Chemically homogeneous polymer layers loaded with oxygen-quenchable luminescent dyes may lead to promising applications for optical oxygen sensing. In this work, luminescence quenching of tris(4,7'-diphenyl-1,10'-phenanthroline)Ru(II) perchlorate, dissolved in a polystyrene layer, has been investigated. Although the dye appears to be molecularly dispersed in this glassy polymer, the Stern–Volmer intensity plot is nonlinear and the luminescence decay is not single exponential. This can be attributed to a spatial disorder in the polymer structure, which is likely to determine the excited state properties. It is shown that an analysis of intensity quenching and luminescence lifetime data based on a multicomponent approach, which was previously developed for dyes in chemically heterogeneous silica matrices, can also be applied to this polymer. Quenching is shown to be dynamic in nature. Some features of polystyrene-based optical oxygen sensors having an enhanced dye concentration are pointed out.

In the past decade, there has been considerable interest in luminescence-based optical oxygen sensors. Sensors based on luminescence quenching of Ru(II) complexes by molecular oxygen have been widely investigated. Sensor design includes immobilization of the dye in a polymer layer; in the case of silicone polymers, ionic dyes insoluble in poly(dimethylsiloxane) matrices have been adsorbed on the surface of carrier particles (e.g., silica) entrapped within the silicone rubber matrix. The structure of such layers can be regarded as macroscopically heterogeneous. Dyes adsorbed on silica are exposed to multiple binding sites.

On a molecular scale, multiple binding sites lead to nonlinear Stern–Volmer plots and complex decay profiles. Alternatively, Ru(II) complexes have been directly dissolved in glassy polystyrene layers. At sufficiently low concentrations, the dyes can be molecularly dispersed in such polymers. Compared to silica carrier particles, there is no evidence for different dye binding sites. Therefore, the structure of the polystyrene layer is considered as homogeneous. Nonetheless, the observed luminescence decays are not single exponential and the Stern–Volmer plots are nonlinear.

In general, the nonradiative relaxation of a luminescent molecule is influenced by the local composition and structure of the matrix in which the molecule is situated. As long as temporal fluctuations of the environment are faster than the excited state decay, variations in matrix influence will be averaged out over the lifetime of the excited state. Such a case is represented by a luminophor dissolved in a liquid solvent. The ensemble of molecules is expected to show a monoexponential decay profile of the emission. In microinhomogeneous environments, this influence may be different for each indicator molecule, if the temporal fluctuations in the environment are slower than the luminescence decay. This gives rise to nonexponential excited state decays and nonlinear Stern–Volmer quenching responses. An extreme case is represented by a chemically heterogeneous matrix, as, for example, the above-mentioned carrier particles in silicone rubber. For these heterogeneous systems, it has been shown that a multiple-exponential decay model satisfactorily describes the quenching behavior. In the present paper, it will be shown that even the decay in a chemically heterogeneous matrix like polystyrene can be successfully treated by a multiexponential approach. The reason for this is that, with respect to the relaxation of the excited state of the dye molecules, the molecular environment is spatially disordered, thus adding complexity to the photophysical properties of the dissolved dyes.
In the presence of a quencher unable to form ground state complexes with the luminescent species, quenching is performed by a diffusion encounter of the dye and the quencher ("dynamic" quenching). This process follows the Stern–Volmer eq 1 for both

\[
\frac{I_0}{I} = 1 + K_{sv}[Q]
\]

(1a)

\[
\frac{\tau}{\tau_i} = 1 + K_{sv}[Q]
\]

(1b)

\[
K_{sv} = k_q\tau_0
\]

(1c)

luminescent intensity \(I\) and lifetime \(\tau\), where \(K_{sv}\) is the Stern–Volmer quenching constant, \(k_q\) is the bimolecular quenching rate constant, and \([Q]\) the concentration of the quencher. The index 0 denotes absence of the quencher.

