

A New Fluorescence Probe for Trace Metal Ions: Cation-Dependent Spectroscopic Properties

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The fluorescence behavior of a new bipyridyl ligand, 2,2'-bipyridyl-3,3'-diol (BPDO), was studied as a function of the metal ion complexed. At pH 7.6, the fluorescence of BPDO is strongly decreased by complexation to Cu(II), but binding to Zn(II) leads to an increase in fluorescence intensity. Time-resolved fluorescence measurements suggest that in the case of Cu(II), a nonfluorescent complex is formed, whereas in the presence of Zn(II), a new, longer decay component appears.

KEY WORDS: 2,2'-Bipyridyl-3,3'-diol; metal ions; cation dependence; fluorescence probe.

INTRODUCTION

Many attempts to design highly selective and sensitive fluorescent chelating agents for trace metal analysis have been described [1,2]. Upon complexation, these fluorescent indicators usually exhibit changes of their absorption and/or emission behavior that are more or less characteristic for the metal ion bound [3]. Furthermore, ligation to a cation can also lead to changes in fluorescence lifetime, thus introducing the emission lifetime as additional parameter for the discrimination between cations [4].

In this paper, the fluorescence behavior of 2,2'-bipyridyl-3,3'-diol (BPDO; Fig. 1) is studied as a function of the metal ion bound [5]. This bipyridyl ligand [5] was chosen as a potential fluorescent indicator for the fluorometric determination of trace metal ions [6] in aqueous solutions since bipyridyl ligands are well-known complexing agents for heavy metal ions showing high stability constants. The strongly fluorescent BPDO can exist in cis/trans isomeric forms and undergoes proton

transfer in the excited state (DPT) [5]. Also, TICT has been reported for BPDO [7].

EXPERIMENTAL

BPDO, copper sulfate, and zinc nitrate were dissolved in bidistilled water. For all the measurements, a phosphate buffer solution ($\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$, pH 7.6) was used. The concentration of BPDO was $7 \times 10^{-6} \text{ M}$. The fluorescence spectra were obtained with a Perkin Elmer LS 50 fluorometer. The optical densities of the samples were <0.1 at the chosen excitation wavelength. For the measurement of the fluorescence decay kinetics, the sample was excited with an MSG 800 N_2 laser (pulse width, 0.5 ns). The fluorescence was de-

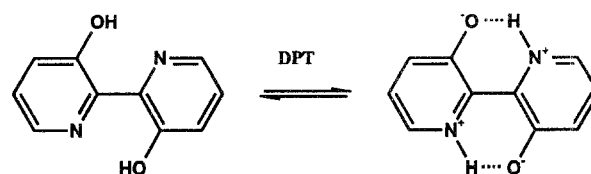


Fig. 1. 2,2'-Bipyridyl-3,3'-diol (BPDO).

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tected with an SP 104 silicon avalanche photodiode (without spectral decomposition) or with a monochromator and an R 4703 photomultiplier. Signal processing was done with an MFA 105 digital sampling oscilloscope, and for the deconvolution procedures the program DecaMax was used.

RESULTS

The effect of the bivalent metal ions Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), and Mn(II) on the fluorescence spectra of BPDO and its fluorescence decay kinetics was studied. Since both the fluorescence and the complexation behavior of BPDO are strongly pH dependent, all the experiments described here were performed at the same pH value, 7.6, where binding of BPDO to the metal ions has the strongest effects on its fluorescence.

Interestingly, depending on the nature of the metal ion bound, either a decrease or an increase in ligand fluorescence occurs as shown in Table I. It can be distinguished between cations such as Cu(II), which decrease the fluorescence intensity, and cations such as Zn(II), which increase the fluorescence intensity of BPDO.

Metal ions such as Cu(II), which decrease the ligand fluorescence, do not considerably influence the shape of the fluorescence spectrum of BPDO as follows from Fig. 2. Interestingly, for both Zn(II) and Cd(II), which enhance the ligand fluorescence, a short-wavelength shoulder at about 420 nm appears as shown for Zn(II) in Fig. 3.

