The spectra, lifetime and laser activity of 2,5-*bis*-2(1-naphthyl)vinylpyrazine and 2,5-*bis*-2(2-naphthyl)vinylpyrazine

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Abstract. Both 2,5-*bis*-2(1-naphthyl)vinylpyrazine (BNVP) and 2,5-*bis*-2(2-naphthyl)vinylpyrazine (B2NVP) diolefinic dyes have relatively short excited-state lifetimes, high fluorescence efficiencies and low photochemical quantum yields. BNVP solutions in dimethyl formamide and methylene chloride give amplified spontaneous emission (ASE) with a maximum at 500 nm. The low solubility of B2NVP in organic solvents does not allow the measurement of ASE for this dye. The excited state absorption spectra (ESA) of BNVP show an absorption band around 525 nm which reduces dye laser efficiency.

Energy transfer from 7-diethylamino-4-methylcoumarin to BNVP and B2NVP has been studied by applying Stern–Volmer plots. The underlying mechanism is a radiative long range energy transfer.

Both BNVP and B2NVP undergo solubilization in anionic as well as cationic micelles.

Keywords. Diolefinic dyes; excited-state lifetimes; fluorescence quantum yields; amplified spontaneous emission.

1. Introduction

Dirolefinic compounds containing pyrazinyl moieties have been reported as important candidates in many research areas. 2,5-Distyrylpyrazine (DSP) was the first reported derivative to undergo solid state four-centre photopolymerization giving rise to a highly crystalline polymer (Hasegawa 1982, 1983; Hasegawa *et al* 1988). Members of this family of compounds have been recently reported as organic electroluminescent crystals giving high brightness at a low DC voltage of about 10 volts (Nohara *et al* 1990).

One of the most important applications of these compounds is their use as laser dyes (Ebeid *et al* 1985, 1986; Hasegawa *et al* 1989). Dye laser emission from DSP (Ebeid *et al* 1985) and 1,4-*bis*(β -pyrazinyl-2-vinyl) benzene (BPVB) (Ebeid *et al* 1986) was observed upon pumping concentrated solutions of these dyes using a nitrogen laser source.

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In the present communication we report the emission characteristics, lifetime values and amplified spontaneous emission of BNVP and B2NVP (chart 1).

2. Experimental

BNVP and B2NVP samples were kindly provided by Professor Masaki Hasegawa of Tokyo University. The last crystallization of BNVP (m.p. 213–214.5°C) was from toluene and that of B2NVP (m.p. 319–320°C) was from xylene. Fluorescence spectra and fluorescence quantum yields (ϕ_f) were measured using a Shimadzu RF 510 spectrofluorophotometer using diphenylanthracene and quinine sulphate as reference standards (Morris *et al* 1976). Photochemical quantum yields (ϕ_c) were measured using a method that has been described earlier (Ebeid *et al* 1986). UV-visible absorption and reflectance spectra were measured using a Shimadzu UV-2100S spectrophotometer. Fluorescence lifetimes were measured using single-photon counting and phase and modulation fluorimetry. In the single-photon counting technique, fluorescence decays were recorded using an ORTEC single-photon counting apparatus equipped with a hydrogen flash lamp operating at about 15 kHz. Excitation wavelengths were selected using a Bausch and Lomb UV-Visible monochromator (type 33–80–07, 1200 grooves/mm). The emission wavelength was selected using appropriate interference filters (Schott, Mainz, Germany). The data were registered in a 400-channel analyser with a linearity of 0.174 ns/channel. The decay profiles were analysed by iterative convolution using autocorrelation and residuals criteria (Grinvald and Steinberg 1974; Demas 1983). Phase and modulation lifetimes were measured using an SLM-48000 fluorimeter. For high dye concentrations, a triangular cuvette was used to minimize reabsorption in both lifetime and fluorescence measurements. For dilute solutions a 4 mm optical length cuvette was used.

Amplified spontaneous emission (ASE) as well as excited state absorption (ESA) were kindly carried out by Professor Ewald Daltrozzi of the University of Konstanz (Germany).

