

# Static and Dynamic Quenching of Luminescent Species in Polymer Media

Paul Hartmann,<sup>1,2</sup> Marc J. P. Leiner,<sup>1,3</sup> and Max E. Lippitsch<sup>2</sup>

Received October 18, 1993

A method developed for quantitative determination of static and dynamic contributions to luminescence quenching is applied to Ru(II) complexes in polymer matrices (silica gel and polystyrene), quenched by oxygen. This method is based on both intensity and lifetime quenching experiments. The curvature of intensity Stern–Volmer plots is related to the results.

**KEY WORDS:** Lifetime; quenching; Ru(II) complexes; oxygen; silica gel; polystyrene.

## INTRODUCTION

In a homogeneous environment (e.g., a liquid solution) most luminescent species show rather simple photophysical and quenching behavior, like monoexponential decay or linear Stern–Volmer plots [1–3]. On the other hand, for Ru(II) complexes entrapped inside a porous silica gel or dissolved in polymers like polystyrene [4], multiexponential decays as well as downward-curved Stern–Volmer plots can be observed [5–7]. We have investigated several systems of Ru(II) complexes immobilized in solid matrices and address in this paper the question of the presence or absence of static quenching in our samples. Possible mechanisms leading to the observed quenching behavior are discussed [5,8,9].

## THEORY

A model for quenching of an indicator's luminescence intensity in any environment including both static and dynamic quenching as well as unquenchable lumi-

nophors at various quencher concentrations  $[Q]$  is presented in Eq. (1):

$$\frac{I_0}{I} = e^{k_s[Q]} \left[ \frac{A}{1 + K_{sv}[Q]} + (1 - A) \right]^{-1} \quad (1)$$

where  $I$  and  $I_0$  are the intensities in the presence and absence, respectively, of the quencher;  $k_s$  is the association constant for static quenching;  $A$  is the fraction of statically unquenched molecules which are subject to dynamic quenching; and  $K_{sv}$  is the dynamic quenching constant.

Static quenching reduces the number of emitting molecules by the factor  $\exp(k_s[Q])$ . The fraction  $(1 - A)$  remains inaccessible for the quencher, whereas the remaining fraction  $A$  is subject to *dynamic* quenching. If there are more unique environments present, this model has to be expanded correspondingly, for example, by a sum of dynamic quenching processes with different quenching constants.

The pulse response of several independently emitting states can be described within the achieved accuracy of the experimental data as a sum of several single-exponential decays.

Static quenching lowers the amplitudes with respect to the unquenched parameters, whereas dynamic quenching appears as a change of time constants.

<sup>1</sup> AVL List GmbH, Kleiststraße 48, A-8020 Graz, Austria.

<sup>2</sup> Institut für Experimentalphysik, Karl-Franzens-Universität, A-8010 Graz, Austria.

<sup>3</sup> To whom correspondence should be addressed.

In the following, a model is briefly outlined that is applicable to luminophors with multiexponential decay:

The intensity  $I$  relative to its unquenched value  $I_0$  of a sample containing both static and dynamic quenching processes at any quencher concentration can be expressed as [6]

$$\frac{I}{I_0} = f_{\text{ns}} f_{\text{nd}} \quad (2)$$

where  $f_{\text{ns}}$  is the fraction of remaining excited molecules after static quenching, and  $f_{\text{nd}}$  is the fraction of excited molecules which remains unaffected by static quenching and is *not* quenched dynamically (the inverse fraction  $1/f_{\text{nd}}$  has the meaning of an average lifetime Stern–Volmer representation). This fraction can be expressed within our model as

$$f_{\text{nd}} = \sum_{j=1}^m \left( \frac{B_{0j} \tau_{0j}}{\sum (B_{0j} \tau_{0j})} \left[ \frac{g_{0j}}{1 + K_{svj} [Q]} + (1 - g_{0j}) \right] \right) \quad (3)$$

where  $j$  is the index of the  $j$ th component of the decay time fit,  $g_{0j}$  is the fractional contribution of excited states accessible for dynamic quenching processes,  $B_{0j}$  is the unquenched amplitude of the  $j$ th decay time component, and  $\tau_{0j}$  the unquenched time constant of the  $j$ th decay time component. This expression includes the fact that the quencher-sensitive decay time components obtained in the fits do not exhibit simple Stern–Volmer quenching. The reason is that the physics behind the decay behavior is more complicated than suggested by the simple multiexponential decay model (distributions of decay times in heterogeneous samples or the presence of unresolved decay time components).

With  $I/I_0$  data from intensity-quenching experiments and the quenching behavior of  $f_{\text{nd}}$  (3) derived from lifetime measurements, we are able to calculate  $f_{\text{ns}}$  and therefore to compare static and dynamic quenching of our samples, regardless of the specific model used for intensity quenching.

## EXPERIMENTAL

To verify the theoretical approach we used different samples with Ru(II) complexes as the luminescent species. Oxygen served as the quencher of the excited states. The preparation of the samples in detail is given elsewhere [4,10].