Considering a more complex matrix, where the luminescent molecules are under different matrix influence on an averaged time scale, multiplexponential decay of the excited states occurs:

\[
i(t) = \sum_{i=1}^{m} B_i e^{-t/\tau_i}
\]

(2)

\(i(t)\) represents the response of the system following a \(\delta\)-pulse excitation, the \(B_i\) are the amplitudes, the \(\tau_i\) are the time constants, and \(m\) is the number of single-exponential components (denoted by index \(i\)) required to describe the decay sufficiently.

Each individual lifetime component fulfills a Stern–Volmer equation (eq 1b):

\[
\frac{\tau_m}{\tau_i} = 1 + K_{sv}[Q]
\]

(3)

For the description of dynamic quenching behavior, a preexponentially weighted mean lifetime \(\tau_m\) can be introduced, similar to the treatment of Demas and co-workers:

\[
\tau_m([Q]) = \frac{\sum_i B_i \tau_i([Q])}{\sum_i B_i}
\]

(4)

For a dynamic quenching process, the amplitudes \(B_i\) are independent of the presence of a quencher. For any quencher concentration, they are expected to be equal to \(B_0\) in the absence of the quencher. Since the lifetimes \(\tau_i\) are only capable of monitoring dynamic quenching processes, \(\tau_m\) is a measure of this contribution to the intensity Stern–Volmer behavior. If quenching is entirely dynamic, intensity and lifetime Stern–Volmer plots will match.\(^{19}\)

To describe luminescence quenching as a function of quencher concentration, a superposition of Stern–Volmer equations has to be applied:\(^{13,14}\)

\[
\frac{I_0}{I} = \left[\sum_i \frac{f_i}{1 + K_{sv}[Q]} \right]^{-1}
\]

(5)

\(f_i\) is the fractional contribution of the \(i\)th component.

This equation provides a Stern–Volmer plot with a downward curvature, since the second derivative of eq 5 is positive for all positive quenching constants. Fractional static (nondiffusional) quenching contributions may introduce a negative deviation of the mean lifetime from the intensity Stern–Volmer equation (eq 5). A parameter \(f_m\) can be defined, which stands for the fraction of excited molecules remaining in this state after static quenching occurs.\(^8\)

\[
\frac{\tau_m}{\tau_i} = \left(\frac{I_0}{I}\right) f_m
\]

(6)

For the variety of local dye environments expected for solid state matrices, including indicators adsorbed on surfaces\(^{15,22}\) or dissolved in polymers,\(^{22,23}\) distributions of relaxation rates have to be considered. The sums in eq 2, 4, and 5 must be replaced by proper integrals. This is not always tractable since assumptions are required about the underlying distributions.

James and Ware\(^{24}\) have shown, that a phenomenological double-exponential approach can reproduce various unimodal and bimodal distributions of lifetimes within the currently used levels of precision of lifetime experiments. This has been verified\(^21\) for simulated distributions having widths \(\sigma\) (defined as one standard deviation over the center lifetime) of at least \(\sigma = 15\%\) (smaller distributions are more properly described by a single-exponential function). The applied center-lifetimes of bimodal distributions deviated by at least a factor of two. The authors also stressed that the Stern–Volmer representations of a double-exponential fit of simulated distributions include linear plots for both revealed lifetime components when a synthetic quenching mechanism with a single quenching constant is applied to the data. Quenching of assumed Gaussian-shaped distributions made them asymmetric and their widths decreased. The synthetic quenching constants were extracted within 10% accuracy by application of the artificial double-exponential model.

However, the underlying synthetic data represented known distributions. To calculate an unknown distribution from decay data or excited state quenching experiments alone is an ill-defined problem.\(^{25}\) Therefore we retain the double-exponential approach as a phenomenological tool for examining real systems where unknown distributions of lifetimes are expected to be present.

