Fluorescence Properties of *p*-Quaterphenyl and *p*-Quinquephenyl Derivatives in Liquid Solvents

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Absorption, fluorescence and emission anisotropy spectra, as well as quantum yields and fluorescence decay times of *p*-quaterphenyl (PQP), 4,4‴-bis-(2-butyloctyloxy)-*p*-quaterphenyl (BBQ), 2,5,2‴‴,5‴‴-tetramethyl-*p*-quinquephenyl (TMI) and 3,5,3‴‴,5‴‴-tetra-*t*-butyl-*p*-quinquephenyl (QUI) were investigated in several nonpolar and polar solvents. It was found that high quantum yield is accompanied by a short (not exceeding 1 ns) lifetime and considerable emission anisotropy in low viscosity solvents. For TMI and QUI, which incorporate as many as 5 phenyl groups, the quantum yield in dioxane is 0.98 and 0.97, respectively. In the case of molecules with 4 phenyl groups, the quantum yield is slightly lower, amounting to 0.91. Rotational motions of terminal phenyl groups cause a lower deactivation of the excitation energy of the singlet state S_1, the longer the linear molecule.

1. Introduction

Some dyes, such as di- and triphenylmethane, auramine 0 and crystal violet, a practically incapable of emitting fluorescence in liquid solutions, unlike when in rigid or high viscosity solvents, where their quantum yield is fairly high. Such a behaviour of dye molecules indicates that the radiationless deactivation process is caused by rotational motions of constituent phenyl groups during the lifetime of the excited singlet state S_1 [1–3].

However, high quantum yield in liquid solvents is observed for a number of aromatic molecules consisting of phenyl groups linked by a single bond, such as *p*-terphenyl or *p*-quaterphenyl [4].

The present paper reports investigation on fluorescence properties of four linear molecules used in dye lasers [5], consisting of four and five phenyl residues. High viscosity solvents were deliberately chosen to demonstrate that in this case rotational motions, resulting in radiationless deactivation, affect the fluorescence quantum yield only slightly.

2. Experimental

p-Quaterphenyl (PQP), 4,4‴-bis(2-butyloctyloxy)-*p*-quaterphenyl (BBQ), 2,5,2‴‴,5‴‴-tetramethyl-*p*-quinquephenyl (TMI) and 3,5,3‴‴,5‴‴-tetra-*t*-butyl-*p*-quinquephenyl (QUI) from Lambda Physik GmbH Goettingen, were laser-grade dyes and were used without further purification (Figure 1). The solvents: cyclohexane, dioxane, chloroform, ethyl acetate, dichloromethane and methanol were spectral grade.

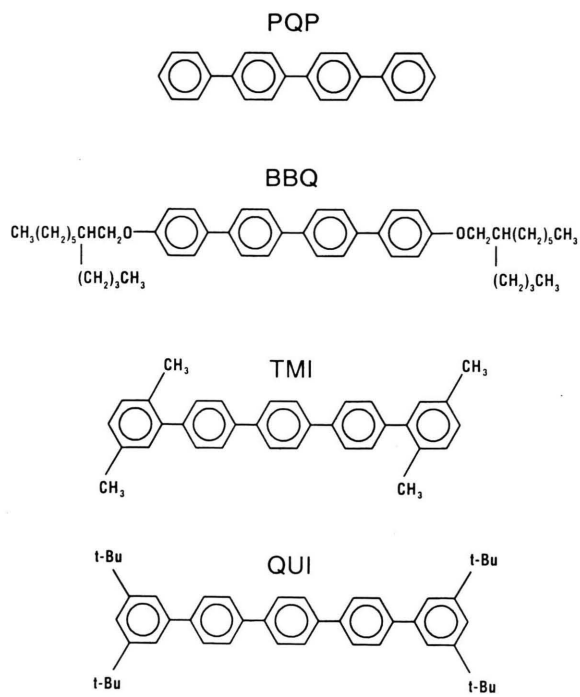

Fig. 1. Structural formulae of PQP, BBQ, TMI and QUI.

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The methods of measuring the absorption and fluorescence spectra and the quantum yields and emission anisotropies were described in [6–11]. The emission anisotropy, r, of the molecules investigated in the above liquid solvents turned out to be distinctly different from the zero value ($r > 0$), thus necessitating the measured quantum yields to be corrected according to formula (1) in [9].