### Sample 1

Tris(2,2'-bipyridyl) Ru(II) chloride (denoted Rubpy) (Strem Chemicals) was adsorbed on silica gel and embedded in a polysiloxane as described in Ref. 10.

### Sample 2

Tris(4,7'-diphenyl-1,10'-phenanthroline) Ru(II) perchlorate (denoted Rudiph) was dissolved in polystyrene ( $c=10^{-2}$  M). A transparent 175- $\mu\text{m}$  polyester sheet (Mylar, Dupont) acts as a support for the 6- $\mu\text{m}$ -thick polystyrene layer.

All measurements were performed at  $25 \pm 1^\circ\text{C}$ .

Emission spectra and luminescence intensity data were obtained with a SPEX Fluorolog II fluorometer.

Gas mixtures were established with a UTAH Medical Products PGM-3 gas mixing device. Nitrogen served as the inert gas component.

Decay time measurements were performed with a PRA LN102 dye laser (pulse width: 300 ps), pumped by a PRA LN103 nitrogen laser, and a fast photomultiplier (Valvo 56 TUVF with a 2-ns rise time), coupled with a Tektronix DSA 601A digital signal analyzer.

## RESULTS

Quencher concentrations are expressed as oxygen partial pressures ( $PO_2$ ). It is assumed that Henry's law is obeyed in the applied region of partial pressure.

Lifetimes and their relative amplitudes resulting from a fit of the experimental decay data with a multiexponential model are given in Table I for both samples. Contributions due to background fluorescence from the matrix are neglected.

The measured intensity quenching data  $I_0/I$  (corrected for background fluorescence) and the values for  $1/f_{\text{nd}}$  calculated from lifetime measurements are shown in Fig. 1.

Quenching of Rubpy on silica gel (sample 1) is mainly dynamic. A slight apparently constant static fraction of several percent seems to be insignificant due to experimental errors.

Quenching of Rudiph in polystyrene (sample 2) appears to be due to both static and dynamic components. The fraction  $f_{\text{ns}}$  of the excited states which are *not* quenched statically is shown in Fig. 2.

It is important to compare the results derived from the samples with the behavior of the chosen dyes in liquid solution: Stern–Volmer plots of Rubpy and Rudiph

**Table I. Lifetimes and Relative Amplitudes Resulting from the Fit of Experimental Decay Curves in the Absence of the Quencher to a Multiexponential Model\***

Component	Sample 1			Sample 2		
	1st	2nd	3rd	1st	2nd	3rd
$\tau_0$ ( $\mu\text{s}$ )	$1.55 \pm 0.04$	$0.775 \pm 0.005$	$0.117 \pm 0.005$	$5.44 \pm 0.01$	$1.17 \pm 0.03$	$0.10 \pm 0.02$
$B_0$	$0.33 \pm 0.02$	$0.55 \pm 0.01$	$0.12 \pm 0.01$	$0.84 \pm 0.01$	$0.09 \pm 0.01$	$0.07 \pm 0.01$

\*Sample 1: Rubpy adsorbed onto silica gel and embedded in polydimethylsiloxane. Sample 2: Rudiph dissolved in polystyrene ( $c=10^{-2} M$ ).

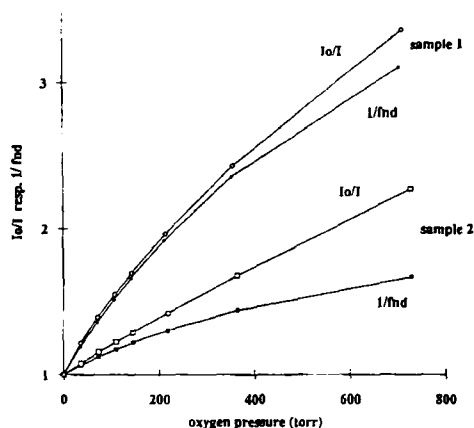


Fig. 1. Quenching behavior of the inverse fraction  $I_0/I$  with respect to the measured luminescence intensity,  $I_0/I$ , for Rubpy entrapped in silica gel and embedded in polysiloxane (sample 1) and Rudiph in polystyrene (sample 2).

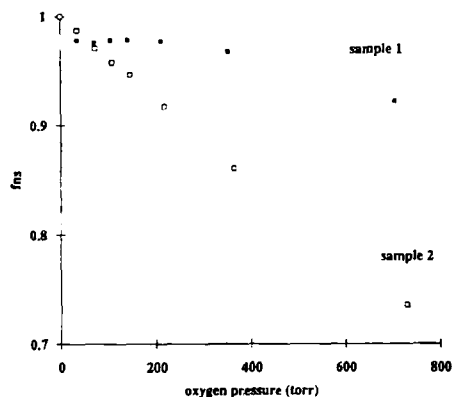


Fig. 2. Fraction  $f_{ns}$  of Rubpy entrapped in silica gel and embedded in polysiloxane (sample 1) and Rudiph in polystyrene (sample 2).

are perfectly linear in liquid solvents. Intensity and lifetime quenching experiments match very well, therefore no static quenching is present in homogeneous solutions. Lifetimes show a pure monoexponential behavior.