We investigated the quenching behavior of the dye tris(4,7'-diphenyl-1,10'-phenanthroline)Ru(II) perchlorate, dissolved in polystyrene, on the basis of the considerations mentioned above. The goal was to establish a reasonable description for the nonlinear Stern–Volmer plots and the nonexponential decay by application of methods that have been successfully applied to surface-adsorbed dyes. The dynamic nature of the quenching process is demonstrated, as well as effects arising from enhanced dye loading. The observed quenching behavior and decay will be discussed with regard to the structural properties of the polystyrene matrix.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Tris(4,7'-diphenyl-1,10'-phenanthroline)Ru(II) perchlorate (denoted as RuPhPhe) was dissolved via

the apolar solvent methyl ethyl ketone in polystyrene (Aldrich, MW = 240 000). Layers were cast by a knife coater. The final concentration of the dye in the layer was \( c = 10^{-3} \) M and alternatively \( c = 10^{-2} \) M. A transparent 100-μm polyester sheet (Mylar, DuPont) or a glass slide was used as a support for the approximately 6-μm-thick polystyrene layers. The samples were stored for 24 h under 90 °C to remove solvent residuals from the polymer.

**Luminescence Intensity Measurements.** Luminescence intensity data were obtained with a SPEX Fluorolog II fluorometer. For the intensity quenching experiments, the excitation wavelength was \( \lambda_{ex} = 470 \) nm and emission was monitored at a wavelength of \( \lambda_{em} = 610 \) nm. Measurements were performed at 25 ± 1 °C.

The samples were fixed with a quartz plate in a steel chamber, with the transparent support facing the incident beam and the oxygen-sensitive layer exposed to the gas stream inside the chamber.

The intensity measurements were performed in front face technique with an angle of 22° between the incident beam and the axis of emission optics. The data are corrected for background fluorescence from the polystyrene polymer and the polyester support (which did not exceed 1.6% of the total emission intensity at \( \lambda_{em} = 610 \) nm in the worst case of the 1 mM sample under 100% oxygen).

Quantum yields were determined by a modified Parker–Rees method, with Rhodamine 101 in ethanol as the reference (\( \Phi_{ref} = 1 \)). For this measurement, identical optical geometries were chosen for both reference solution and polymer samples. Absorption values at the wavelength of excitation of the quantum yield experiment were determined by a Shimadzu UV-PC 2101 spectrophotometer. Quantum yield measurements were performed at ambient air. The respective values \( \Phi_0 \) in the absence of oxygen were calculated by regarding the known intensity quenching behavior \( I_0/I_{air} \) of the respective sensors:

\[
\Phi_0 = \Phi_{air}I_0/I_{air} \tag{7}
\]

Gas mixtures were established by a UTAH Medical Products PGM-3 gas-mixing device. Nitrogen served as the inert gas component. For quenching experiments, oxygen content was varied in eight steps between 0% and 100% oxygen.

Since the concentration of oxygen in the polymer is not accurately known due to the lack of knowledge about accurate gas solubility, quencher concentrations are expressed as oxygen partial pressures (\( PO_2 \)). The validity of Henry's law in the applied region of partial pressure will be discussed.

**Luminescence Decay Time Measurements.** Decay time measurements were performed with a PRA LN102 dye laser, pumped by a PRA LN103 nitrogen laser, and a fast PMT (Valvo 56 TVUP with 2 ns rise time), coupled to a Tektronix DSA 601A sampling oscilloscope. The exciting pulse (\( \lambda_{ex} = 470 \) nm, pulse width \( t = 300 \) ps) was treated as a δ-pulse with respect to the measured decay time components. No deconvolution was necessary. Emission was monitored through a 550-nm cut-off filter (Schott KV550). Measurements were performed at 25 ± 1 °C.


![Figure 1](image_url) **Figure 1.** Stern–Volmer plots of RuPh2phen dissolved in polystyrene (c = 1 mM): Data of intensity (squares) and preexponentially weighted mean lifetime \( \tau_m \) (triangles) vs applied partial pressure of oxygen \( PO_2 \); solid line, best fit of the two-component model (eq 5) to the intensity data; dashed lines, schematic representation of the respective quenching constants \( K_{q1} \) and \( K_{q2} \) of the fit.

The geometry of decay time measurements involved a 30° angle of incidence for the exciting laser pulse respective to the plane of the sample and a 90° angle between exciting pulse and emission optics.

