Monatshefte für Chemie 129, 835–842 (1998)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Excitation Energy Transfer and Photodecomposition of Some Diolefinic Laser Dyes

Samy A. El-Daly

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

Summary. Energy transfer from 1,4-*bis*-(β-pyridyl-2-vinyl)-benzene (*P2VB*, **1**), 2,5-distyrylpyrazine (*DSP*, **2**), and 2,5-*bis*-2-(1-naphthylvinyl)-pyrazine (*BNVP*, **3**) to N,N′-*bis*-(2,5-di-*tert*-butylphenyl)-3,4:9,10-perylene-*bis*-dicarboximide (*DBPI*, **4**) has been studied in dimethyl formamide by steady state emission measurements. It was found that the *Stern-Volmer* relation is obeyed from which the rate constants of energy transfer were determined as 5.6×10^{12}, 6.8×10^{12}, and $9.1\times10^{12}\,\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$ for **1/4**, **2/4**, and **3/4**, respectively. The corresponding experimental critical transfer distances have been calculated as 5.3, 5.7, and 8.45 nm, indicating a *Förster* type energy transfer mechanism. The activation energies associated with the fluorescence quenching of **1–3** by **4** in *DMF* were calculated as 5.5, 5.2, and $4.8\,\mathrm{kJ\cdot mol^{-1}}$. The excited state lifetime and the role of molecular oxygen in deactivation of the excited singlet state of **1–3** have been studied and the second order quenching rate constants have been determined. The photochemical quantum yields ($\lambda_{ex} = 365$ nm) of **1–3** were studied in CCl_4.

Keywords. Diolefinic dyes; Laser dyes; Energy transfer; Lifetime; Quenching.

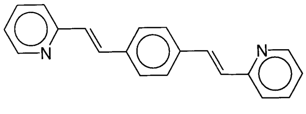
Anregungsenergieübertragung und photochemische Zersetzung von diolefinischen Laserfarbstoffen

Zusammenfassung. Die Übertragung von Energie von 1,4-*bis*-(β-Pyridyl-2-vinyl)-benzol (*P2VB*, **1**), 2,5-Distyrylpyrazin (*DSP*, **2**) und 2,5-*bis*-2-(1-Naphthylvinyl)-pyrazin (*BNVP*, **3**) auf N,N′-*bis*-(2,5-di-*tert*-Butylphenyl)-3,4:9,10-perylen-*bis*-dicarboxamid (*DBPI*, **4**) wurde durch *steady-state*-Emissionsmessungen in Dimethylformamid untersucht. Die Systeme gehorchen der *Stern-Volmer*-Beziehung, aus der sich die Geschwindigkeitskonstanten der Energieübertragung zu $5.6\cdot10^{12}$, $6.8\cdot10^{12}$ und $9.1\cdot10^{12}\,\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$ für die jeweiligen Paare **1/4**, **2/4** und **3/4** ergeben. Die entsprechenden kritischen Übertragungsabstände wurden zu 5.3, 5.7 und 8.45 nm errechnet. Die Daten lassen auf einen Energieübertragungsmechanismus nach *Förster* schließen. Die mit der Fluoreszenzlöschung von **1–3** durch **4** verbundenen Aktivierungsenergien ergeben sich zu 5.5, 5.2 und $4.8\,\mathrm{kJ\cdot mol^{-1}}$. Die Lebensdauer des angeregten Zustands sowie der Einfluß von molekularem Sauerstoff auf die Deaktivierung der angeregten Singlettzustände von **1–3** wurden ermittelt und die Geschwindigkeitskonstanten zweiter Ordnung der Fluoreszenzlöschung wurden bestimmt. Die photochemischen Quantenausbeuten ($\lambda_{ex} = 365$ nm) von **1–3** in CCl_4 wurden gemessen.

