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A new diolefinic laser dye: 2,5-bis-2-(2-naphthyl) vinyl pyrazine (B2NVP)

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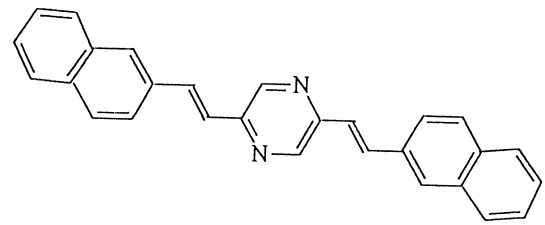
Abstract

The title dye acts as a laser dye upon pumping with nitrogen laser ($\lambda_{ex} = 337.1$). B2NVP in *N*,*N*-dimethylformamide (DMF) gives amplified spontaneous emission (ASE) with a maximum at about 470 nm, but only low laser activity upon nitrogen laser pumping. The difference between σ_E (emission cross-section) and σ_E^* (from ASE calculated effective emission cross-section) is interpreted as S_1–S_n absorption, the maximum of this absorption occurring in DMF at around 500 nm. Thereby the laser efficiency of the dye is strongly reduced. Investigations on the photochemical stability, photochemical quantum yields, and the dependence efficiency of the dye. B2NVP has short excited state lifetimes, high fluorescence efficiencies and low photochemical quantum yields. The dye undergoes solubilization in anionic micelles with subsequent increase in fluorescence efficiencies. Energy transfer from B2NVP to rhodamine6G (R6G) in dimethylsulfoxide (DMSO) has been studied giving a second order quenching rate constant of $8.7 \times 10^{13}\ M^{-1}\ s^{-1}$.

Keywords: Diolefins; Amplified spontaneous emission

1. Introduction

Diolefinic 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-center photopolymerization giving highly crystalline polymer [1–3]. Members of this family of compounds have been recently reported as organic electroluminescent crystals giving high brightness at low DC voltage of about 10 V [4]. One of the most important applications of these compounds is their use as laser dyes. Laser emission from DSP [5] and 1,4-bis(β-pyrazinyl-2-vinyl) benzene (BPVB) was observed [6] upon pumping concentrated solutions of these dyes using a nitrogen laser source. The naphthyl analog of DSP is expected to emit at longer wavelengths and to show a strongly supposed *trans–cis* isomerization process [7] due to changes in bond lengths on going from the S_0 to the S_1 state. In this communication we report the emission characteristics, lifetime and amplified spontaneous emission of 2,5-bis-2-(2-naphthyl) vinyl-pyrazine (B2NVP).



B2NVP

2. Experimental

The final crystallization of B2NVP[1] was from xylene (mp 319–320°C). Fluorescence spectra and fluorescence quantum yields (ϕ_f) were measured using a Shimadzu RF 510 spectrofluorophotometer using diphenylanthracene and quinine sulphate as reference standards [8]. Quantum yields of the *trans–cis* photoisomerization of B2NVP (ϕ_c) were measured using a modified method that takes into account the

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[1]The B2NVP sample was kindly provided by Professor Masaki Hasegawa of Toin University, Yokohama, Japan.

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change in absorbance with proceeding photoisomerization [9].

UV–Vis absorption spectra were measured using a Shimadzu UV-1200 S spectrophotometer. Fluorescence lifetimes were measured by the single photon counting technique using an air flash lamp operating between 20 and 40 kHz. Excitation wavelengths were selected using a bandpass filter (260–380 nm), the emission wavelengths were selected by appropriate filters (Schott, Mainz, Germany). The data were registered in a 1000 channels analyzer with a resolution of 24 channels/ns. The decay profiles were analyzed by iterative convolution using autocorrelation and residual criteria [10]. ASE was measured using a nitrogen laser (type 1M 50A, Lambda Physics; $\lambda_{ex} = 337.1$ nm, pulse duration = 5 ns) as excitation source and an optical multichannel analyzer (type OMA II, Princeton Applied Research Corp.) as detector [11]. The dye cuvette was placed in the focus of a cylindrical lens, which concentrates the N_2 laser beam to a narrow line. The dye concentration was 6.32×10^{-5} M in DMF solvent. Eight ASE spectra were recorded for different pulse energies (between 0.1 and 1.5 mJ). All spectra were measured in the unsaturated light amplification region. Within the model used [11], the relation between ASE intensity I and excitation pulse intensity P is given by equations (Eqs. (1)–(3)):

