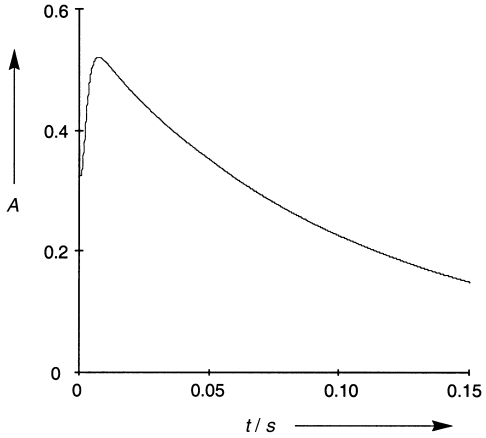

Figure 2. Generation and decay of $\mathbf{1}^+$ observed after dissolving **1**-Cl in TFE/CH_3CN (20:80 (v/v)) containing 1.0 M of $LiClO_4$.

the diarylmethyl cation $\mathbf{1}^+$. The carbocation, which was formed with a rate constant (k_i) of $5 \times 10^2\ s^{-1}$ was consumed with a rate constant (k_{TFE}) of 10.4 s^{-1} under these conditions (Table 2, entry 15). Analogously, formation and consumption of $\mathbf{1}^+$ was observable in other TFE/CH_3CN mixtures containing alkali metal perchlorates[14] (Table 2, entries 12 and 14).

The direct observation of the carbocationic intermediate demonstrated in this experiment is certainly not a singular case. Increasing stabilization of the carbocation and decreasing solvent nucleophilicity transform the generally accepted energy profiles of S_N1 reactions with carbocations as short-lived intermediates (Figure 3, upper graph) into energy profiles which imply the buildup of significant concentrations of the intermediate carbocations (Figure 3, lower graph).

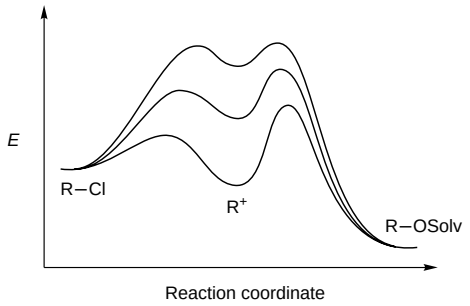

Figure 3. Schematic energy profiles for solvolytic displacement reactions in TFE. Upper graph: Slow ionization (conventional S_N1). Lower graph: Rate-determining carbocation–nucleophile combination with directly observable intermediate. Ion-pairing and proton transfer steps are neglected.

The occurrence of such scenarios can easily be predicted from available ionization and combination rate constants as demonstrated herein. Since ionization and nucleophile addition must be uncoupled when the intermediate is observable, the investigation of such reaction cascades may open a new era in the study of solvolytic displacement reactions. As salt and solvent effects on the two steps of the reaction can now be studied separately, many ambiguities in the earlier interpretations of the mechanisms of solvolytic displacement reactions can be resolved.

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A Europium-Ion-Based Luminescent Sensing Probe for Hydrogen Peroxide**

Otto S. Wolfbeis,* Axel Dürkop, Meng Wu, and Zhihong Lin

Molecular probes and molecular sensors for hydrogen peroxide (H_2O_2) are important in the environmental and bioanalytical sciences for a number of reasons. H_2O_2 is present in small but significant concentrations in the atmosphere[1] and the marine environment.[2] It is widely used in industry for bleaching, cleaning, and disinfection,[3] and released to the environment in large quantities.[4] H_2O_2 is one of the products of the activity of almost all oxidases,[5] and this enables a quantitative assay of a) the activity of the respective enzyme, b) numerous substrates including glucose,[6] and c) a so-called

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enzyme-linked immunoassay (ELISA) to be carried out, if an oxidase is used as a label.[7] Finally, H_2O_2 is known to be the cause of various kinds of DNA damage in mammalian[8] and plant[9] cells; an area of particular current research activity. Obviously, molecular probes for H_2O_2 are of broad interest in environmental and biochemistry research, in clinical assay and screening.