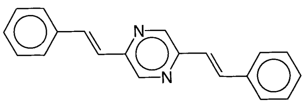
Introduction

Diolefinic heterocyclic compounds of the general formula Ar′-CH=CH-Ar-CH=CH-Ar′ are used extensively as monomers for solid state four-center type photopolymerization [1, 2], laser dyes [3–8], photographic sensitizing dyes [9], electroluminescent devices [10], electrochromic displays, and optical imaging devices [11, 12]. Some of them act as antifungal and antibacterial compounds [13].

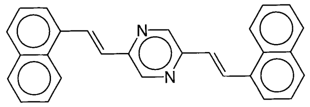
In this paper we report on the excitation energy transfer and photodecomposition of 1,4-*bis*-(β-pyridyl-2-vinyl)-benzene (*P2VB*, **1**), 2,5-distyryl-pyrazine (*DSP*, **2**), and 2,5-*bis*-2-(1-naphthylvinyl)-pyrazine (*BNVP*, **3**).



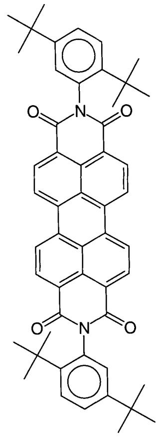
1



2



3



4

Results and Discussion

Figure 1 shows the fluorescence quenching of $1\times10^{-5}\,M$ **1** and **2** by **4** in *DMF*. The quenching process obeys the *Stern-Volmer* relation (Eq. (2)) [20].

$$\frac{I_o}{I} = 1 + K_{ET}\,\tau_f\,[A] \tag{2}$$

I_o and I represent the fluorescence intensity of the donor in the absence and presence of **4**, K_{ET} is the rate constant of the energy transfer, and $[A]$ is the acceptor concentration.

Figure 2 shows the *Stern-Volmer* plots of the fluorescence quenching of **1**, **2**, and **3** in *DMF* using **4** as a quencher. They are linear, and the second order quenching rate constants K_{ET} were calculated from the slopes and the donor solution lifetime in *DMF* (Table 1). The rate constant of energy transfer is much greater than the diffusion rate constant in *DMF* at room temperature, indicating a diffusionless mechanism for the energy transfer [21]. Figure 3 shows the overlap between the emission spectra of **1**, **2**, and **3** and the electronic absorption spectrum of **4**.

The critical transfer distances R_o were calculated from the emission spectrum of the donor and the absorption spectrum of the acceptor using *Förster*'s formula [21] (Eq. (3)) where φ_D is the emission quantum yield of the donor in the absence