$$I(L,\lambda,P) = F(\lambda)N_1(P)\int_0^L \exp\left[N_1(P)\sigma_E^*(\lambda) - N_0(P)\sigma_A(\lambda)\right]\mathrm{d}x \tag{1}$$

$$N_1(P) = N\frac{\sigma_{ex}k_\tau P}{\sigma_{ex}k_\tau P + 1/\tau} \tag{2}$$

$$N = N_0 + N_1 \tag{3}$$

where N is the total dye concentration in molecules/cm^3, N_0 and N_1 are the populations of the ground state (S_0) and the first excited singlet state (S_1) respectively, σ_A is the absorption cross-section of the S_0, σ_{ex} is σ_A at 337.1 nm, σ_E^* is the effective emission cross-section, L is the length of the excited region within the dye cuvette (16–19 mm), τ is the lifetime of the S_1 state, k_τ is a correction factor and F is a factor depending on fluorescence intensity, detector sensitivity, and geometrical conditions. The factor k_τ gives the deviation of N_1 from the value obtainable under steady state conditions and depends on the ratio excitation pulse duration to S_1 lifetime τ. The difference between σ_E^* (effective emission cross-section) and σ_E (emission cross-section) we interpret as the absorption cross sections σ_A^* of $S_n \leftarrow S_1$ transitions. F as well as σ_E^* are determined from the ASE spectra by curve fitting. The emission cross section σ_E is calculated form relation (Eq. (4)), where E means the normalized fluorescence lineshape function, which is correlated with fluorescence quantum yield ϕ_f by equation (Eq. (5)).

$$\sigma_E(\lambda) = \frac{E(\lambda)\lambda^4}{8\pi\tau c n^2} \tag{4}$$

$$\int E(\lambda)\,\mathrm{d}\lambda = \phi_F \tag{5}$$

where n is the refractive index of the dye solution, c is the velocity of light in vacuum, $E(\lambda)$ is obtained from solutions whose absorptivities are low to avoid reabsorption processes (optical density at absorption maximum $\leq$0.1). The excited state absorption cross-section σ_A^* is calculated from the difference ($\sigma_E - \sigma_E^*$) [11].

3. Results and discussion

Table 1 summarizes some spectral data of B2NVP in different solvents. The absorption of B2NVP is not strongly affected by solvent polarity, whereas the emission spectra

Table 1
Spectral data, ϕ_f and ϕ_c values of B2NVP in different solvents

Solvent	λ_{max} (F). (nm)	λ_{max}(abs) (nm)	ϵ (M^{-1} cm^{-1})			ϕ_f		ϕ_c	pK	pK^*
			$\lambda_{(max)}$	λ_{336}	λ_{337}	$\lambda_{(max)}$	λ_{337}			
DMF	462	402	45 700	27 200	14 500	0.51	0.47	1.9×10^{-3}	2.16	1.79
Ethylene glycol	484	406	–	–	–	0.56	0.60	–	–	–
CH_3CN	457	393	–	–	–	0.49	0.42	–	–	–
Isopropanol	476	399	42 700	26 300	15 400	0.54	0.41	7.0×10^{-4}	–	–
CH_2Cl_2	458	397.5	–	–	–	0.61	0.40	–	–	–
Dioxane	450	398.5	–	–	–	0.51	0.40	–	–	–
$CHCl_3$	464	402	–	–	–	0.57	0.26	–	–	–
CCl_4	451	402.5	–	–	–	0.21	0.13	–	–	–
O/W	468	401.5	32 100	–	–	–	–	1.4×10^{-3}	–	–
EtOH	472		–	–	–	0.64	0.45	–	–	–
MeOH	482	397	41 000	–	–	0.65	0.42	–	–	–
Acetone	–		–	–	–	0.64	0.58	–	–	–
BuOH	–	–	–	–	–	0.75	0.46	–	–	–
n–Hexane	448	401	–	–	–	–	–	–	–	–
DMSO	470	398.5	–	–	–	0.74	0.57	–	–	–