H_2O_2 can be optically detected with extreme sensitivity by chemiluminescence[10] (CL) or electroluminescence,[11] however usually at pH values above 8.0 only. A sensitivity similar to that of CL assays is achieved by using (laser-induced) fluorescence. The reaction of H_2O_2 with certain phenols in the presence of peroxidase yields fluorescent dimers (excitation at around 320 nm; emission maximum at 415 nm), which can be used to visualize and detect H_2O_2,[12] ideally through the long-decaying fluorescence of the respective europium complexes.[13] This method requires, however, the use of several reagents including a) a fluorogenic precursor; b) a peroxidase, c) a lanthanide ion such as Eu^{3+}, and d) in some instances a fluorescence-enhancing solution.

We present a new fluorescent probe for hydrogen peroxide and its use for sensitive but simple detection of H_2O_2. The procedure is based on the rather surprising finding that the Eu^{3+}–tetracycline complex[14] referred to herein as [Eu(tc)], when used as an aqueous solution in a 4-morpholine propanesulfonic acid (MOPS) buffer,[15] binds H_2O_2 to form a strongly fluorescent complex ([Eu(hp)(tc)]) that can be excited at 390 to 405 nm, for example, by using a 405-nm diode laser. On addition of H_2O_2 to [Eu(tc)], a 15-fold increase in luminescence intensity at 616 nm occurs (Figure 1). Simultaneously,

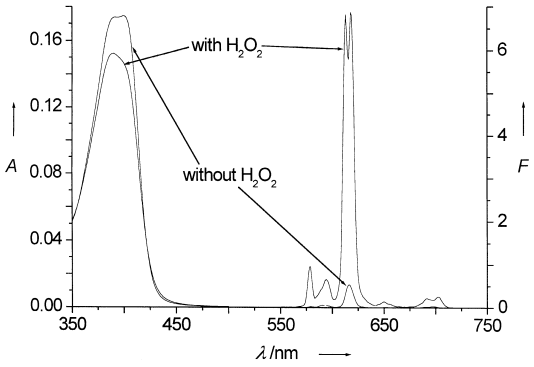

Figure 1. Absorption and emission spectra of the Eu^{3+}–tetracycline complex ([Eu(tc)][15]) in pH 6.9 buffer, in the presence and absence of 0.8 mmol·L^{-1} of hydrogen peroxide. Fluorescence excitation at λ_{exc} 405 nm.

large changes are observed in the luminescence decay time of [Eu(tc)], which was reported to be in the 10–20 μs range and highly pH-dependent.[14,16] The increase is most pronounced at physiological pH values and does not require the presence of an enzyme. The effects observed are constant over time which implies that a) they are not caused by chemiluminescence, and b) that the reagent and the product of its reaction with H_2O_2 do not measurably photobleach.

Eu^{3+}–ligand complexes of the type of [Eu(tc)] have coordination numbers of eight or nine.[17,18] Both [Eu(tc)] and [Eu(hp)(tc)] display the typical absorption and emission spectra of a lanthanide–ligand complex. The absorption band (with peaks at 398 and 405 nm) is caused by the presence of the tetracycline ligand which—in its uncomplexed form—has a very similar absorption spectrum. As in other complexes of this type, the photonic energy absorbed by the ligand is transferred from the triplet state of the ligand to the central Eu^{3+} ion with its typical emission spectrum[18] of a main band which peaks at 616 nm ($^5D_0 \rightarrow {}^7F_2$) and several side bands centered at 579, 597, 654, and 688 nm, respectively (Figure 1). In the case of [Eu(hp)(tc)], the main emission band is split into two bands when the concentration of [Eu(tc)] exceeds 1 μmol L^{-1}, provided a spectrometer is used with a resolution of < 1 nm.

The probe [Eu(tc)] is highly specific for H_2O_2. Its luminescence is not affected by alkali and ammonium ions, nor by chloride, sulfate, or nitrate anions in concentrations of up to 100 mmol L^{-1}. However, citrate and phosphate interfere, leading to an increase in fluorescence. The emission intensities of [Eu(tc)] and [Eu(hp)(tc)] are strongest at pH 6.6–7.2 and rapidly drop outside this range. In fact, the fluorescence is only 15% of the maximum intensity at pH 8.0, and 8% at pH 6.0. The quantum yield of [Eu(tc)] in MOPS buffer solution of pH 6.9 is 0.003 ± 0.002 at 22 °C, which increases to 0.040 ± 0.001 on addition of excess H_2O_2.

