

APPLICATION NOTE

Photoinduced Electron-Transfer Quenching of Long-Lived Luminescent Ru(II) Complexes

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EDINBURGH
INSTRUMENTS

INTRODUCTION

Luminescence quenching refers to any process by which the emission intensity of a chemical species decreases in the presence of an external agent (the analyte itself or a relay species in the case of luminescent photochemical sensors). This competitive pathway in the radiative electronic excited state desactivation may occur by electron, proton or energy transfer to/from the quencher. Dynamic quenching in isotropic solution obeys the so-called Stern-Volmer equation (1), where τ_0 and τ are the excited state lifetimes in the absence and in the presence of the quencher (Q), respectively, [Q] is the quencher concentration, and the Stern-Volmer constant (K_{sv}) is actually the product of the unquenched excited state lifetime (τ_0) and the kinetic quenching rate constant (k_q).^{1,2} A long-lived excited state and a fast photochemical process provide the highest analytical sensitivity, therefore, phosphorescent ruthenium(II) polypyridyl complexes are particularly suitable for this purpose.³ The excited state responsible for the emission of these dyes is a triplet metal-to-ligand charge transfer (³MLCT) one, generated quantitatively by very fast intersystem crossing from the initial singlet MLCT state reached upon the absorption of light in the uv to blue-green region. The presence of a metal core determines their characteristic phosphorescence lifetimes (ca. 0.1 μ s to 7 μ s) at room temperature.

$$\frac{\tau_0}{\tau} = 1 + K_{sv}[Q] \quad (1)$$

The bimolecular deactivation of the ³MLCT state can proceed by electron transfer reactions with a variety of organic and inorganic quenchers.⁴ The feasibility of a photoinduced electron transfer is determined by the redox potentials of the luminescent excited state of the dye and those of the quencher.

In addition to acting as electron, energy and proton transfer partners, and their relatively long emission lifetimes, ruthenium(II) polypyridyl complexes offer other advantages for their use as phosphorescent indicator dyes to develop *optical chemical sensors*: high (photo)stability, strong absorption in the blue and emission in the red, and tunability of their photochemical and physical properties by a judicious selection of the coordinating polyazaheterocyclic ligands.³ Examples of relevant analytes monitored with Ru(II)-based sensors are O₂, pH, CO₂, humidity, temperature, metal ions, herbicides, etc. Dedicated instruments for oxygen monitoring are now commercially available, and are phasing out the widely used Clark-type electrodes for in situ water analysis.⁵



FLS980 Spectrometer

METHODS AND MATERIALS

Luminescence lifetimes were measured by TCSPC in a FLS980-xD2-T Photoluminescence Spectrometer equipped with a sub-ns 463 nm laser diode source, and a 500 nm-blazed double monochromator in the emission channel. A 467-nm bandpass

interference filter was used to polish the laser diode blue emission. Luminescence from the dye solutions was detected at 620 nm with a red-sensitive photomultiplier tube. The emission lifetimes were extracted from the exponential raw decay data (4096 channels) by using a non-linear Marquardt fitting algorithm contained in the F980 software package. All measurements were performed in aqueous solutions of tetrasodium tris(diphenyl-1,10-phenanthroline-4,7-disulfonate)ruthenate(II), abbreviated Na₄[Ru(dpds)₃], the synthesis of which has been described.⁶ Methyl viologen dichloride dihydrate (MV²⁺, Fluka) and potassium hexacyanoferrate(III) (abbreviated HCF³⁻, Sigma-Aldrich) were used as quenchers of the Ru(II) polypyridyl luminescence. The luminescence lifetime titration was carried out by addition of the corresponding μ L aliquots of a concentrated stock of the quencher directly on 2.00 mL of a 2.45 $\times 10^{-5}$ mol L⁻¹ solution of the Ru(II) dye. Type I water was from a Millipore Direct-Q3-UV system (Bedford, MA). All the experiments were run at atmospheric pressure (~715 Torr) and 25.0 °C.



The new FLS1000. The next generation of photoluminescence spectrometer.

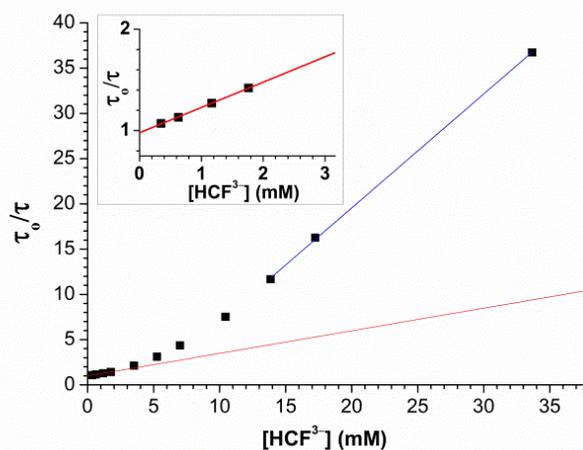
RESULTS - DISCUSSION

The luminescence lifetime of [Ru(dpds)₃]⁴⁻ in air-equilibrated water, both in the absence and in the presence of increasing concentration of quencher, was measured from the fit of the (purely) exponential decay data (Table 1). Stern-Volmer plots (Figure 1) have been used for the analysis of the μ s lifetime quenching ($\tau_0 = 992$ ns) in the absence of quencher. This initial lifetime progressively decreases due to the increase of the quencher concentration (Figure 1).