Fluorescence decays were measured using time-correlated single photon counting technique [12] by means of an apparatus shown in Figure 2. The samples were excited by light pulses with wavelength $\lambda_{exc} = 290$ nm, time halfwidth of ~ 5 ps, with a frequency of 720 kHz. A fast Antel ARS-3 photodiode triggered the START channel of the time-to-amplitude converter, and the STOP pulses were generated by a Philips XP 2020Q photomultiplier. The decay curves were recorded by a multichannel PCA-8000 Nucleus/Tennelec amplitude analyzer inserted into a PC486 computer. The CU system served to control the frequency of the STOP pulses so that the proper statistics of the measurement be maintained (i.e. $f_{START}/f_{STOP} = 100:1$). The experimental data were deconvoluted using an FLA-900 programme (Edinburgh Analytical Instruments, Great Britain), involving the nonlinear least squares method based on the Marquardt algorithm [13]. For illustration, Fig. 3 shows the result of the fluorescence decay measurement of BBQ in dioxane.

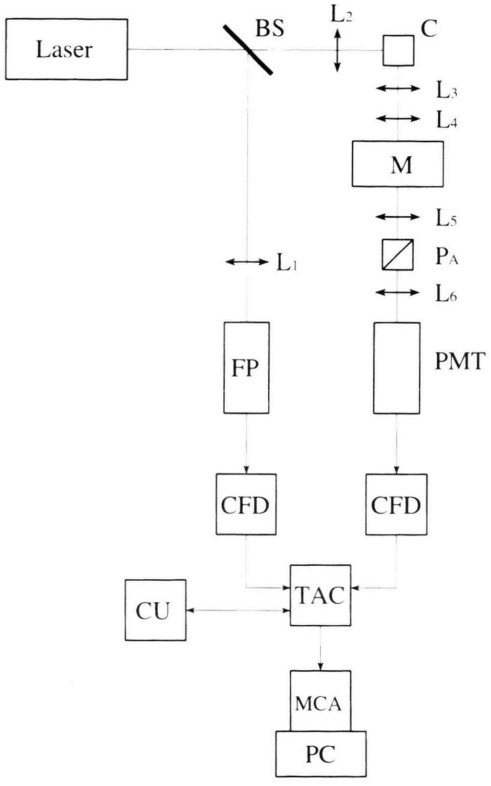

Fig. 2. The time-correlated single photon counting method: LASER, YAG Nd:$^{3+}$ Antares 76 laser with the mode locker and frequency doubler, Rhodamine 6G dye laser model 700 with Model 7200 Cavity Dumper, all from Coherent, USA; additional, external frequency doubler Model 390 of Spectra Physics to obtain 290 nm. BS, beam splitter. $L_1 \div L_6$, lenses. FP, fast photodiode Model ARS-3, Antel, Canada. CFD, Quad Constant Fraction Discriminator, CTC 454, Tennelec, USA. TAC, time-to-amplitude converter, TC 864, Tennelec, USA. CU, control unit with counter and signalization, selfmade. C, cuvette. M, monochromator. P_A, analyzing polarizer, used only in case of emission anisotropy decay measurements. PMT, XP 2020Q photomultiplier, Philips, Netherland. MCA, multichannel analyser, PCA 8000, Nucleus/Tennelec, USA, plug-in PC board. PC, personal computer.

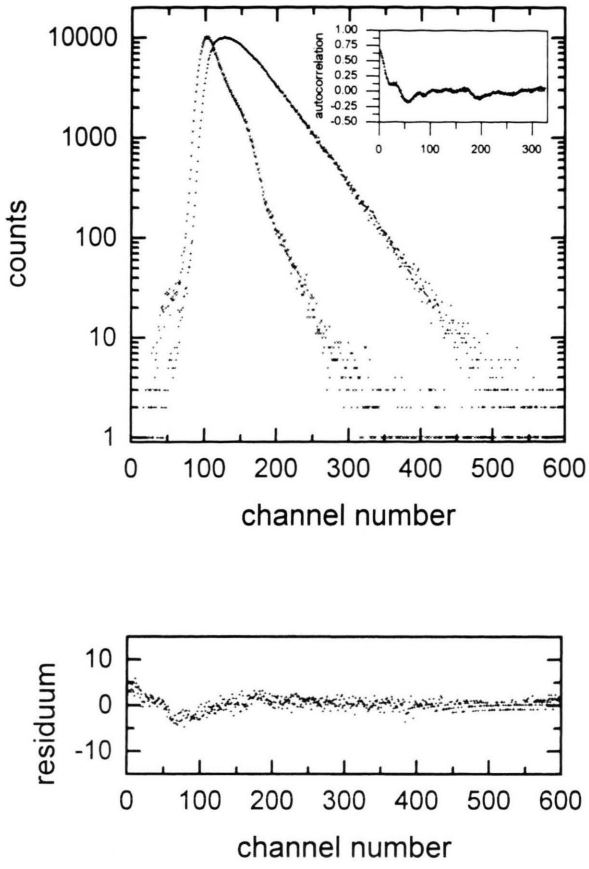

Fig. 3. Fluorescence decay of BBQ in dioxane ($\chi^2 = 2.45$).