Decay curves were fitted by a Gauss–Newton least-squares algorithm to a superposition of a minimum number of single-exponential decays. The decay curves exhibited very short (a few nanoseconds) but strong components which are attributable to the fluorescence of the polymer and of the polyester support. These short components were as far as possible omitted in the fits.

**X-ray Diffraction Measurements.** X-ray diffraction patterns were recorded with a Siemens D 501 diffractometer, using a Cu Kα radiation source.

**RESULTS AND DISCUSSION**

**Intensity and Lifetime Quenching Experiments.** The Stern–Volmer intensity plot of RuPh2phen in polystyrene is represented in Figure 1 (squares). On examining oxygen partial pressures up to 1 atm, the downward curvature of the plot becomes apparent.

A two-component model (eq 5) sufficed to fit the corrected intensity quenching data of the layer containing 1 mM dye (solid line). The analysis revealed two intensity-based quenching constants, \( K_{q1}^{\text{int}} \) and \( K_{q2}^{\text{int}} \), differing by a factor of 4 (Table 1). These parameters are schematically represented as dashed lines in Figure 1. The fractional contributions of the components are listed in Table 1.

Excited state decays were recorded at various quencher concentrations. After neglecting the very short (a few nanoseconds) contributions of the polymer and the support, all decay curves could be conveniently described by a double-exponential model (represented by eq 2 with \( m = 2 \)). This two-component approach is justified as the simplest applicable phenomenological
Table 1. Comparison of Stern–Volmer Quenching Constants

<table>
<thead>
<tr>
<th>components</th>
<th>intensity data</th>
<th>lifetime data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K'_q$ (Torrs$^{-1}$)</td>
<td>$S$</td>
</tr>
<tr>
<td>1</td>
<td>$(3.6 \pm 0.2) \times 10^{-3}$</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>$(0.8 \pm 0.2) \times 10^{-3}$</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Fitted parameters $K'_q$ and $S$ of the two-component analysis (eq 5) of intensity quenching data; slopes $K_m$ obtained from the linear Stern–Volmer quenching behavior of the individual lifetimes; lifetimes $t_0$, respectively, the relative amplitudes $B_0$ in the absence of the quencher.

Figure 2. Excited state decay of RuPhphen dissolved in polystyrene ($c = 1$ mM): solid line, best fit using a double-exponential function (eq 2). Residual plot.

Figure 3. Dependence of the reciprocals of the two main lifetimes of RuPhphen dissolved in polystyrene ($c = 1$ mM) on the applied partial pressure of oxygen $PO_2$: $1/t_1$ (full squares); $1/t_2$ (empty squares).

model. A typical decay curve is shown in Figure 2 along with the residuals of the fit. The unquenched lifetimes $t_0$ and $t_0'$ differ by a factor of ~2 (Table 1); the relative amplitudes $B_1$ and $B_2$ are almost constant for all applied quencher concentrations. The higher relative amplitude $B_2$ varies between 0.51 and 0.57 for the applied oxygen concentrations.

The dependence of the reciprocals of the two lifetimes on quencher concentration is shown in Figure 3. The plots appear fairly linear. The slopes and unquenched lifetimes give the lifetime-based quenching constants $K_{q1}$ and $K_{q2}$ (Table 1). It is remarkable that the higher of the two lifetimes corresponds to the lower quenching constant, as indicated in Table 1.

Description of intensity and lifetime quenching behavior of this system within the two-component model is adequate for both intensity and lifetime quenching. Calculation of the preexponentially weighted mean lifetime (eq 4) and its quenching behavior (triangles in Figure 1) leads to matching intensity and lifetime Stern–Volmer plots, indicating an exclusively dynamic quenching process.

Behavior in Liquid Solution. It is of importance to compare the results derived from the solid state sample with the behavior of RuPhphen in liquid solution (absolute ethanol, at 25°C). The lifetime of the single-exponential decay is $t_0 = 5.2 \pm 0.1$ μs, the quenching constant is $K_m = 0.12 \pm 0.02$ Torr$^{-1}$, and the molar quenching constant is $K_{m,M} = 9700 \pm 100$ M$^{-1}$. A liquid low-viscosity solution represents a homogeneous environment for dissolved molecules. Solvent relaxation is rapid compared to the lifetime of the excited state of the indicator. The Stern–Volmer plots of both intensity and lifetime are linear and match, as expected for indicators dissolved in a homogeneous environment.