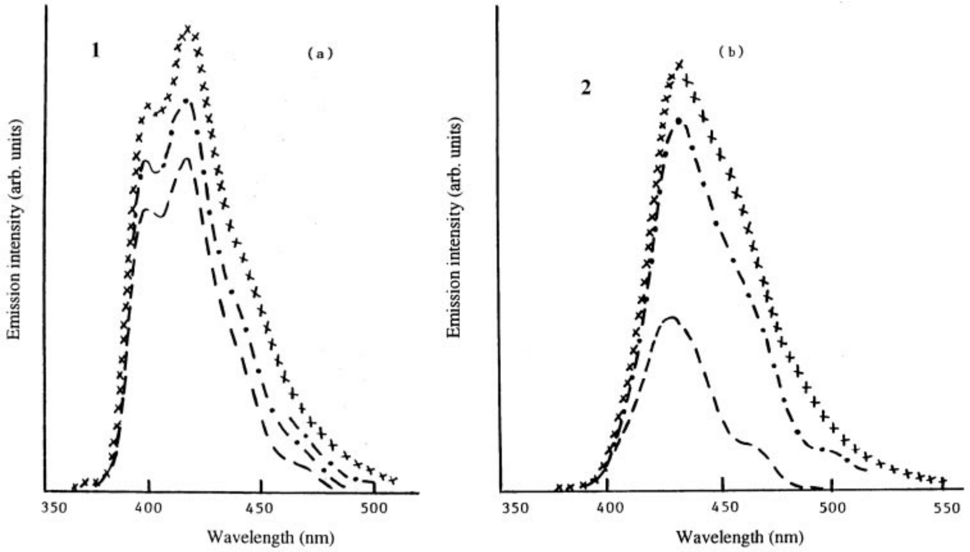


Fig. 1. (a) Emission spectra of $1 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ of **1** in *DMF* ($\lambda_{ex} = 337\,\mathrm{nm}$) in presence and absence of **4**; the concentrations of **4** at decreasing emission intensities are 0.0, 2×10^{-5}, and $5 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ (b) Emission spectra of $1 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ of **2** in *DMF* ($\lambda_{ex} = 337\,\mathrm{nm}$) in presence and absence of **4**; the concentrations of **4** at decreasing emission intensities are 0.0, 1×10^{-5} and $5 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$

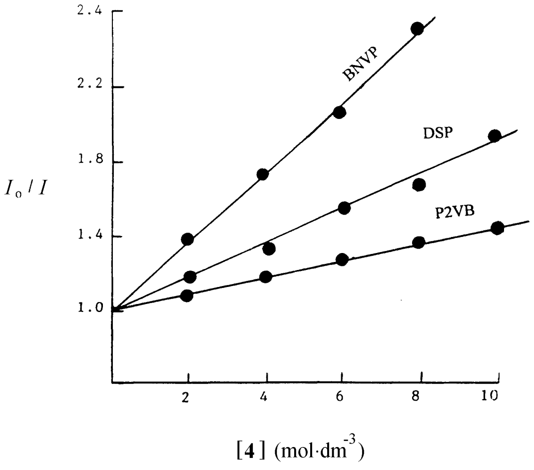


Fig. 2. *Stern-Volmer* plots of the fluorescence quenching of 1×10^{-5} *M* **1**, **2**, and **3** in *DMF* using **4** as a quencher

of acceptor, n is the solvent refractive index, the integral represents the overlap integral for the fluorescence spectrum of the donor normalized to unity (F_D) and the absorption spectrum of the acceptor (ε_A) divided by the fourth power of the wavenumber ($\bar{\nu}$), R_o is the distance at which energy transfer and emission processes are equally probable. The R_o values are also listed in Table 1.

$$R_o^6 = 1.25 \times 10^{-25} \frac{\Phi_D}{n^4} \int_0^\infty F_D(\bar{\nu}) \varepsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \quad (3)$$

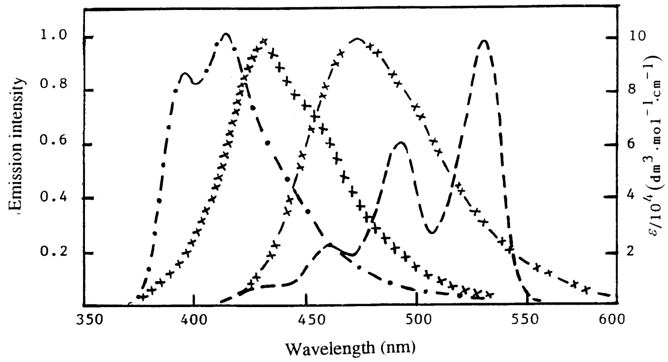


Fig. 3. Absorption spectrum (- - -) of $1 \times 10^{-5}\,M$ **4** and emission spectra of $1 \times 10^{-5}\,M$ **1** (-··-), $1 \times 10^{-5}\,M$ **2** (xxx), and $1 \times 10^{-5}\,M$ **3** in *DMF* (-xx-) ($\lambda_{ex} = 337\,\text{nm}$)

Table 1. Fluorescence quantum yields (φ_F), fluorescence lifetimes (τ), energy transfer (K_{ET}), overlap area (J), and critical transfer distances (R_o) of **1**, **2** and **3** with respect to **4** in *DMF* at room temperature ($\lambda_{ex} = 337\,\text{nm}$)