In contrast to Hirschy et al.[14] we find the decay characteristics of [Eu(tc)] to be rather complex. The decay profile of in pH 6.9 buffer solution has two main components, one having a decay time of 8.7 μs (weighting 58%), the other of 30.4 μs (40%). We also found a third component (2%) which, with a decay time as long as 174 μs, indicates a quite different deactivation channel. The decay of the [Eu(hp)(tc)] also has two main components, of which the decay times are 13.2 μs (34%) and 59.4 μs (64%), respectively. The third component (2%) is present as well and has a decay time of 158 μs. From these results it is obvious that time-resolved measurements are best performed after a lag time of > 30 μs to detect the major (59.4 μs) component of the [Eu(hp)(tc)] selectively. Fortunately, this lag time can be programmed into many fluorescence (and microplate) readers.

Complexes of Eu^{3+} with organic ligands are known to contain water as an additional ligand, usually at the ninth coordination site.[17] From the experimental findings we conclude that on exposure to H_2O_2 the water ligand is replaced by H_2O_2, without the occurrence of a redox reaction. This interpretation is based on the findings that the absorption spectrum of [Eu(hp)(tc)] is very similar in shape to that of [Eu(tc)] (Figure 1) and that the H_2O_2 in [Eu(hp)(tc)] is still available to reduction (e.g. by thiosulfate). We assume that the binding of the H_2O_2 ligand causes a structural rearrangement of the [Eu(tc)] complex in solution, such that the tc ligands come closer to the central metal ion, which would lead to a distinctly more efficient transfer of energy from the ligand to the central ion (i.e. a higher quantum yield and less quenching) and to an increase in luminescence decay time (for the two main fractions; we also assume that water molecules act as quenchers). Unfortunately, and despite many attempts, we failed to obtain crystals of the obviously weak complex formed between [Eu(tc)] and H_2O_2.

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The potential of the above findings is demonstrated by applying the Eu complex in the detection of trace levels of H_2O_2, a kinetic enzyme-activity assay (glucose oxidase), a kinetic assay for glucose, and an optical sensor for H_2O_2. The respective procedures are rather simple. The first[19] consists of the addition of [Eu(tc)] to the buffered (pH 6.9) sample; the reaction is complete in about 10 min. In contrast to previous methods, the addition of an enzyme (or an enzyme mimetic) is not needed. The plot of intensity versus concentration of H_2O_2 in Figure 2 shows that H_2O_2 can be determined in the 2–400

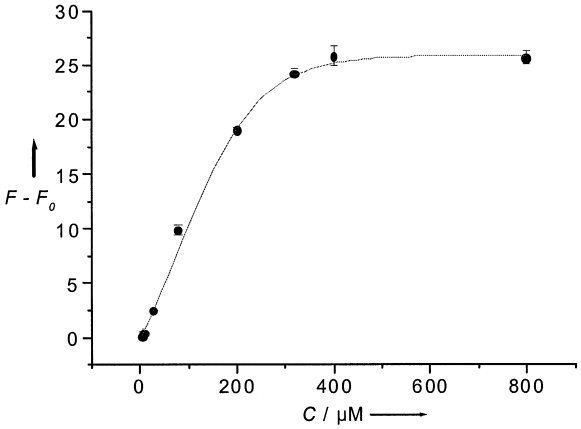

Figure 2. Plot of $(F-F_0)$ versus concentration of H_2O_2 including error bars (for n = 6) at pH 6.9, showing the dynamic range of the system. Here, F_0 is the initial fluorescence of the system (caused by [Eu(tc)]), which increases to F on addition of H_2O_2 because of the formation of the strongly fluorescent [Eu(hp)(tc)]. The linear range is from 0 to about 200 µmol·L^{-1}.

µmol L^{-1} concentration range. The limit of detection (LOD; defined as 3σ/slope) is 1.8 µmol L^{-1}. This LOD is not comparable to the extremely sensitive methods based on chemiluminescence, but better by a factor of ten than the peroxytitanyl ion method, which has the additional disadvantages that it is a nonfluorescent system and requires a pH value of <3, so that it is not applicable to probing biological systems.

