

THE FLUORESCENCE OF 2,2'-BIPYRIDYL

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Summary

Absorption, fluorescence and luminescence excitation spectra of 2,2'-bipyridyl (bipy), of the protonated species bipyH^+ and bipyH_2^{++} , and of the Zn(bipy)^{++} complex ion were measured in rigid and in fluid media. A weak fluorescence which has previously been ascribed to bipy or bipyH^+ appears to be due to the strongly fluorescent species Zn(bipy)^{++} which results from the contamination of polar solvents with traces of Zn^{++} . The quantum yields of fluorescence of Zn(bipy)^{++} and bipyH_2^{++} were determined.

A weak fluorescence of bipyH^+ , which is markedly Stokes shifted, is reported.

1. Introduction

2,2'-Bipyridyl (bipy) has for many years been considered to be non-fluorescent, resembling in this respect the parent molecule pyridine. Recently, fluorescence from bipy solutions has been reported [1, 2]. It has been ascribed to two different states of bipy, $^1(n, \pi^*)$ or $^1(\pi, \pi^*)$, in different solvents [1], or to the hydrated forms of the free base or of the monovalent cation bipyH^+ [2]. In attempting to reproduce and check these results we arrived at a different and quite unexpected conclusion.

2. Experimental

Bipy (POCh, Gliwice) was recrystallized from hexane, sublimed, and checked for purity by gas and thin-layer chromatography. Water was distilled four times over KMnO_4 . n-Propanol was purified by shaking with active charcoal and by fractional distillation. 2-Methyltetrahydrofuran (MTHF) was dried, passed through an Al_2O_3 column and distilled. CH_3COOH was distilled. CH_3OH (fluorescence grade, Merck), ZnSO_4 and concentrated H_2SO_4 were used without further purification. All solvents and ZnSO_4 solutions were checked for luminescence and absorption before use.

Luminescence and low temperature absorption spectra were measured by means of a Jasný spectrofluorimeter [3] and were fully corrected for the spectral response of the instrument. The luminescence quantum yields were measured using 2-aminopyridine ($\phi_F = 0.73$ [4]) and 2-aminopurine ($\phi_F = 0.82 - 0.83$ depending on $\tilde{\nu}_{exc}$ [5]) as standards. In low temperature experiments the changes of refractive index due to cooling of the solvent were taken into account.

3. Results

The absorption, emission and excitation spectra of approximately 10^{-5} M bipy were measured in MTHF, propanol or methanol + H_2O (4:1) at room temperature and in low temperature glasses (Figs. 1 - 3). All the curves are normalized to unity and the absorbances are thus presented in arbitrary units.

The phosphorescence excitation spectra of bipy and bipyH⁺ fit well to the corresponding absorption spectra (Fig. 3), whereas the fluorescence excitation spectra do not (Fig. 2).

Henry and Hoffman [2] have ascribed the fluorescence to a hydrated form bipy $\cdot H_2O$ (or bipyH⁺ $\cdot H_2O$) which is present only in aqueous solutions. However, we observed the same fluorescence, although much weaker, in