X-ray Diffraction of the Polymer. To support the interpretation of the nonexponential decay in the polymer, the structure of the polystyrene film was verified by examination of the X-ray diffraction pattern of the polymer. For this purpose, polystyrene layers were coated on glass slides. The diffraction patterns had smooth shapes for samples both with and without indicator loading, identical within the accuracy of sample positioning in the diffractometer, and typical for a fully amorphous polymer. They represent continuous distance distributions of scattering centers (electron density fluctuations), providing static spatial disorder of the indicator's microenvironment (inhomogeneity of the medium). Partially crystalline polystyrene would have shown pronounced Bragg reflection peaks superimposed on the signal from the amorphous regions.

In the following, possible sources other than spatial disorder leading to a nonexponential decay profile or a nonlinear Stern–Volmer plot are addressed:

1. Nonexponential decay may be caused by transient diffusion effects. Based on the diffusion coefficient of oxygen in polystyrene, these effects are expected in the range of up to $t = 10$ ns for this material. They are therefore irrelevant for the observed decay.

2. Nonlinear Stern–Volmer plots may be caused by the appearance of unquenchable background emission, originating for

example from the polyester support. This influence has been corrected. Unquenchable emission from aggregates of the complex might also be regarded. The Ru(II) complex is dissolved in amorphous polystyrene via its aromatic ligands, and there is no evidence for precipitation of the indicator at a concentration of \( c = 1 \text{ mM} \) (vide infra).

(3) Dual or continuous gas sorption in the polymer may also have an influence on the curvature of the intensity Stern–Volmer plot.\(^{12}\) Inhomogeneity of a glassy polymer represents a distribution of site geometries and interaction energies not only for the dissolved indicator but also for gas sorption. These density fluctuations have been approximated by the simple division of the polymer into bulk and holes, thus leading to a dual-sorption mechanism\(^{31}\) describing the diffusion and condensation behavior of gases in glassy polymers. Recently this model was refined by introduction of a continuous distribution of Langmuir isotherms.\(^{32}\)

Based on the results obtained with the help of the dual-sorption model, which is still a convenient approach, this influence is negligible for sorption of a noncondensing gas in glassy polystyrene up to 1 atmosphere.\(^{31}\)

Thus, the only source of nonexponential decay and nonlinear Stern–Volmer response is expected to be inhomogeneity due to spatial disorder of the amorphous environment. The modeled two-component excited state decay has to be interpreted as caused by such an underlying distribution. This is appropriate also for the intensity Stern–Volmer behavior; it is not sufficient to postulate the existence of two distinct environments.

The appearance of two different quenching constants in the intensity as well as lifetime Stern–Volmer analysis is due to the phenomenological double-exponential model. It cannot be concluded that there are two different diffusion processes involved.

Effects of Tempering. To examine the influence of the thermal history of the sample, the membrane was stored for several days at a temperature \( T = 120^\circ \text{C} \), which is above the glass transition temperature \( T_g \) (which is \( T_g = \approx 100^\circ \text{C} \) for the employed polystyrene type).\(^{33}\) A third lifetime \( (\tau_3 = 1.3 \mu\text{s}) \) appeared in the excited state decay, showing no significant response to the presence of the quencher. This may be attributed to the formation of aggregations of the indicator since the decay of neat crystals of RuPhphen under air is dominated by a lifetime of \( \tau = 1.4 \mu\text{s} \). The excited state decay of neat crystals is not significantly quenched by oxygen, since the diffusion of the quencher in crystals is rather limited.

The temperature dependence of the diffusion coefficient of molecules in a medium follows an Arrhenius law, providing a constant activation energy for diffusion \( E_d \). At the glass transition temperature \( T_g \) of a polymer, a discontinuity appears in the Arrhenius plot: \( E_d \) for diffusion is smaller above \( T_g \) compared to \( E_d \) at ambient temperature.\(^{34}\) Aggregation can therefore proceed in the sample, which has been stored for several days above \( T_g \), due to both enhanced temperature and reduced activation energy.