	φ_F	τ_F (ns)	J ($M^{-1} \cdot \text{cm}^3$)	$K_{ET}/10^{12}$ ($\text{M}^{-1} \cdot \text{s}^{-1}$)	R_o (nm)
1	0.46	0.69	2.99×10^{-13}	5.6	5.3
2	0.35	1.20	6.52×10^{-13}	6.8	5.7
3	0.74	1.70	27.7×10^{-13}	9.1	8.4

It was observed that the values of R_o are much greater than the values for the collision energy transfer (0.4–0.6 nm, [22]) and that the rate constant of energy transfer increases with increasing overlap area. The large values of K_{ET} and R_o found in this investigation indicate that the dominant mechanism responsible for energy transfer is resonance energy transfer due to long-range dipole-dipole interactions between excited state donor and ground state acceptor molecules.

The changes in the emission intensity of the acceptor **4** ($\lambda_{ex} = 337\,\text{nm}$, $\lambda_{em} = 530\,\text{nm}$) in the presence of different concentrations of donor in *DMF* were followed and are shown in Fig. 4. The emission intensity of acceptor **4** at 530 nm increase with increasing donor concentration.

The effect of temperature on the energy transfer from **1**, **2**, and **3** to **4** was also studied in *DMF* in the range of 20–45°C. The activation energy values E_a associated with K_{ET} were calculated by assuming the *Arrhenius* equation to be valid for K_{ET} (Eq. (4)).

$$K_{ET} = A \exp\left(-E_a/RT\right) \tag{4}$$

The values obtained are 5.5±0.24, 5.2±0.14, and 4.8±0.22 $\text{kJ} \cdot \text{mol}^{-1}$ for **1/4**, **2/4** and **3/4**, respectively. These values are smaller than the activation energy associated with solvent viscosity ($E_\eta = 10\text{–}13\,\text{kJ} \cdot \text{mol}^{-1}$) and distinctly below the value for diffusion control as reported earlier [23, 24].

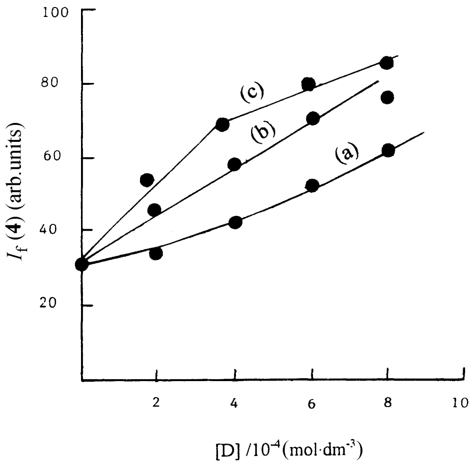


Fig. 4. Changes in the emission intensity of 1×10^{-5} *M* **4** in *DMF* as a function of increasing concentration of (a) **1**, (b) **2** and (c) **3** ($\lambda_{ex} = 337$ nm, $\lambda_{em} = 530$ nm)

The role of molecular oxygen in the deactivation of the excited singlet state of **1**, **2**, and **3** has been studied. The quenching rate constants (K_q) have been determined in different solvents applying the *Stern-Volmer* relation where $[O_2]$ is the concentration of oxygen and τ_o and τ are the fluorescence lifetimes ($\lambda_{ex} = 337$ nm) in the absence and presence of oxygen (Eq. (5)). The results are summarized in Table 2.

$$K_q[O_2] = \frac{1}{\tau} - \frac{1}{\tau_o} \qquad (5)$$

The photodecomposition of **1**, **2** and **3** has been studied in carbon tetrachloride. A rapid deterioration has been observed in CCl_4 upon irradiation at 366 nm ($I_o = 11.4 \times 10^{-6}$ Ein/min) as shown in Fig. 5. The photochemical quantum yields φ_c were calculated as 0.18, 0.006, and 0.005 for **1**, **2**, and **3** respectively.