The determination of the activity of the enzyme glucose oxidase (GOx) requires the addition of only glucose and the reagent [Eu(tc)].[20] This process is much simpler than any other optical assay reported to date. The determination of glucose (which is important in clinical analysis, in food chemistry, and in the monitoring of processes occurring in bioreactors) becomes possible by addition of only GOx and [Eu(tc)].[21] Figure 3 gives time plots of a typical kinetic glucose assay.

Finally, we have obtained an optical sensor by immobilizing the [Eu(tc)] complex in an optically transparent layer of a polyurethane hydrogel. The sensor enables continuous monitoring of H_2O_2 in the 0.001–0.3 % concentration range. By analogy to the imaging of chemical species by using ruthenium probes with relatively long decay times,[22] we are currently performing experiments to visualize H_2O_2 by fluorescence imaging using the new [Eu(tc)] probe.

While steady-state luminescence intensity was used as the analytical information in the experiments described so far,

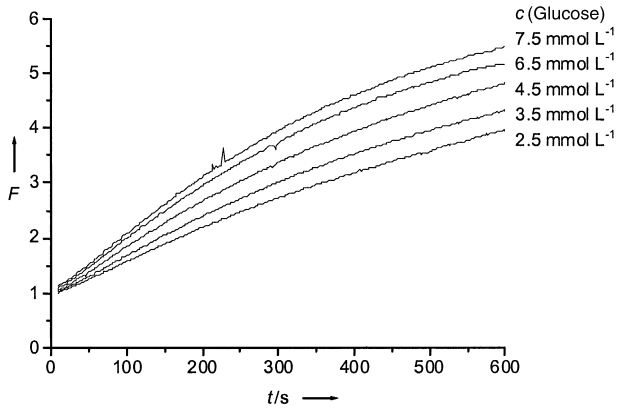

Figure 3. Time-dependent oxidation of glucose (2.5 to 7.5 mmol·L^{-1}) by glucose oxidase (15 units in 3 mL) in MOPS buffer at pH 7.0, monitored by the formation of [Eu(hp)(tc)]. Luminescence excitation was at 405 nm and measurements at 616 nm.

gated measurements may also be performed using a time-resolving fluorometer. In a typical experiment, the delay time of a time-resolving fluorometer[23] was set to 30 µs and the integration time to 100 µs. This led to an eight–ten-fold reduction in background luminescence (resulting from both the sample and the microtiterplate). However, it has to be noted that gated measurements with the [Eu(tc)] probe do not lead to complete suppression of background luminescence, because background luminescence is always predetermined by the fraction of free [Eu(tc)] present. The luminescence of [Eu(tc)] is weaker than that of the [Eu(hp)(tc)] complex by a factor of 15, but has spectral characteristics which are virtually identical to those of [Eu(hp)(tc)]. Fortunately, the main component of the three (at 59.4 µs) is well separated from that of the [Eu(tc)] complex (30.4 µs), so that the latter is largely eliminated by gating.

In conclusion, the new luminescent probe for H_2O_2 has unique properties;[24] it works at neutral pH values, has the general advantages of a fluorescent probe (e.g. sensitivity), displays a very large Stokes shift (210 nm) and a µs fluorescence decay time. The latter enables gated assays, and also provides decay-time-based information (not discussed here). Unlike other europium labels, which can only be excited by diode lasers by using two-photon excitation or second-harmonic generation, the new probe can be directly excited with the violet (405 nm) diode laser. Finally, [Eu(tc)] is the first probe for the determination of H_2O_2 that does not require the presence of an enzyme (such as peroxidase) or an enzyme mimic to form a fluorescent product.

The findings may be exploited in a) the detection of H_2O_2 in the environment and in process control, b) the determination of the activity of oxidases, either directly as shown here, or in ELISAs or gene assays, c) the determination of enzyme inhibitors, in particular heavy-metal ions, and d) the quantification of substrates for oxidases. Europium reagents that are covalently linked to appropriate biomolecules are widely used in binding assays, known for example as the DELFIA or FIAGEN immunoassays, and in gene assays,[25] some based on the use of nanobeads and lanthanide phosphors that, ideally, may be adapted to microarray formats.[26] The new europium reagent [Eu(tc)] is an attractive alternative because it need

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not be covalently attached to a receptor and it does not require the addition of a detergent to enhance fluorescence intensity.

