach the theoretical encounter-controlled limit.

It is commonly assumed that fluorescence quenching of aromatic molecules with inorganic anions occurs by electron transfer [28]. In the present study this assumption is strongly supported by the observation of polyhalide anions and the reduced $[\text{Sb}^{\text{III}}(\text{TPP})]^+$ metalloporphyrin sensitizer as permanent photoproducts. The possible overall multielectron transfer pathways related to similar substrate conversion reactions of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ have previously been discussed [29]. In this context, the quenching experiments performed in the present study can supply detailed informations about the primary processes and reactive excited states of the metalloporphyrin complex involved. It is rather clear now that the photoredox reactions of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ with halide and pseudohalide anions are initiated by a reductive quenching of the lowest singlet excited state of the sensitizer. Since the rates of these quenching reactions are situated below their dif-

Table 2

Estimated rate constants, diffusion coefficients, outer-sphere reorganizational energies and standard free energy changes for the reductive quenching of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]^+$ by X^- at 298 K in CH_3CN

Donor X^-	k_q ($\text{M}^{-1}\text{s}^{-1}$)	D_{AB} ($\text{m}^2 \text{ s}^{-1}$)	k_d ($\text{M}^{-1}\text{s}^{-1}$)	λ_{out} (kJ mol^{-1})	ΔG_{et}^0 (kJ mol^{-1})	k_{et} (s^{-1})
Cl^-	2.8×10^{10}	6.3×10^{-9}	2.1×10^{11}	260.8	-48.2	4.5×10^9
Br^-	4.7×10^{10}	6.5×10^{-9}	2.2×10^{11}	268.0	-86.8	8.2×10^9
I^-	7.3×10^{10}	6.4×10^{-9}	2.1×10^{11}	263.2	-135.1	1.5×10^{10}
SCN^-	2.9×10^{10}	5.6×10^{-9}	2.0×10^{11}	224.3	-48.2	4.6×10^9

fusion-controlled limit, it is possible to get an estimate for the corresponding primary electron transfer rate constants k_{et} (Table 2). For the calculation of the k_{et} values a standard bimolecular reaction mechanism was applied [24], which includes diffusion of the reactants *A* and *B* together to form an encounter complex *AB*, followed by an irreversible electron transfer step. Secondary processes yield permanent redox products or result in a re-formation of the ground state reactants via reverse electron transfer. Assuming steady-state kinetics, the following expression can be derived [24], where k_{AB} is the equilibrium constant for the formation of the encounter complex:

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{K_{AB}k_{\text{et}}} \quad (3)$$

The k_{et} rates listed in Table 2 were obtained from Eq. (3) with an estimate of k_{AB} calculated according to the Fuoss–Eigen model [24]:

$$K_{AB} = \frac{4}{3} \pi R_{AB}^3 N \exp \left(\frac{e^2}{4\pi\epsilon\epsilon_0 kTR_{AB}} \right) \times 1000. \quad (4)$$

For the present system, large outer-sphere reorganization energy values (λ_{out}) between 2.3 and 2.8 eV are obtained according to the classical Marcus theory of electron transfer reaction rates [30]. These values can be regarded as an estimate for the total reorganization energy ($\lambda \approx \lambda_{\text{out}}$) of the photoinduced electron transfer step, which prior to subsequent chemical bond changes produces the neutral quencher radical *X* and the delocalized metalloporphyrin π -radical anion $[\text{Sb}^{\text{V}}(\text{TPP}^-)(\text{OH})_2]$ with $E_{1/2} = -0.15$ V vs NHE as the primary products [29]. The overall free energy changes ΔG_{et}^0 that can be calculated for this primary process (Table 2) fulfill the relation $\Delta G_{\text{et}}^0 > -\lambda$, which corresponds to normal Marcus region conditions. Accordingly, the k_{et} values for the photoinduced electron transfer step increase with an increasing electron donor strength of the quencher anions, which is also reflected by the redox potentials given in Table 1.

5. Conclusions

In summary, it can be concluded from the present results that the bimolecular fluorescence

quenching of the dihydroxy antimony(V) tetraphenylporphine cation by Cl^- , Br^- , I^- and SCN^- ions is a fast and efficient reaction. The process is obviously facilitated by electrostatic interactions and occurs via an electron transfer mechanism, which finally leads to permanent redox products. While the discovery of efficient quenching reactions is an interesting observation in its own right with relevance to the design of halide-selective optical sensors [31], these findings have implications for several other current research fields. The photochemical oxidation of halide anions by visible light has been repeatedly suggested for solar energy conversion processes [32,33]. In this context solar chemical brine-splitting and fuel cell applications might be considered as the final goals. A further application of the reactions described could be the photochemical modeling of the function of oxidoreductase enzymes [34,35] such as chloroperoxidase [14] or the halide-binding myeloperoxidase [36].

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