Carbon tetrachloride forms weak charge transfer complexes with numerous electron donor molecules in their electronic ground state because its significant

Table 2. Fluorescence lifetimes in the presence and absence of molecular oxygen and quenching rate constants K_q of diolefinic laser dyes using O_2 as a quencher ($\lambda_{ex} = 337$ nm)

Solvent	$[O_2]$ (m*M*)	**1**			**2**			**3**		
		τ_o (ns)	τ (ns)	$K_q/10^{10}$ ($M^{-1} \cdot s^{-1}$)	τ_o (ns)	τ (ns)	$K_q/10^{10}$ ($M^{-1} \cdot s^{-1}$)	τ_o (ns)	τ (ns)	$K_q/10^{10}$ ($M^{-1} \cdot s^{-1}$)
MeOH	2.12	0.46	0.42	9.7	1.50	1.44	1.3	1.90	1.77	1.8
Acetone	2.4	0.73	0.67	5.1	1.20	1.16	1.2	1.70	1.60	1.5
CH_3CN	1.33	0.69	0.65	6.7	1.20	1.17	1.6	1.65	1.50	2.8
2-PrOH	2.11	0.56	0.54	3.1	1.36	1.31	1.6	1.78	1.72	1.9
BuOH	1.80	0.63	0.61	2.9	1.37	1.31	1.8	1.87	1.77	1.7

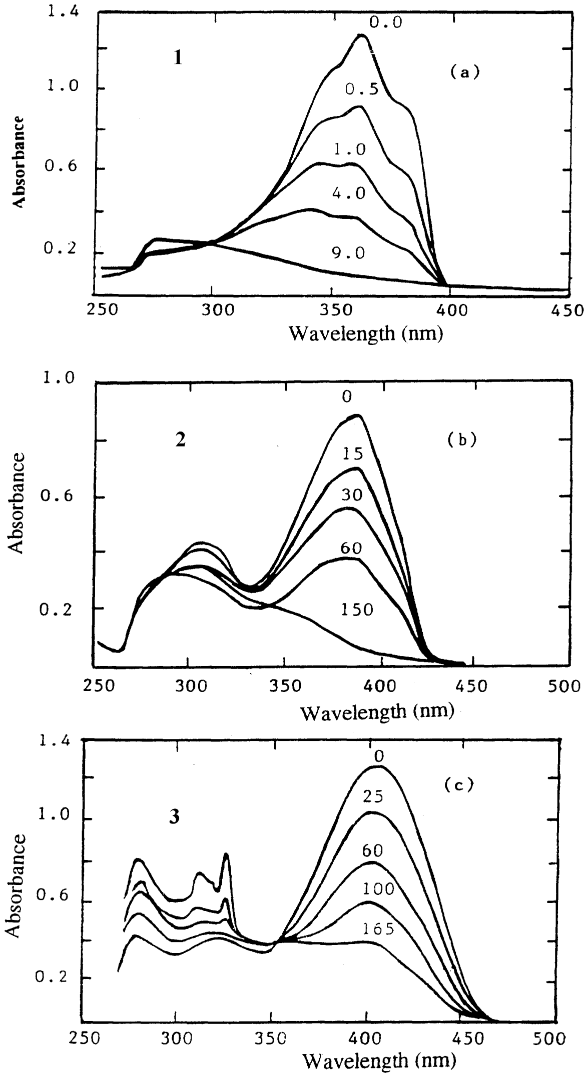


Fig. 5. Effect of irradiation ($\lambda_{ex} = 366\,nm$, $I_o = 11.4 \times 10^{-6}$ Einstein·min^{-1}) on the electronic absorption spectra of $2 \times 10^{-5}\,M$ (a) **1**, (b) **2** and (c) **3** in CCl_4 (irradiation time (min) indicated on each curve)

electron affinity [25]. The excited states of aromatic molecules are therefore expected to be involved in charge transfer interaction with carbon tetrachloride through exciplex formation. The low energy of the C-Cl bond in carbon tetrachloride [26] and also the low activation energy of the dissociative process of electron attachment [27] promote the chemical activity of carbon tetrachloride.