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[15] Reagent: A solution containing $EuCl_3 \cdot 6H_2O$ (9.6 mg) and tetracycline hydrochloride (4 mg) in a MOPS buffer (200 mL, 10 mmol L^{-1}) of pH 6.9. The absorbance at 405 nm is $\approx 0.78 \pm 0.01$ cm^{-1}. The reagent is stable for at least 1 month if stored at 4 °C in the dark.

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[19] Assay protocol for H_2O_2: The aqueous sample (1 mL; containing 1 to 2 $\mu g \cdot mL^{-1}$ of H_2O_2) was added to the [Eu(tc)][15] (1 mL) in a cuvette, and the increase in luminescence intensity at > 616 nm was measured after 10 min (excitation at 405 nm). If a time-resolving reader was available, the lag time was adjusted to > 30 μs and the integration time to 100 μs.

[20] GOx assay procedure: The following solutions were placed in the wells of a microtiterplate: a) A [Eu(tc)] solution (in the ten-fold concentration of that given in [15], except for the buffer concentration); b) a solution of GOx (of unknown activity) in the same buffer; c) enough buffer to fill up to a volume of 200 μL; d) β-D-glucose (50 μL, 28 mmol L^{-1}) in buffer, to start the reaction. The increase in fluorescence intensity between 610 and 630 nm was measured over 10 min (ΔI_{10min}). The activity of GOx was calculated by use of a calibration graph, established by plotting ΔI_{10min} versus known activities of GOx. Note: citrate and phosphate interfere.

[21] Procedure for glucose assay: The [Eu(tc)] reagent solution[15] (1 mL) was placed in a cuvette, to which a solution of GOx (2 mL, 15 units, from Sigma, product no. G 2133) in MOPS buffer (10 mL) was added. The reaction was initiated by adding 2 mL of a sample containing between 2 and 10 mmol L^{-1} of glucose. The increase in luminescence intensity after 10 min (ΔI_{10min}) at 616 nm (excitation at 400–440 nm) was measured, and ΔI_{10min} used to read off the glucose concentration using a calibration graph established with β-D-glucose. Note: citrate and phosphate interfere.

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Conversion of *arachno*-Nonaborane into Azanonaborane: Unexpected Loss of a Firmly Integrated Boron Atom**

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The polyhedral azanonaborane $(RH_2N)B_8H_{11}NHR$ (R = *i*Pr, **1**) is easily prepared by treating dimethylsulfido *arachno*-nonaborane 4-$(Me_2S)B_9H_{13}$ with three equivalents of a primary amine.[1] The reaction has been shown to proceed stepwise, by an initial ligand exchange to give 4-$(RH_2N)B_9H_{13}$, which reacts with an additional amine NH_2R^1 to give the mixed species $R^1H_2NB_8H_{11}NHR$.[1b] These compounds have been shown to constitute a good entry into azacarbaborane[2] and azametallaborane chemistry[3] and may also be useful in neutron capture therapy.[4] The transformation of $(Me_2S)B_9H_{13}$ to $(RH_2N)B_8H_{11}NHR$ involves the loss of one boron atom and cluster rearrangement. Herein we report the conversion of boron-substituted nonaboranes into azanonaboranes. These experiments make it possible to determine which boron atom is eliminated, and to speculate on the mechanism of the cluster rearrangement.

A variety of B-substituted $B_{10}H_{14}$ derivatives are known.[5] These can be converted readily by a two-step process via 6,9-$(Me_2S)_2B_{10}H_{12}$ derivatives into the corresponding *arachno*-nonaborane system.[6] We prepared some ethyl, bromine, and deutero derivatives of decaborane(14), which are stable under the reaction conditions (neither the bromine atom nor the ethyl group can be removed by Et_3N,[6a] and no deuterium exchange has been noted on heating the tetradeuterated $(Me_2S)B_9H_{13}$ with diethylamine under reflux in benzene[6c]).

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