## DISCUSSION

### Sample 1

It is evident from Figs. 1 and 2, that no significant static quenching appears in the system Rubpy, entrapped inside silica gel and embedded in polysiloxane. For such a complex environment it is not surprising that decay kinetics require more than a simple multiexponential analysis. However, the multiexponential approach gives good fits of the decay time data, but with restricted physical meaning of the resulting lifetime components. This restriction is compensated for by the introduction of a model for the apparent quenching behavior of  $f_{nd}$  (3). On returning to a description for the intensity Stern–Volmer behavior for sample 1, model (1) cannot be applied directly. For a phenomenological description without direct mechanistic content, it can be modified in that  $k_s=0$  and the term describing dynamic quenching has to be replaced by a sum of (at least) two similar expressions.

### Sample 2

For sample 2 (Rudiph dissolved in polystyrene) the deviations of the lifetime from the intensity Stern–Volmer quenching behavior rises with oxygen concentration, which is evidenced by the apparently linearly decreasing fraction  $f_{ns}$  in Fig. 2 [for small arguments  $\exp(k_s[Q])$  in model (1) is expandable to  $(1+k_s[Q])$ ].

The quenching behavior of the inverse of the remaining fraction  $f_{nd}$  (Fig. 1) is satisfactorily covered by a model introducing two lifetimes instead of the first component ( $\tau_1 = 5.44 \mu\text{s}$ ) revealed by the fit of the excited-state decay (Table I): One of them is dynamically quenched by oxygen. The other component is inaccessible by the quencher, which is manifested in the lifetime Stern–Volmer plot as an unquenchable background. Within this treatment a Stern–Volmer plot of luminescence intensity is received, which can be summarized by model (1).

The parameter  $g_{01}$  (3) is, in this case, practically identical to the fraction  $A$  of model (1).

Excited states of molecules may be deactivated statically by adjacent quencher molecules [8]. The presence of water in the relatively thin layers also has to be considered [11], whereas diffusion and surface effects [12] can definitely be ruled out by theoretical considerations.

The consequence of this different lifetime and intensity quenching behavior has to be stressed: It is clearly not sufficient to characterize the quenching behavior of related samples only by means of intensity data. It is not sufficient to attribute the comparatively low curvature of the intensity Stern–Volmer plot of sample 2 to a well-defined solvation of the indicator Rudiph in the polystyrene matrix (which contains an aromatic structure as well), where the luminophor would exist within only one well-defined environment on an average time scale. For the above results it appears that, in this case, the curvature rather originates from a complex superposition of photophysical processes, possibly containing static quenching and dynamic quenching fractions, and an unquenchable component.

## CONCLUSIONS

This work demonstrates clearly the necessity of applying more predicative parameters and techniques, for example, lifetime and its measurements, to explore the

mechanisms responsible for the behavior of intensity-based experiments.

## ACKNOWLEDGMENTS

We would like to thank I. Klimant for preparation of sample 2 and interesting discussions. We also are indebted to the AVL Company and to FWF (No. S 5703) for funding the project and to Professor H. Kauffmann for supplying the dye laser.

## REFERENCES

1. C. J. Timpson, C. C. Carter, and I. J. Olmsted (1989) *J. Phys. Chem.* **93**, 4116–4120.
2. J. N. Demas, E. W. Harris, and R. P. McBride (1977) *J. Am. Chem. Soc.* **99**, 3547–3551.
3. J. R. Lakowicz (1982) *Principles of Fluorescence Spectroscopy*, Plenum Press, New York.
4. W. R. Gruber, I. Klimant, and O. S. Wolfbeis (1993) *Proc. SPIE* **1885**, 448–457.
5. E. R. Carraway, J. N. Demas, B. A. DeGraff, and J. R. Bacon (1991) *Anal. Chem.* **63**, 337–342.
6. E. R. Carraway, J. N. Demas, and B. A. DeGraff (1991) *Anal. Chem.* **63**, 332–336.
7. M. E. Lippitsch, J. Pusterhofer, M. J. P. Leiner, and O. S. Wolfbeis (1988) *Anal. Chim. Acta* **205**, 1–6.
8. M. R. Eftink (1991) in J. R. Lakowicz (Ed.), *Topics in Fluorescence Spectroscopy, Vol. 2*, pp. 53–126.
9. X.-M. Li and K.-Y. Wong (1992) *Anal. Chim. Acta* **262**, 27–32.
10. O. S. Wolfbeis, M. J. P. Leiner, and H. E. Posch (1986) *Mikrochim. Acta* **1986**, 359–366.
11. J. Janata (1992) *Anal. Chem.* **64**, 921A–927A.
12. S. Wolfgang and H. D. Gafney (1983) *J. Phys. Chem.* **87**, 5395–5401.