Room-temperature phosphorescence of 2,2'-biquinoline in polymeric matrices

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Abstract. An original and very strong long-lived emission of 2,2'-biquinoline is observed in hydrogen-bonded polymeric matrices only. This long-lived emission ($\tau_D = 1$ s) is ascribed to room-temperature phosphorescence (RTP) because of the large value of the decay time, the temperature-dependence, and the polarization results.

The existence of hydrogen-bonded complexes in the ground state is assumed to be the origin of the RTP. They involve changes in the conformation of the 2,2'-biquinoline.

Keywords. H-bonded polymeric matrices; room-temperature phosphorescence; 2,2'-biquinoline.

1. Introduction

The photophysics and photochemistry of ligand molecules of various complexes of metals and ligands have been investigated because of their particular relevance in a large range of applications (Ohno and Kato 1974; Clarke *et al* 1980; Vinodgopal and Leenstra 1985; Yagi *et al* 1985; 1991). The double molecule 2,2'-biquinoline (2,2'-BQ) is a typical chelating agent for metal ions with possible *cis* and *trans* conformations. Properties of the triplet state of 2,2'-BQ have been studied by various techniques; by steady state ESR (Higuchi *et al* 1980) and by Raman and ODMR techniques (Clarke *et al* 1982). Some studies on 2,2'-biquinoline complexes have stressed the close connection between the metal complex formation and the conformational changes in the ligand molecule (Klassen 1976; Frederiks *et al* 1979; Higuchi *et al* 1980, 1986).

Our interest in this molecule arises from earlier observations on other double molecules such as 1,1' and 2,2'-binaphthyl. In a previous study on the luminescence of 2,2'-binaphthyl solutions, we showed an anomalous dependence of the ratio $I_{\text{phos}}/I_{\text{fluor}}$, versus excitation, at nitrogen liquid temperature (Fadouach *et al* 1992). This anomalous behaviour is due to the charge transfer (CT) character of highest singlet states (S^*); we assumed the existence of various conformers more or less twisted as

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the origin of this behaviour. These conformers seemed, to be depending on the viscosity of the environment and its ability to form hydrogen bonds. The present study on the 2,2'-BQ is now performed, largely to increase the phosphorescence (and make the phenomenon more sensitive) because the presence of the lone pair orbital of intracyclic nitrogen has to increase the intersystem crossing (and, thus the phosphorescence), due to the presence of the n, π^* states. In the present study, when including the 2,2'-BQ in various polymeric matrices, we show evidence for an original and strong room temperature phosphorescence (RTP). This RTP only appears in the case of hydrogen-bonded polymeric matrices.

In recent years the phenomenon of RTP has attracted large interest, and so also its application in spectroscopic analysis (Vo-Dinh 1984). In 1974, Winefordner and coworkers (Wellon *et al* 1974; Vo Dinh and Hooyhman 1979) established the general use of RTP as an analytical technique. Although many basic aspects of RTP remain to be explained, this phenomenon received immediate attention and rapidly found its place as a new spectrochemical technique for trace organic analysis.

2. Experimental techniques

2,2'-Biquinoline was purchased from Fluka Chemica AG, and checked for luminescent impurities by thin layer chromatography (TLC). As no impurities were observed, the compound was used without further purification. All solvents (Aldrich) used were of spectroscopic grade. Polyethylene (PE) films, of thickness about 50 and 100 μ , are commercially available. Polyvinylchloride (PVC) films were either XVPH type of thickness about 17 and 19 μ (kindly donated by Grace Society) or O'Kay type commercially available of about the same thickness. Polyvinylalcohol (PVA) films were made in the laboratory with rhodoviol pellets (Rhône-Poulenc 30S). Melamine formol (MF) was graciously provided by Polyrey, SA.

2,2'-Biquinoline was introduced into the matrices by direct inclusion during film elaboration (PVA, MF) or by absorption from an *n*-hexane solution and evaporation of the solvent (PE, PVC). All the films were washed with *n*-butylchloride and dried carefully before use. All absorption spectra were recorded on a Cary 118 Varian spectrometer, and emission and excitation spectra on a Jobin-Yvon JY3CS spectrofluorimeter with a 150 W xenon lamp. 2,2'-BQ concentration in the films was of the order of 10^{-5} M.