Differential thermal analysis (DTA) was carried out using a Shimadzu XD-30 thermal analyser. Molecular weights of irradiated and unirradiated BNVP and B2NVP samples were monitored using a Knauer Vapour Pressure Osmometer.

3. Results and discussion

BNVP and B2NVP are of the same molecular weight, yet the reported melting point of B2NVP is nearly 100°C higher than that of BNVP. This has been confirmed by using DTA. DTA thermograms also indicate the absence of thermal processes other than melting up to $\approx 350^\circ\text{C}$. The wide difference in melting points reflects different molecular packing and interactions in crystalline samples. Excitation ageing of

crystalline BNVP and B2NVP samples results in a decrease in emission and excitation intensities indicating photochemical reactivity. This is a particularly significant phenomenon since both BNVP and B2NVP thin films have been applied (Nohara *et al* 1990) in electroluminescent devices and photochemical reactivity is an undesired phenomenon in that respect.

Reflectance spectra of BNVP and B2NVP crystals also indicate a solid state photochemical reaction in these samples. The reflectance maxima at ≈ 420 nm in BNVP and that at ≈ 400 nm in B2NVP decrease in intensity with concomitant appearance of reflectance maxima at 280 and 220 nm for BNVP and B2NVP samples, respectively. Further studies are needed to identify the photochemical product(s) that are believed to be oligomers obtained by π - π addition of the olefinic double bonds as reported earlier for similar diolefinic derivatives (Hasegawa 1982, 1983).

The electronic absorption, emission and excitation spectra of BNVP and B2NVP solutions in DMSO solvent are shown in figure 1. The electronic absorption spectrum of BNVP in DMSO consists mainly of symmetrical absorption bands around

Figure 1. The emission, excitation and absorption spectra of (a) BNVP, and (b) B2NVP solutions in DMSO (10^{-5} mol dm $^{-3}$). (—) emission ($\lambda_{\text{ex}} = 410$ nm) and excitation (following the respective emission maxima and (---) Absorption spectra.

≈ 405 nm with molar absorptivity $\varepsilon_{\max} = 45,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; the emission spectrum is unsymmetrical with a maximum at 480 nm ($\lambda_{\text{ex}} = 410$ nm).

For B2NVP both absorption and emission spectra in DMSO are unsymmetrical with an absorption maximum at 410 nm and an emission maximum at 460 nm. The emission from BNVP occurs at lower energy as compared to that from B2NVP, a phenomenon that is related to excited state solvation. The longer lifetime of BNVP as compared to that of B2NVP (*vide infra*) allows greater solvation of the BNVP excited state as compared with that of B2NVP.

The position of emission maxima for both BNVP and B2NVP is dependent upon the solvent polarity Δf , where Δf is given by the relation (Rao *et al* 1976; Brecht 1986).

$$\Delta f = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^2 - 1)}{(4n^2 + 2)},$$

where ε and n are the dielectric constant and the refractive index of the solvent respectively. A linear correlation exists between $\lambda_{\max}$ (emission) and Δf for both BNVP and B2NVP with $\lambda_{\max}$ increasing as Δf increases. The effect of medium polarity on the absorption maxima of both dyes is insignificant. These phenomena are diagnostic for excited states that are more polar than the ground state (Griffith 1976). The electronic absorption, emission and excitation spectra of BNVP and B2NVP dilute solutions ($\approx 10^{-5} \text{ mol dm}^{-3}$) undergo change upon UV-irradiation ($\lambda_{\text{ex}} = 365$ nm). The underlying photoreaction in such dilute solutions of diolefinic derivatives is thought to be a *cis-trans* photoisomerization.

The photochemical quantum yields (ϕ_c) are low and the ϕ_c and fluorescence quantum yields ϕ_f are summarized in table 1.