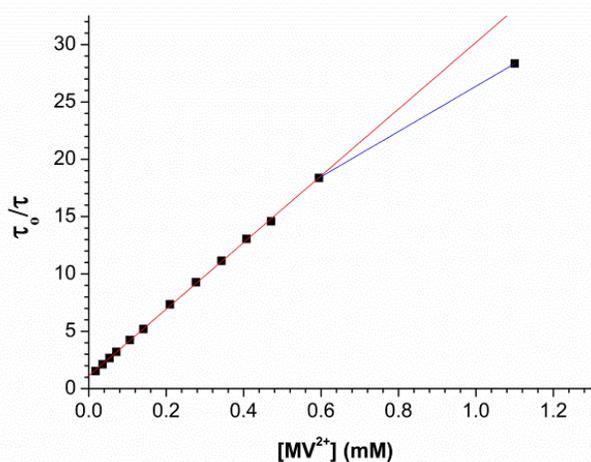
Table 1: Luminescence lifetime quenching of [Ru(dpds)₃]⁴⁻ by potassium hexacyanoferrate (III) (HCF³⁻) and methyl viologen (MV²⁺) in aerated water (uncertainty: $\pm 0.5\%$).

τ (ns)	[HCF ³⁻] (mM)	τ (ns)	[MV ²⁺] (mM)
992	0.00	992	0.00
926	0.35	646	0.02
877	0.63	468	0.04
783	1.17	373	0.05
700	1.76	310	0.07
469	3.52	234	0.11
320	5.26	191	0.14
228	7.00	135	0.21
132	10.45	107	0.28
85.1	13.86	89.2	0.34
61.1	17.24	76.0	0.41
27.4	33.67	68.3	0.47
		54.1	0.59
		35.7	1.10

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(a)



(b)

Figure 1: Stern-Volmer plots for the luminescence lifetime quenching of $[\text{Ru}(\text{dpds})_3]^{4+}$ in aqueous media by a) hexacyanoferrate (III) and b) methyl viologen.

The resulting K_{SV} and k_{q} values are shown in Table 2 for different concentration ranges. Since $[\text{Ru}(\text{dpds})_3]^{4+}$ and the tested quenchers are charged species, a strong effect of the solution ionic strength on the photoinduced electron transfer rate is to be expected according to the Debye-Smoluchowski effect.⁷ Specifically, the powerful electrostatic repulsion of $^3[\text{Ru}(\text{dpds})_3]^{4+}$ and HCF^{3-} is severely attenuated upon increasing the ionic strength, so that the quenching rate constant increases 5-fold; conversely, the strong electrostatic attraction of $^3[\text{Ru}(\text{dpds})_3]^{4+}$ and MV^{2+} is weakened as the salinity of the medium increases, lowering the quenching rate constant 1.5-fold.

The 2-orders of magnitude difference between the quenching rate constants extrapolated at zero ionic strength must be attributed to the dramatic electrostatic effect, in spite of the much larger driving force of the photoinduced electron transfer quenching of $^3[\text{Ru}(\text{dpds})_3]^{4+}$ by HCF^{3-} compared to that of MV^{2+} (0.96 vs 0.16 V taking into account that the redox potentials of hexacyanoferrate(III), methyl viologen, and the photoexcited Ru(II) complex are 0.36, -0.44 and -0.60 V vs SHE⁸).

Table 2: Stern-Volmer (K_{SV}) and bimolecular quenching constants (k_{q}) extracted from the linear fits to eq.1 of the luminescence lifetime-based data in Figure 1.

Quencher	Conc. range (mM)	K_{SV} (mM^{-1})	k_{q} ($\text{M}^{-1}\text{s}^{-1}$)	r^2
$[\text{HCF}^{3-}]$	0.35 - 1.76	0.25	$(2.52 \pm 0.02) \times 10^8$	0.998
	10.45 - 33.67	1.26	$(12.70 \pm 0.05) \times 10^8$	0.999
$[\text{MV}^{2+}]$	0.02 - 0.47	29.07	$(2.90 \pm 0.07) \times 10^{10}$	0.999
	0.59 - 1.10	19.72	2.0×10^{10}	1.000

^aRegression coefficient of the corresponding linear fit.

CONCLUSION

A precise determination of photoinduced electron-transfer kinetics of photoexcited phosphors is possible with the FLS980 due to its capability of measuring luminescence lifetimes in the μs to ns region with no changes to the instrument hardware.

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