The primary photophysical and photochemical processes of diolefinic dyes in the presence of carbon tetrachloride are outlined in the following scheme.

$$D + h\nu \longrightarrow {}^1D^* \qquad (a)$$

$${}^1D^* \longrightarrow D + h\nu \text{ (fluorescence)} \qquad (b)$$

$$
{}^1D^* + CCl_4 \begin{array}{l} \nearrow {}^3D^* + CCl_4 \\ \searrow D + CCl_4 \end{array} \tag{c}
$$

$$
{}^1D^* + CCl_4 \longrightarrow {}^1[D^{\delta+} \cdots CCl_4^{\delta-}]^* \text{ (excited exciplex)} \tag{d}
$$

$$
{}^1[D^{\delta+} \cdots CCl_4^{\delta-}]^* \begin{array}{l} \nearrow {}^3D^* + CCl_4 \\ \searrow {}^1D^* + CCl_4 \end{array} \tag{e}
$$

$$
{}^1[D^{\delta+} \cdots CCl_4^{\delta-}]^* \longrightarrow [D^{+\cdot} \cdots Cl^- \cdots {}^{\cdot}CCl_3] \tag{f}
$$

$$
[D^{+\cdot} \cdots Cl^- \cdots {}^{\cdot}CCl_3] \longrightarrow \text{photoproducts formed in the solvent cage} \tag{g}
$$

$$
[D^{+\cdot} \cdots Cl^- \cdots {}^{\cdot}CCl_3] \longrightarrow D^{+\cdot} + Cl^- + {}^{\cdot}CCl_3 \tag{h}
$$

We propose that the electron transfer from the singlet excited state (D) to carbon tetrachloride in the transient excited charge transfer complex (exciplex) is the main primary photochemical process which initiates a chemical reaction. It leads to the radical cation, a chloride ion, and a trichloromethyl radical in the solvent cage (step f).

Experimental

Both **1** and **2** were prepared according to *Hasegawa et al.* [14]. Purification was achieved by recrystallization and column chromatography on silica gel using methylene chloride as eluent. The materials were then vacuum sublimed in the dark. A sample of **3** was kindly provided by Prof. *Masakai Masegawa* of Tokyo university.

4 (Aldrich) was dissolved in a minimum volume of chloroform, filtered, and the dye was precipitated by addition of methanol. The precipitate was collected by filtration and dried in vacuum. All solvents used in this work were of spectroscopic grade. Steady state emission spectra were measured with a Shimadzu RF 510 spectrophotometer using a rectangular quartz cell ($0.2 \times 1.0\,\mathrm{cm}^2$). Electronic absorption spectra were measured using a Shimadzu UV 160 A spectrophotometer.

Room-temperature fluorescence quantum yields (φ_f) were calculated relative to the fluorescence quantum yield of 9,10-diphenylanthracene in ethanol according to Eq. (1) [15] where the indices s and r denote sample and reference, respectively, the integrals represent the corrected fluorescence peak areas, and A and n are the absorbance at excitation wavelength and the refractive index of the applied solvents.

$$
\frac{\Phi_f(s)}{\Phi_f(r)} = \frac{\int I_s(\bar{\nu})\,d\bar{\nu}}{\int I_r\,(\bar{\nu}\,d\bar{\nu}} \cdot \frac{A_r}{A_s} \cdot \frac{n_s^2}{n_r^2} \tag{1}
$$

The use n^2 affords *ca.* 5% higher φ_f values compared with the values obtained upon using n in Eq. (1). Correction of the fluorescence for machine response was carried out by comparison of the fluorescence spectrum of $1.0 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ anthracene in benzene with those reported by *Melhuish* [16]. In the quenching studies, the emission intensities were corrected for reabsorption and absorption at excitation wavelengths according to the method described by *Marciniak* [17].