The effects of the medium on the spectra of BNVP and B2NVP have been further studied in relation to the acidity of the medium and the micellization phenomenon. The electronic absorption spectra of both dyes in ethanol do not change significantly on lowering the pH of the medium down to a value of 1. In 0.8 mol dm^{-3} ethanolic

Table 1. ϕ_f and ϕ_c values of BNVP and B2NVP in different media at room temperature.

Dye	Medium	$\phi_f, \lambda_{\text{ex}} =$		ϕ_c $\lambda_{\text{ex}} = 365 \text{ nm}$
		365 nm	337 nm	
BNVP	EtOH	0.52	0.47	1.03×10^{-4}
	BuOH	0.67	0.56	
	DMSO	0.72	0.64	
	Cyclohexane	0.72	0.66	
	SDS ($8 \times 10^{-3} \text{ mol dm}^{-3}$)	0.60	0.52	
	CTAC (0.1 mol dm^{-3})	0.50	0.38	
B2NVP	EtOH	0.64	0.45	2.6×10^{-4}
	MeOH	0.65	0.42	
	BuOH	0.75	0.46	
	DMSO	0.74	0.57	
	Acetone	0.64	0.58	
	CHCl_3	0.63	0.56	
	Ethylene glycol	0.49	0.26	

solutions of HCl, a yellow protonated product is obtained and fluorescence efficiencies of both dyes decrease substantially. The effect of acidity of the medium on the emission properties is particularly important in relation of pH-tuning in dye lasers (Weller 1961; Dienes 1975).

Both BNVP and B2NVP undergo solubilization in anionic (e.g. sodium dodecyl sulphate, SDS) and cationic (e.g. cetyltrimethylammonium chloride, CTAC) micelles. The solubilization process is associated with an increase in the fluorescence intensities. Plots of the surfactant concentrations versus fluorescence intensities of both dyes show abrupt increase in fluorescence intensities at surfactant concentrations corresponding to the critical micelle concentrations (cmc) of SDS and CTAC which is the case for many organic dyes (Muthuramu and Ramamurthy 1984).

The lifetimes of BNVP and B2NVP in DMSO are summarized in table 2.

Table 2. Lifetime values of BNVP and B2NVP in DMSO at room temperature.

Sample	Concentration (mol dm ⁻³)	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)			
				Single photon	Phase + modulation	Phase only	Modulation only
BNVP	10 ⁻⁵	405	485	1.82	1.77	1.76	1.78
	10 ⁻³	365	485	2.11	—	—	—
B2NVP	10 ⁻⁵	410	481	1.38	1.32	1.31	1.34
	$\approx 10^{-4}$	365	481	1.33	—	—	—

The lifetimes are short both for dilute and concentrated solutions. We found no evidence for molecular aggregation in concentrated solutions (10⁻⁴ mol dm⁻³) of both dyes, giving emission spectra that are slightly red-shifted compared with those of dilute dye solutions due to reabsorption. The lifetimes also reveal one decay component in both dilute and concentrated solutions. The absence of molecular aggregation is of great significance since molecular aggregation is usually associated with fluorescence quenching via excimer formation (Jones 1990; Gilbert and Baggott 1991) and is conducive to bimolecular photochemical reactions (Suzuki *et al* 1974). The lifetimes in DMF and CH₂Cl₂ are close to those in DMSO. For BNVP the lifetimes are 1.66 and 1.53 ns in DMF and CH₂Cl₂, respectively.

Solutions of BNVP in dimethyl formamide (DMF) and in methylene chloride (CH₂Cl₂) of concentration 2.98×10^{-4} mol dm⁻³ give amplified spontaneous emission (ASE) with a maximum at 500 nm. The solubility of B2NVP in both solvents was too low to allow any ASE measurements and laser emission was not observed from B2NVP solutions solely because of lack of solubility. The excited singlet-state absorption (ESA) cross-section σ_A^* of BNVP is shown in figure 2. The ground state absorption cross-section (σ_A), the emission cross-section (σ_E) as well as the effective emission cross section σ_E^* are also shown in figure 2.