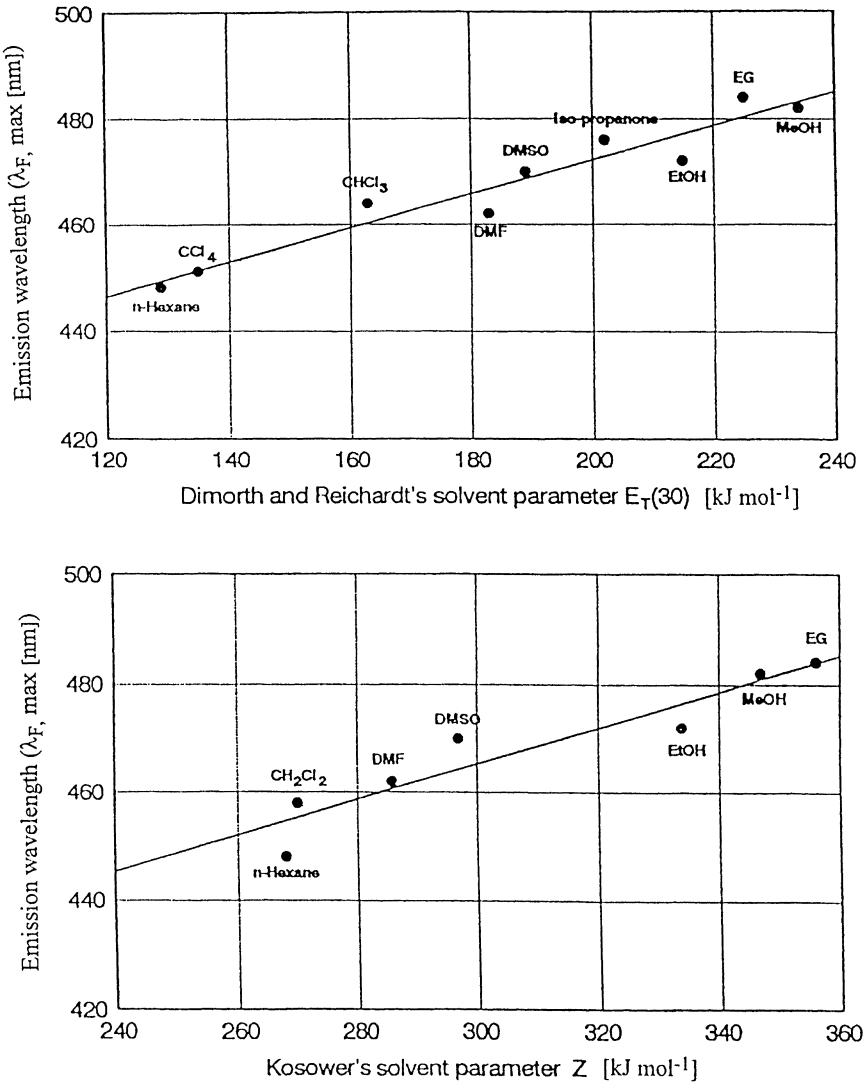


Fig. 1. Plot of emission maxima of B2NVP against (a) Dimroth–Reichardt's solvent parameter E_T and (b) Kosower's solvent parameter Z.

are significantly influenced by the medium. With increasing solvent polarity, the fluorescence maximum shifts to longer wavelengths from 448 nm in *n*-hexane ($E_T = 129$ kJ mol^{-1}) to 484 nm in ethylene glycol ($E_T = 225$ kJ mol^{-1}). In Fig. 1 the fluorescence maxima are plotted against Dimroth–Reichardt's (E_T) and also against Kosower's solvent parameters (Z) [12,13]. Due to hindrance around the naphthyl ethylenic bonds, the existence of different rotamers has to be taken in account. The existence of such rotamers is substantiated by both semiempirical calculations and the non-structured broad S_0–S_1 absorption as well as the dependence of the fluorescence and fluorescence excitation spectra on the exciting and observing wavelengths. Likewise, the fluorescence quantum yields are wavelength-dependent. This phenomena could be ascribed to two different, energetically preferred rotamers (conformers).