3. Experimental results

3.1 Absorption

2,2'-Biquinoline is included in several polymeric matrices, more or less polar, able or not, to undergo hydrogen bonding: PE or PVC was the nonhydrogen-bonded matrix and MF or PVA was the hydrogen-bonded matrix. The absorption spectra in these different matrices are very similar to those in solution; the first structured band between 355 and 280 nm looks like that of quinoline (same global shape, same structure) but red-shifted (about 40 nm), involving a larger delocalization of the aromatic ring orbital. The second unstructured band presents a similar quasi red-shift

Figure 1. Absorption spectra of 2,2'-BQ in different polymeric matrices at room temperature (concentration $\approx 10^{-5}$ M), with optical density calibrated on the maximum (260 nm) of the second absorption band: — MF matrix; ——— rigid PVA matrix; - - - - soft PVA matrix; ····· PVC matrix.

($\lambda_{\text{max}} \approx 260$ nm). The increasing of the matrix polarity does not change very much with the absorption spectra (from PE to PVC), but the relative oscillator strengths of these first bands are very sensitive to increase of hydrogen bonding. Figure 1 shows the absorption spectra of the 2,2'-BQ in MF (of very strong rigidity), in PVA (rigid and soft matrix successively), and PVC. A similar effect of hydrogen bonding on the absorption spectra of 2,2'-BQ has been observed by decreasing the temperature of solutions in methylcyclohexane containing some traces of water in it, proof of stabilization of the hydrogen-bonded complexes at low temperature (unpublished results).

The relative variation of the oscillator strengths of the two first bands of 2,2'-BQ is probably due to deformation of the conformation, involving coupling of the two quinolic parts. The large flexibility of this molecule is coherent with the calculation results: very weak energetic barrier around the C_2-C_2 bond (about 1 kcal). A similar deforming role of hydrogen bonding has been already shown in the case of various TICT molecules (Cazeau-Dubroca 1991; Cazeau-Dubroca *et al* 1992).

3.2 Emission

In nonhydrogen-bonded polymeric matrices, only normal fluorescence is observed at room temperature. In hydrogen-bonded polymeric matrices, a very intense long-lived emission also appears (figure 2a). This emission is ascribed to room temperature phosphorescence (RTP) because of the following reasons:

(a) the large similitude of the emission shape (same structure) to that of the one observed at liquid nitrogen temperature, in the case of solutions or polymeric matrices (figure 2b- α).

(b) the polarization of this long-lived emission is negative, when excited by both the first bands of the absorption spectrum ($S_0 \rightarrow S_1^*$), ($S_0 \rightarrow S_2^*$), and involves the $^3\pi, \pi^*$ character of the emissive triplet state (figure 2b- β) at room temperature as at liquid nitrogen temperature (more negative indeed, in this last case).

(c) the very large value of the lifetime, τ_D (decay time), in the range of about one second (figure 3a), is specific of either a phosphorescence issue to a $^3\pi, \pi^*$ triplet state or an α -delayed fluorescence (as in the case of DMABN in PVA at room temperature, for instance (Cazeau-Dubroca *et al* 1983, 1986), the emissive TICT state being populated through the highest vibrational levels of the triplet state).

(d) the temperature dependence is specific of phosphorescence: a continuous decrease of emission intensity on increasing the temperature, from liquid nitrogen temperature to room temperature, is observed (figure 3b).

Elsewhere this RTP depends on excitation wavelength: the ratio $I_{\text{phos}}/I_{\text{fluor}}$ increases on increasing the wavelength excitation; the 340 nm wavelength seems to be "optimum" for the excitation of RTP, this means a larger efficiency for the RTP owing to more "red" conformer corresponding to the less energetic spectrum. The excitation spectra of fluorescence and phosphorescence, respectively, are the same. Indeed, this RTP is very dependent on the rigidity of the matrix.