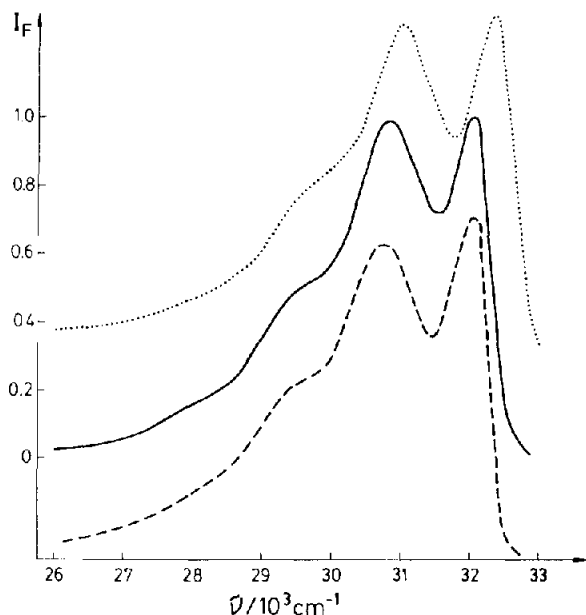


Fig. 1. Low temperature fluorescence spectra in $CH_3OH + H_2O$ (4:1 by volume) at 93 K (curves displaced vertically by 0.3 units): — — —, bipy, $\tilde{\nu}_{exc} = 34\,000\text{ cm}^{-1}$; . . . , bipyH⁺, $c(H_2SO_4) = 5 \times 10^{-3}\text{ M}$, $\tilde{\nu}_{exc} = 34\,600\text{ cm}^{-1}$; — — —, $Zn(bipy)^{2+}$, $c(Zn^{2+}) = 0.1\text{ M}$, $\tilde{\nu}_{exc} = 34\,300\text{ cm}^{-1}$.

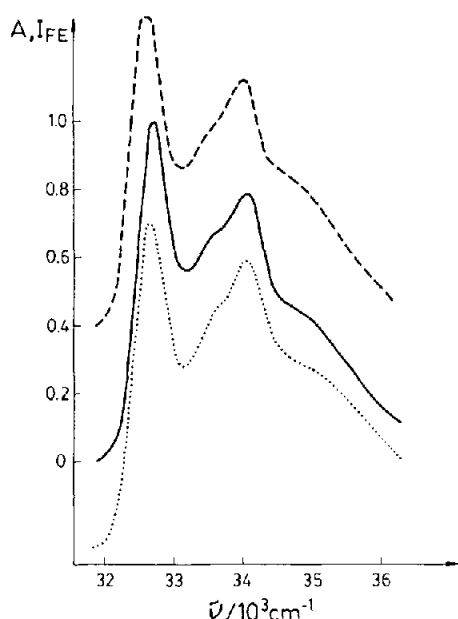


Fig. 2. Low temperature absorption and fluorescence excitation spectra in $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ (4:1) at 93 K (successive curves displaced vertically by 0.3): — — —, bipy, fluorescence excitation, $\tilde{\nu}_{\text{obs}} = 28\,000\text{ cm}^{-1}$; . . . , bipyH⁺, fluorescence excitation, $\tilde{\nu}_{\text{obs}} = 29\,000\text{ cm}^{-1}$, $c(\text{H}_2\text{SO}_4) = 5 \times 10^{-3}\text{ M}$; —, $\text{Zn}(\text{bipy})^{++}$, absorption spectrum, $c(\text{Zn}^{++}) = 0.1\text{ M}$.

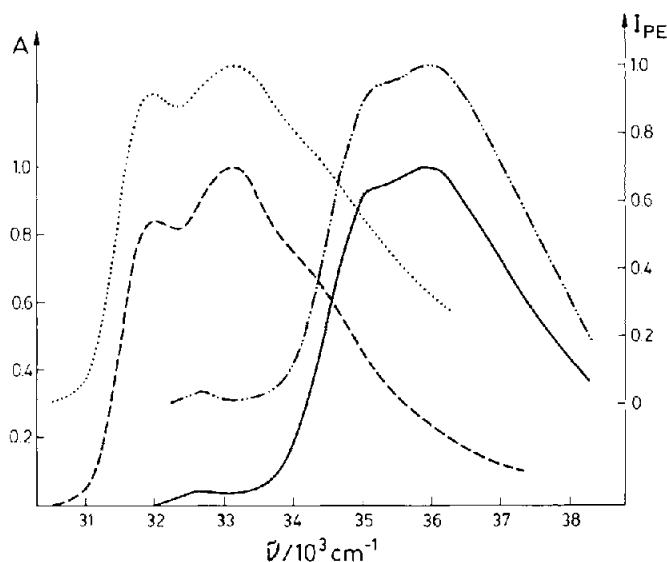


Fig. 3. Low temperature absorption and phosphorescence excitation spectra in $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ (4:1) at 93 K: —, absorption and, — · · · —, phosphorescence excitation ($\tilde{\nu}_{\text{obs}} = 21\,000\text{ cm}^{-1}$) spectra of bipy; — — —, absorption and, . . . , phosphorescence excitation ($\tilde{\nu}_{\text{obs}} = 21\,000\text{ cm}^{-1}$) spectra of bipyH⁺, $c(\text{H}_2\text{SO}_4) = 5 \times 10^{-3}\text{ M}$.

propanol glass (propanol had to be substantially dried in order to get a transparent glass). No fluorescence was detected in rigid or fluid MTHF. The 4,4'-bipyridyl was found to be non-fluorescent, although it could be expected to form analogous hydrates (provided no specific geometry of a hydrate is required).