B2NVP undergoes solubilization in anionic micelles (sodium dodecyl sulphate (SDS)) The solubilization process is associated with an increase in the fluorescence intensity as shown in Fig. 2. Plots of the surfactant concentrations versus fluorescence intensities of the dye show a distinct increase in fluorescence intensities at surfactant concentration corresponding to the critical micelle concentration (cmc) of SDS. This is shown in Fig. 2.

The protonation constant of the ground state (pK) was calculated using relation (Eq. (6))

$$\mathrm{pH} = \mathrm{p}K - \log \frac{[\mathrm{B}]}{[\mathrm{BH}^+]} \tag{6}$$

where [B] is the concentration of the non-protonated form expressed in terms of its absorbance at 395 nm, [BH^+] is the concentration of the protonated form expressed in terms of the decrease in absorbance at 395 nm.

The protonation constants of the excited state pK^* were calculated using relation Eq. (7) [14]:

$$pK - pK^* = 2.10 \times 10^{-3}(\bar{\nu}_{\mathrm{BH}^+}) - \bar{\nu}_{\mathrm{B}}) \tag{7}$$

The quantities $\bar{\nu}_{\mathrm{BH}}, \bar{\nu}_{\mathrm{B}}$ represent the wave numbers of (pure)

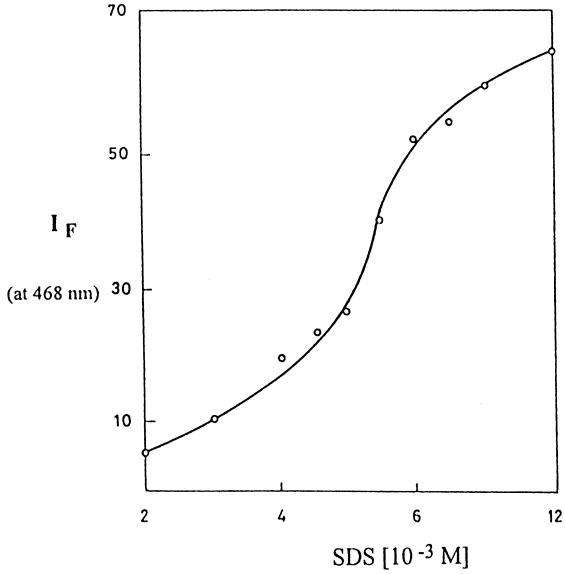
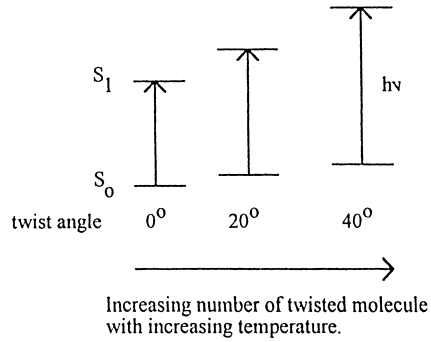


Fig. 2. Effect of concentration of SDS on the fluorescence intensity I_f of 10^{-5} M solutions of B2NVP.

electronic transitions in acid and conjugate base, respectively. The wave numbers obtained from electronic absorption spectra give pK^* values, termed pK^*_{ab}. Wave numbers obtained form fluorescence spectra give pK^* values, termed pK^*_f. For B2NVP in DMF $pK = 2.16$ and $pK^*_{ab} = 1.79$ are determined.

From quantum chemical calculation, the bond order between the naphthalene and the ethylenic moiety increases in the excited state leading to reduction of rotational frequencies with the consequence of rather high fluorescence quantum yield.