We have to note that this RTP looks like that of the quinoline (very weak, increased by heavy atoms) in a special matrix (chalk and paper) (Ford and Hurtubise 1979). The

Figure 2.(a)

Figure 2. (a) Emission spectra of 2,2'-BQ in different polymeric matrices at room temperature (concentration $\approx 10^{-5}$ M): — MF matrix ($\lambda_{\text{exc}} \approx 340$ nm); - - - PVA rigid matrix ($\lambda_{\text{exc}} \approx 340$ nm); $\circ - \circ$ - PVA soft matrix ($\lambda_{\text{exc}} \approx 330$ nm); $\bullet - \bullet$ - PVC matrix ($\lambda_{\text{exc}} \approx 310$ nm). (b) α - Emission spectra of 2,2'-BQ in rigid PVA excited at 340 nm at room temperature ($\bullet \bullet \bullet$) and at nitrogen liquid temperature (—). β - Polarization spectra of the emission of 2,2'-BQ in rigid PVA excited at 340 nm at room temperature ($\bullet \bullet \bigcirc \bullet \bullet$) and at nitrogen liquid temperature ($\bigcirc \bigcirc \bigcirc$).

presence of the two chromophores (two quinolines) with some special conformation with respect to each other (induced by hydrogen bonding), increases the RTP phenomenon. The hydrogen bonding stains the complex to a conformation different from that of the bare molecule. Recently, Higuchi *et al* (1980) assigned the EPR signal of 2,2'-BQ in the stretched PVA film to the *trans* conformer. Furthermore, we have

Figure 3. (a) Phosphorescence decay curve monitored at 500 nm of 2,2'-BQ in rigid PVA matrix, at room temperature, excited at 340 nm. (b) Evolution of maximum of the phosphorescence intensity ($\lambda_{max} \approx 500$ nm) against the temperature of the 2,2'-BQ in rigid PVA matrix, excited at 340 nm.

observed the absorption and luminescence spectra of 2,2'-BQ in the stretched PVA rigid film at room temperature (the stretched 250% films are obtained by a similar process as that of Higuchi *et al* 1980). Hence, the RTP, observed in hydrogen-bonded matrices, is assigned to the *cis* conformer of the molecule. The reasons for this assignment are as follows.

- In the stretched PVA rigid film, the observed absorption spectrum shows a relatively weak first band (relative to the second band) and a ratio I_{phos}/I_{fluo} weaker than in unstretched PVA rigid films cf. figures 4a and b.

Figure 4. (a) Absorption spectra of 2,2'-BQ at room temperature (concentration $\approx 10^{-5}$ M); — in unstretched rigid PVA film; --- in stretched rigid PVA film. (b) Emission spectra of 2,2'-BQ excited at 340 nm at room temperature: — in unstretched rigid PVA film; --- in stretched rigid PVA film.

●Furthermore, the results of the calculated intermolecular interactions, simulating the hydrogen-bonded complex of the 2,2'-BQ, are consistent with the *cis* conformer, while the more stable conformation of the bare molecule is the *trans* one (unpublished results). Moreover, the simulated spectroscopic results, by CNDO/s are coherent with the relative variation of the oscillator strengths, for the two conformers respectively *cis* and *trans* (unpublished results). The deforming role of hydrogen bonding in the ground state has been already stressed by some of us, it seems to be a general phenomenon.

4. Conclusions

In the present study, we show a strong long-lived emission in some hydrogen-bonded polymeric matrices. This long-lived emission is ascribed to a room temperature phosphorescence issue to a $^3\pi, \pi^*$ triplet state, because its negative polarization by both excitations of the two first absorption bands. This RTP is very dependent on the temperature and on the viscosity of the matrix. Furthermore, the appearance of the RTP is correlated to the presence of hydrogen-bonded complexes in the ground state, according to the absorption spectra. We assume that these hydrogen-bonded complexes in the ground state correspond to a different conformation of the 2,2'-BQ, owing to the very large difference in the ratios of the oscillator strengths of the two first absorption bands, in comparison with that of the bare molecule (absorption in nonhydrogen-bonded matrix, for instance). A further study simulating the hydrogen bonded complex (and its probable deformation) will be presented subsequently.

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