In contrast to bipy and bipyH⁺, where the lowest excited singlet state may be a ¹(n,π*) state with a low radiative rate, the second protonation should lead to a lower ¹(π,π*) state. Indeed, in H₂SO₄ + CH₃COOH (3:1), where the equilibrium was shifted towards the diprotonated species, a strong fluorescence appeared: $\phi_F = 0.45$ in fluid and $\phi_F = 0.46$ ($\phi_F = 0.052$) in rigid media. The excitation spectrum reproduces the absorption spectrum of bipyH₂⁺⁺ (Fig. 4).

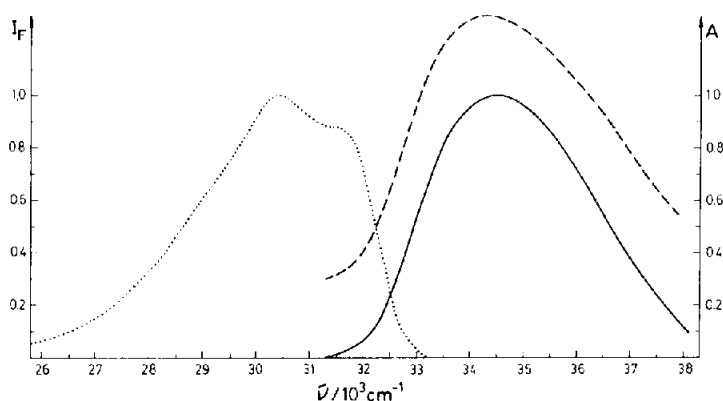


Fig. 4. Low temperature spectra of bipyH₂⁺⁺ in H₂SO₄ + CH₃COOH (3:1) at 158 K: —, absorption; . . ., fluorescence, $\tilde{\nu}_{\text{exc}} = 33\,400\text{ cm}^{-1}$; — —, fluorescence excitation, $\tilde{\nu}_{\text{obs}} = 29\,000\text{ cm}^{-1}$.

The lone pairs at the nitrogen atoms can also bond to coordinating ions, *e.g.* to a Zn⁺⁺ ion. Fluorescence of such complexes is already known [6]. Our experiments demonstrated that the excitation spectra of the fluorescences ascribed to bipy or bipyH⁺ closely match the absorption spectrum of the complex (Figs. 1 and 2) at both low and room temperatures.

The concentration of bipy was 10⁻⁵ M and that of the Zn⁺⁺ ions, in the appropriate experiments, was 0.1 M. The stability constants of the bipy-Zn⁺⁺ complexes are log $K_1 = 5.2$, log $K_2 = 4.4$ and log $K_3 = 3.8$ [7]. Hence practically only the 1:1 complex was present in the solution. The fluorescence quantum yield of Zn(bipy)⁺⁺ was found to be high (ϕ_F is 0.36 at room temperature and 0.57 in the low temperature glass; $\phi_F = 0.052$) so that the spectra were easily measurable even at very low concentrations. Because of its high yield the Zn(bipy)⁺⁺ fluorescence appears in solutions of bipy whenever they are contaminated by Zn⁺⁺ which is usually dissolved from glass by water and possibly also by alcohols. An addition of 1 × 10⁻⁶ M Zn⁺⁺ doubled the fluorescence intensity. In another series of experiments methanol and water were distilled in an all quartz apparatus and were kept in

quartz vessels, the only exception being the use of glass pipettes. This procedure lowered the fluorescence intensity sixfold.