The absorption spectra of B2NVP in ethanol show a red shift of ≈23 nm is going from room temperature to 125 K. This is explainable by low rotational barriers for the naphthalene–ethylenic bonds in the ground state resulting in an equilibrium between the coplanar and twisted conformations. Due to strengthening of these very bonds in the S_1 state, twisted conformers are at significantly higher energies compared with the energy of the coplanar. With lower temperatures the amount of coplanar molecules with correspondingly long wavelength absorption increases resulting in a long wavelength shift of the absorption band with decreasing temperature. Correspondingly, the half-width of the first electronic transition is reduced.



Saturated solutions of B2NVP in DMF give ASE with a maximum at 465 nm. 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 shown in Fig. 3.

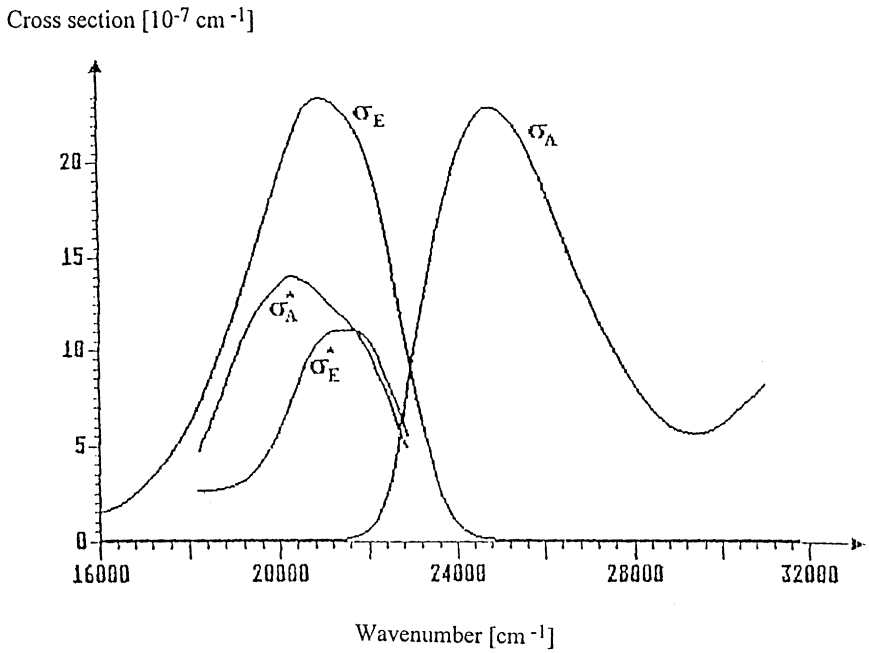


Fig. 3. The cross-sections (in units of cm^2) for some processes of B2NVP in DMF. σ_A and σ_E are the ground state absorption and emission cross-sections, respectively. σ^*_A and σ^*_E are the excited state absorption cross section and the effective emission cross-section, respectively.

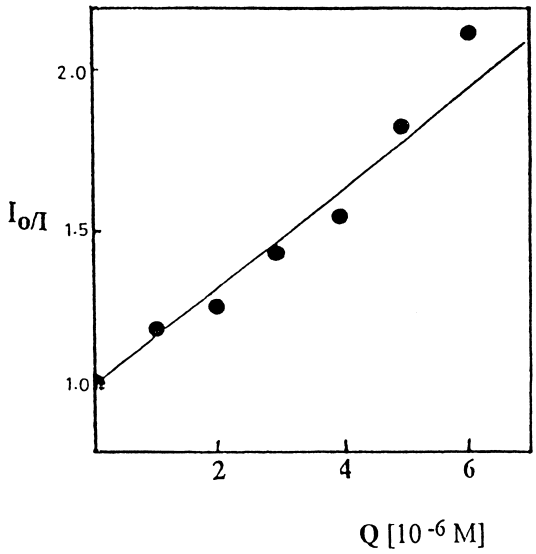


Fig. 4. Stern–Volmer plots for the quenching of B2NVP fluorescence using R6G as a quencher in DMSO at room temperature ($\lambda_{ex} = 337$ nm, $\lambda_{em} = 480$ nm). The concentration of B2NVP is 5×10^{-6} M.