Excited state lifetimes were measured using the facilities at the Chemistry Laboratory, Kyoto Institute of Technology, Japan and were based on an experimental set-up that has been described elsewhere [18]. The photochemical quantum yield φ_c was calculated using a published method [19] which was modified using a new C++ language program to determine absorbance at infinite irradiation periods (A_∞).

Acknowledgements

We thank Prof. *S. Hirayama*, Kyoto Institute of Technology, Japan for lifetime measurements.

References

[1] Hasegawa M (1982) Advan Polym Sci **42**: 1; (1983) Chem Rev **83**: 507; (1986) Pure Appl Chem **58**: 1179
[2] Dilling WL (1983) Chem Rev **83**: 1
[3] Ebeid EM, Issa RM, El-Daly SA, Sabry MMF (1986) Chem Soc Faraday Trans 2, **82**: 1981
[4] Ebeid EM, Sabry MMF, El-Daly SA (1985) Laser Chem **5**: 223
[5] Warden JT, Gough (1971) Appl Phys Lett **19**: 345
[6] El-Daly SA, Ebeid EM, El-Hazymy SM, Babaqi AS, El-Gohary Z, Duportail G (1993) Proc Indian Acad Sci **105**: 651
[7] El-Daly SA, Al-Hazmy, SA, Ebeid EM, Vernigor EM (1995) J Photochem Photobiol A **91**: 199
[8] El-Daly SA, Al-Hazmy SA, Ebeid EM, Bhasikuttan AC, Plit DK, Spare AV, Mittal JP (1996) J Phys Chem **100**: 973
[9] Norland K, Ames A, Taylor T (1970) Photogr Sci Eng **14**: 401
[10] Hosokawa C, Kusumoto T, Tokailin H, Higashi H (1990) Eur Patent Appl
[11] Hirohashi A, Akutagawa K, Sumiya M, Ito Y (1988) Jpn Kokai Tokyo Koho
[12] Bykh AI, Golovenko VM, Rozhitskii NN (1982) Deposited Doc SPSTL 1114 Khp D-82
[13] Osman AM (1957) J Chem Soc **79**: 966
[14] Hasegawa M, Suzuki Y, Suzuki F, Nakanishi H (1969) J Polym Sci Part A-1, **7**: 743
[15] Demas JN, Crosby GA (1971) J Phys Chem **75**: 1991
[16] Melhuish WH (1960) J Phys Chem **64**: 762
[17] Marciniak B (1986) J Chem Edu **63**: 998
[18] Hirayama S, Shimono Y (1984) J Chem Soc Faraday Trans 2, **80**: 941
[19] Ebeid EM, Issa RM, Ghoneim MM, El- Daly SA (1986) J Chem Soc Faraday Trans 1, **82**: 909
[20] Braun AM, Maurette MT, Oliverso E (eds) (1991) Photochemical Technology. Wiley, New York, p 41
[21] Benzer GR, Brown SB (eds) (1980) An Introduction to Spectroscopy for Biochemists. Academic Press, New York, p 86
[22] Turro NJ (1967) Molecular Photochemistry. Benjamin, New York
[23] Marshal EJ, Philipson A, Philling MJ (1976) J Chem Soc Faraday Trans 2, **72**: 1980
[24] Aguirre MJ, Lissi EA, Olea AF (1987) J Photochem **36**: 177
[25] Biondic MC, Erra-Balsells R (1990) J Photochem Photobiol A, **51**: 341
[26] Pardo A, Reyman D, Martin E, Poyato JML, Camacho JJ, Hidalgo J, Sanchez M (1988) J Luminesc **42**: 163
[27] Encinas MV, Rubio MA, Lissi EA (1982) J Photochem **18**: 137

Received December 22, 1997. Accepted March 3, 1998