As free bipy is generally in a large excess with respect to the complex, an inner filter effect may be observed. Free bipy *phosphoresces*, while $\text{Zn}(\text{bipy})^{++}$ *fluoresces* strongly and is only weakly phosphorescent. Thus the apparent phosphorescence yield is independent of $\tilde{\nu}_{\text{exc}}$, while the yield of fluorescence drops markedly with excitation wavenumber above $34\,000\text{ cm}^{-1}$ where bipy starts to absorb. The ratio of phosphorescence (excited at $34\,200\text{ cm}^{-1}$) to fluorescence ($\tilde{\nu}_{\text{exc}} = 32\,400\text{ cm}^{-1}$) markedly increases with increasing concentration of bipy. This indicates that the fluorescence-promoting impurity, e.g. Zn^{++} , is not introduced with the crystalline bipy but with the solvent.

For the monocation solutions these dependences are less spectacular since both species, i.e. bipyH^+ and $\text{Zn}(\text{bipy})^{++}$, absorb in the same spectral region.

Apart from the fluorescence reproduced in Fig. 1, the monocation exhibits another fluorescence which is very weak ($\phi_F \approx 5 \times 10^{-4}$), broad, structureless and has a maximum at about $22\,800\text{ cm}^{-1}$; it is detectable only at room temperature (Fig. 5). In rigid media the much stronger phosphorescence appears in the same spectral region. The fluorescence excitation (as observed at $\tilde{\nu}_{\text{obs}} \approx 23\,000\text{ cm}^{-1}$) matches the bipyH^+ absorption spectrum within experimental error (Fig. 5), whereas the observation at $\tilde{\nu}_{\text{obs}} = 28\,000\text{ cm}^{-1}$ results in the excitation spectrum characteristic of $\text{Zn}(\text{bipy})^{++}$. A similar long wavelength emission has been reported [2] and ascribed to $\text{bipyH}^+ \cdot \text{H}_2\text{O}$.

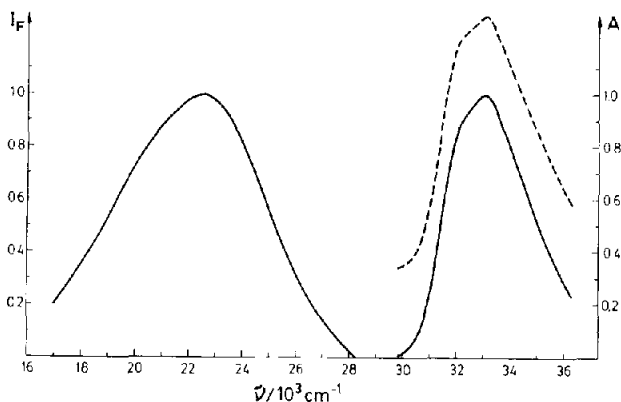


Fig. 5. Room temperature spectra of bipyH^+ in CH_3CN ($c(\text{H}_2\text{SO}_4) = 5 \times 10^{-3}\text{ M}$, H_2O content of about 2 vol.%): —, absorption and fluorescence, $\tilde{\nu}_{\text{exc}} = 32\,000\text{ cm}^{-1}$; ---, fluorescence excitation, $\tilde{\nu}_{\text{obs}} = 23\,000\text{ cm}^{-1}$.

Several other ions were checked for their effects on the fluorescent properties of bipy. In contrast to the coloured complexes (Cu^{++} , Fe^{++} , ...) the colourless complex with Mg^{++} revealed a similar behaviour. As the complexes of bipy with Mg^{++} and alkaline earth cations are much less stable than those with Zn^{++} , we directed our attention to Zn^{++} .

4. Conclusions

(1) Weak fluorescence appearing in rigid or fluid solutions of bipy or bipyH⁺ in the spectral region 30 000 - 32 000 cm⁻¹ is due to the strongly fluorescent Zn(bipy)⁺⁺ complex formed with Zn⁺⁺ ions that are supplied from polar solvents (and probably eluted from glass). Only the phosphorescence could be unambiguously ascribed to bipy.

(2) Double protonation converts the molecule into the strongly fluorescent species, as is expected from molecular orbital schemes.

(3) The singly protonated species bipyH⁺ undergoes in fluid solutions an adiabatic process of structural relaxation and emits a weak fluorescence at about 23 000 cm⁻¹ which is strongly Stokes shifted. The nature of the structural change is not yet clear.

(4) The Zn(bipy)⁺⁺ fluorescence may be used as a sensitive analytical test for Zn⁺⁺.

Acknowledgment

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