To obtain more information on chelation-induced fluorescence changes, the fluorescence decay kinetics of BPDO were measured in the presence of either Cu(II) or Zn(II). The ligand BPDO shows a monoexponential fluorescence decay with a lifetime of 0.6 ns. The addition of Cu(II) does not lead to a shortening of the fluo-

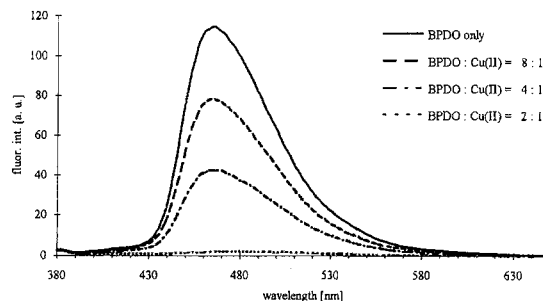


Fig. 2. Emission spectra of BPDO with Cu(II).

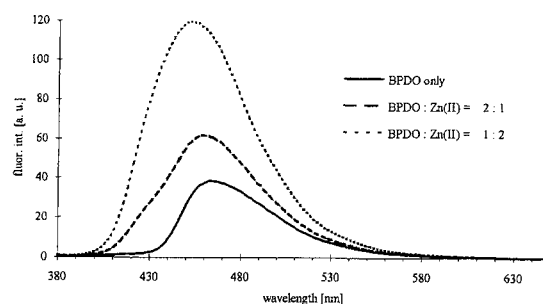


Fig. 3. Emission spectra of BPDO with Zn(II).

rescence lifetime, thus indicating that the observed decrease in BPDO fluorescence intensity is caused by a decrease in the number of emitting BPDO molecules. This suggests the formation of a nonfluorescent Cu(II)-BPDO complex.

In the presence of Zn(II), an additional decay component with a lifetime of 6.0 ns appears as shown in Table II. In the investigated Zn(II) concentration range, the amplitude of the long decay component increases sublinearly with increasing amounts of Zn(II) added, and correspondingly, the amplitude of the short decay component decreases.

The parallel increase in both the emission intensity of the short-wavelength shoulder at about 420 nm and the amplitude of the long decay component suggests a relation between the effects. This relation is further confirmed by the fact that the contribution of the long decay component depends on the emission wavelength (96% at 424 nm and 68% at 500 nm, respectively, for BPDO:Zn(II) = 1:2).

CONCLUSION

For the first time, the fluorescence behavior of complexes of BPDO with various metal ions was studied.

Table I. Spectral Properties of BPDO

Metal ion	Relative fluorescence intensity (AU)	Max. emission wavelength (nm)
None	100	467
Zn(II)	160	460
Cd(II)	114	463
Pb(II)	95	467
Mn(II)	96	467
Co(II)	19	467
Ni(II)	5	471
Cu(II)	<1	n.d.

Table II. Fluorescence Intensity Decay of BPDO

Substance	Amplitude		Fluorescence intensity		
	a_1^a	a_2^b	I_1^a	I_2^b	I_{total}
BPDO	47.5 ± 1.0	0.00	28.5 ± 0.5	0.0	28.5 ± 1.0
BPDO:Zn ^(II) (2:1)	41.0 ± 1.0	2.9 ± 1.0	24.6 ± 0.5	17.4 ± 0.3	42.0 ± 0.6
BPDO:Zn ^(II) (1:2)	30.5 ± 1.0	8.8 ± 0.5	18.3 ± 0.5	52.8 ± 3.0	71.1 ± 3.0

^a For $\tau_1 = (0.6 \pm 0.1)$ ns.

^b For $\tau_2 = (6.0 \pm 0.5)$ ns.

The emission spectra of the ligand are only slightly dependent on the metal ion complexed but the fluorescence intensity is strongly affected by ligation. In the presence of Cu(II), the ligand emission strongly decreases, whereas the addition of Zn(II) causes an enhancement of the fluorescence. Time-resolved fluorescence measurements suggest that in the case of Cu(II), the fluorescence decrease is caused by the formation of a nonfluorescent Cu(II)–BPDO complex. Chelation-enhanced fluorescence is observed only for the diamagnetic cations Zn(II) and Cd(II). For Zn(II), the chelation-enhanced fluorescence can be correlated with both the appearance of an emission shoulder and a new decay component. This suggests that complexation to Zn(II) can affect the contributions of the different BPDO isomers, thus changing the fluorescence.

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