The emission cross-section σ_E was calculated from the relation (Nair 1982)

$$\sigma_E(\lambda^4 E(\lambda) \phi_f) / (8\pi\tau_f c n^2),$$

where $E(\lambda)$ is the normalized fluorescence lineshape function at a certain wavelength (λ) such that

$$\int_0^\infty E(\lambda) d\lambda = \phi_f,$$

Figure 2. The cross-sections (in units of cm^2) of some processes in BNVP in (a) DMF, and (b) CH_2Cl_2 . σ_A and σ_E are the ground state absorption and emission cross-sections. σ_A^* is the excited state absorption cross-section and σ_E^* is the effective emission cross-section where $\sigma_E^* = (\sigma_E - \sigma_A^*)$.

n is the refractive index of the dye solution, τ is the fluorescence lifetime and c is the velocity of light. $E(\lambda)$ was obtained from the fluorescence spectra of dilute dye solutions to minimize reabsorption.

The ground-state absorption cross-section σ_A was calculated in terms of values of

molar absorptivities $\epsilon(\lambda)$ (Nair 1982) where

$$\sigma_A(\lambda) = 3.82 \times 10^{-21} \epsilon(\lambda).$$

Both emission and absorption cross-sections are given in units of cm^2 .

The effective emission cross section σ_E^* is given as the difference $(\sigma_E - \sigma_A^*)$. In DMF and CH_2Cl_2 , the results are similar, showing an absorption band around 525 nm in the first excited singlet state. This absorption reduces the dye laser efficiency and seems to be common for the derivatives with a central pyrazine ring system e.g. 2,5-distyryl pyrazine (DSP) and 1,4-bis(β -pyrazinyl-2-vinyl) benzene (BPVB) (El-Daly *et al* 1993). Members of the same diolefinic laser dye series containing pyridyl moieties namely 1,4-bis(β -pyridyl-2-vinyl) benzene (P2VB) and its isoelectronic dye 1,4-bis(4-pyridyl-2-vinyl)benzene (P4VB) are more efficient laser dyes as compared to BNVP, BPVB and DSP. It was shown (El-Daly *et al* 1993) that σ_A^* values in case of diolefinic dyes containing a pyrazinyl moiety are higher than those in dyes containing a pyridyl moiety. This view, however, has to be substantiated by examining more compounds.

The harvesting of BNVP and B2NVP to pump nitrogen laser photons can be improved by using mixtures of these dyes with other suitable laser dyes, e.g. 7-diethyl amino-4-methylcoumarin in the form of the energy transfer dye laser (ETDL) system.

Figure 3. Stern-Volmer plots of the quenching of 7-diethylamino-4-methylcoumarin fluorescence using (●) BNVP and (○) B2NVP as quenchers in DMSO at room temperature $\lambda_{\text{ex}} = 337 \text{ nm}$ and $\lambda_{\text{em}} = 450 \text{ nm}$.

Both BNVP and B2NVP act as good photon acceptors from 7-diethylamino-4-methyl-coumarin that has maximum absorption at 373 nm in ethanol and maximum emission at 450 nm. Figure 3 shows the Stern–Volmer plots of quenching of 7-diethylamino-4-methylcoumarin fluorescence using BNVP and B2NVP as quenchers. The room temperature second-order quenching rate constants k_q in DMSO have been calculated from the slopes and the lifetime of 7-diethylamino-4-methyl coumarin of 3.6 ns (Masilamani and Sivaram 1982). The quenching rate constants (k_q) for BNVP and B2NVP in DMSO at room temperature are 1×10^{13} and $4.36 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. These values are about three orders of magnitude higher than the diffusion rate constant (k_{diff}) in DMSO at room temperature ($= 0.37 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The high quenching rate constant, together with the overlap between the donor emission and the acceptor absorption, indicates a diffusionless long range radiative energy transfer mechanism.

Acknowledgements

We thank Professor Masaki Hasegawa of Tokyo University for providing BNVP and B2NVP samples. We also thank Professor Ewald Doltrozzo of Konstanz University, Germany, for measuring the ASE and ESA using apparatus not available to us.

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