The value of the main lifetime component of the neat crystals of the indicator is short compared to the lifetime of the dye in solution. This is due to the strong intermolecular interactions between the molecules in a crystal.

The interference of this short component restricts the possibility of conveniently describing the expected distribution of relaxation rates of the dissolved molecules accurately within the double-exponential model. Instead, only average lifetimes with nonlinear quenching behavior can be observed.

Spectral and quenching properties of the 1 mM sample are not significantly affected by the tempering process since the concentration of the precipitates is very low.

Concentration Effects. To enhance the luminescence intensity, polystyrene layers with a 10-fold higher dye loading (10 mM) have been prepared. The Stern–Volmer intensity plot remains almost the same compared to the more dilute (1 mM) layer. The excited state decay exhibits the short lifetime attributed to aggregates of the indicator already in the freshly prepared layer: As a consequence of the high concentration, the dye was not completely dissolved. Dependent on manufacturing conditions, aggregation of the indicator even at room temperature is more or less pronounced. Similar effects have been reported for the dye tris(2,2'-bipyridyl)Ru(II) dichloride in poly(vinyl alcohol) and poly(vinylpyrrolidone) matrices\(^{36}\) and recently for RuPhphenCl\(_2\) in plasticized cellulose acetate.\(^{35}\)

For this 10 mM sample, the relative contribution of the aggregates to the decay in absence of the quencher was \( B_0 = 0.1 \) and increased to \( B_0 = 0.6 \) after thermal treatment above \( T_g \) for 4 days. The thermal treatment also caused a decrease in the Stern–Volmer slopes. An analysis of the intensity quenching data with respect to the two-component model shows that all relevant parameters are affected (Table 2). The emission spectrum shows a red shift upon tempering (from \( \lambda_{\text{max}} = 612 \text{ nm} \) in the native sample to \( \lambda_{\text{max}} = 630 \text{ nm} \)). The emission of neat crystals of the dye has its maximum at \( \lambda_{\text{max}} = 665 \text{ nm} \). Therefore, the redshift is likely due to strong precipitation.

Independent of the thermal history of the 10 mM sample, a calculation of the preexponentially weighted mean lifetime \( \tau_n \) for all quencher concentrations results in a lifetime Stern–Volmer plot that significantly deviates from the Stern–Volmer intensity plot for this highly concentrated sample.\(^{17}\) In view of the dynamic nature of quenching reported for the 1 mM sample, this deviation is rather an artifact of the multieponential analysis of a complex decay than real static quenching.

Quantum Yields. The quantum yield \( \Phi_0 \) in absence of the quencher was \( \Phi_0 = 0.6 \pm 0.1 \) for both the 1 and 10 mM samples. After thermal tempering of the 10 mM sample, \( \Phi_0 \) dropped to 0.21 \pm 0.08. These values are not corrected for possible multiple

<table>
<thead>
<tr>
<th>Temperature Treatment</th>
<th>prior to tempering</th>
<th>after tempering</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_0 )</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>( f_0 )</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>( k_w ) (Torr(^{-1}))</td>
<td>3.4 \times 10^{-3}</td>
<td>2.8 \times 10^{-3}</td>
</tr>
<tr>
<td>( k_w ) (Torr(^{-1}))</td>
<td>1.0 \times 10^{-3}</td>
<td>0.5 \times 10^{-3}</td>
</tr>
</tbody>
</table>

* Measurements at room temperature.


reflections of the emission at the polymer interfaces and thus represent rather lower limits. The decrease in quantum efficiency upon thermal treatment is in part caused by enhanced emission scattering by the aggregates.

Generally the observed behavior of this highly loaded sample shows the difficulties one has to be aware of by overloading a sensor layer with the dye to be capable of highest possible luminescence intensities.

A possible alternative to the chosen phenomenological mathematical treatment in this work is the application of lifetime distribution models on a sound physical basis. Investigations on that point are in progress.

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