The cross-section values are given in units of cm^2. The cross-section σ_A^* is given from the difference ($\sigma_E - \sigma_E^*$). We interpret this difference as the first excited singlet state absorption band which reduces dye laser efficiency. Members of the diolefinic laser dye series containing pyridyl moieties e.g. 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 compared with B2NVP, BPVB and DSP because of significantly higher σ_E^* values and low σ_A^* values [11].

The B2NVP/rhodamine6G (B2NVP/R6G) system represents a useful energy transfer dye laser (ETDL) system achieving better harvesting of light photons at 337.1 nm (the wavelength of pumping nitrogen laser). Fig. 4 shows the Stern–Volmer plot of B2NVP fluorescence quenching using R6G as a quencher. The Stern–Volmer relation (Eq. (8))

$$\frac{I_0}{I} = 1 + k_q \tau_f [Q] \tag{8}$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher of concentration [Q] (mol dm^{-3}), k_q ($dm^3\ mol^{-1} s^{-1}$) the second-order quenching rate constant and τ_f the fluorescence lifetime which is taken as 1.32 ns in DMSO [15]. From the slope (Fig. 4) k_q is calculated to be 12×10^{13} $dm^3\ mol^{-1} s^{-1}$. This value is much higher than the diffusion rate constant (k_{diff}) in DMSO (0.37×10^{10} $dm^3\ mol^{-1}\ s^{-1}$) at room temperature. The high quenching rate constant value together with the overlap of the donor emission and the acceptor absorption indicate a diffusionless energy transfer mechanism. The emission intensity of donor in the presence of acceptor (R6G) was corrected against both reabsorption of donor emitted photons by R6G and absorption of excitation light by R6G using equations described earlier [16].

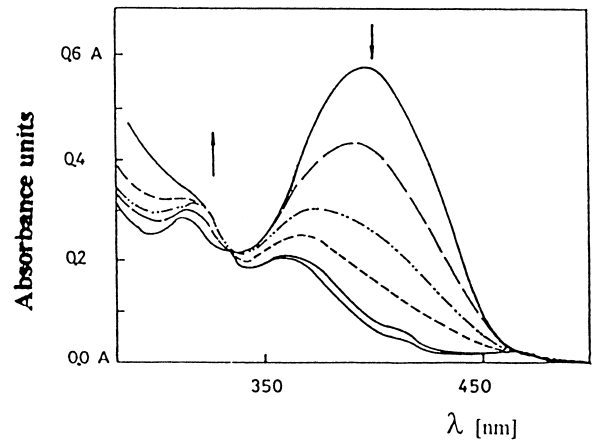


Fig. 5. Deterioration of B2NVP in CCl_4 using 254 nm light in excitation. The changes in absorption spectra of 1×10^{-5} M solution of B2NVP in CCl_4 as a result of UV irradiation ($\lambda_{ex} = 254$ nm). The irradiation times at decreasing absorbance are 0, 2, 4, 6, 16 and 26 min.

The photostability of B2NVP has been studied in different media. The electronic absorption and emission spectra of B2NVP dilute solutions (ca. 10^{-5} mol dm^{-3}) undergo change upon UV irradiation (λ_{ex} 365 nm). The underlying photoreaction in such dilute solutions of diolefinic derivatives is interpreted as *trans-cis* photoisomerization. The photochemical quantum yield (ϕ_c) value in ethanol is given in Table 1. A rapid deterioration of the dye has been observed in carbon tetrachloride (CCl_4) upon irradiation with 254 nm light as shown in Fig. 5. We propose an initial electron transfer from singlet excited B2NVP to CCl_4 leading to the formation of a transient (exciplex). This is followed by the formation of an intermolecular ion pair [$B2NP^{\cdot+} \cdots {}^{-}CCl_4$], which gives [$B2NP^{\cdot+} \cdots {}^{-}Cl \cdots {}^{-}CCl_3$] via the well-known $CCl_4 + e \rightarrow {}^{\cdot}CCl_3 + {}^{-}Cl$ reaction. The photostability of several electron donor molecules in halomethane solvents has been examined earlier [17–21].

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