3. Results and Discussion

3.1. Absorption, Fluorescence and Emission Anisotropy Spectra

Figures 4 and 5 show absorption, fluorescence and emission anisotropy spectra of PQP in cyclohexane and dichloromethane and of BBQ in dioxane and dichloromethane. In the case of both nonpolar elongated luminescent molecules, slight band shift towards long wavelengths is observed when passing from nonpolar to polar solvent. Similar behaviour of absorption and fluorescence spectra can be observed for TMI and QUI (Figures 6 and 7). In all cases, the emission anisotropy in the longwave absorption band and in the fluorescence band does not change, thus demonstrating the occurrence of luminescent centres of one kind.

The slight shift of the absorption and fluorescence bands for nonpolar luminescent molecules in the longwave direction is due to dispersive interactions between the luminescent molecules and the surrounding solvent. According to Liptay [14], there exists a linear dependence between the position of the absorption

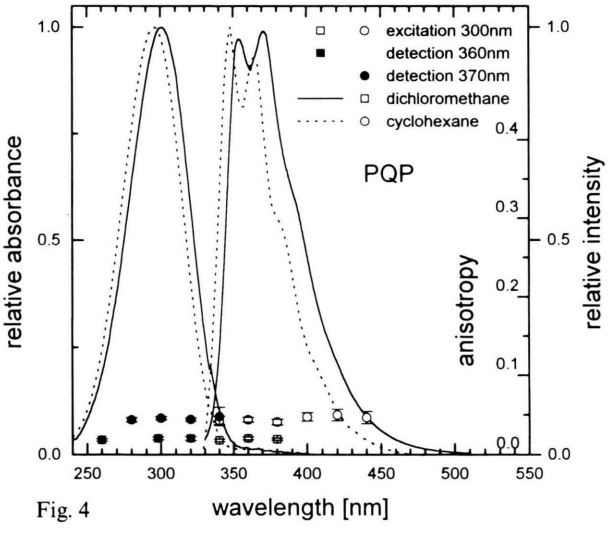

Fig. 4

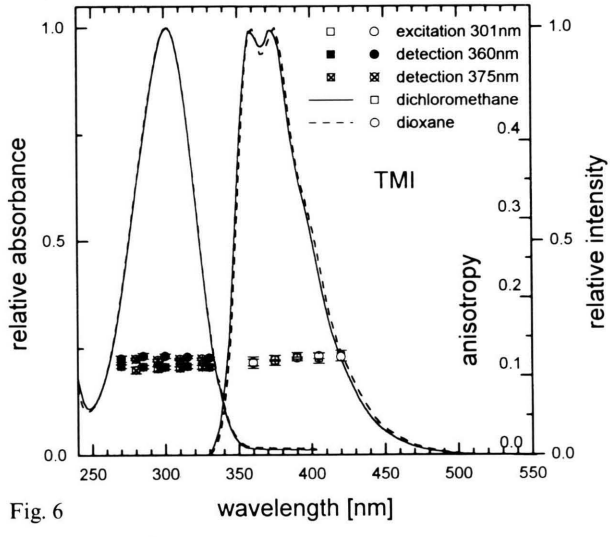

Fig. 6

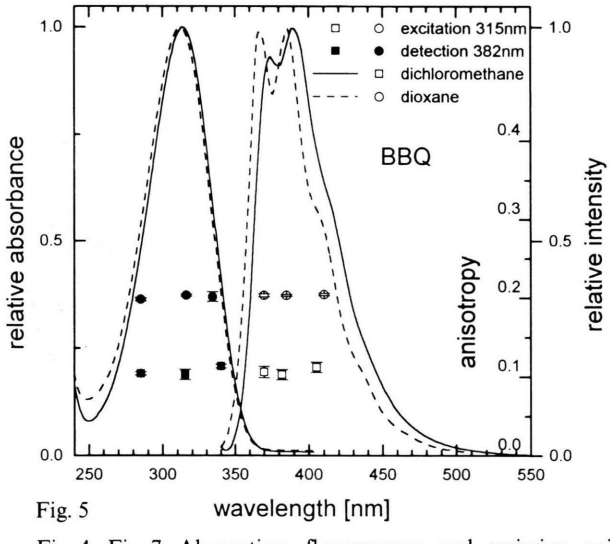

Fig. 5

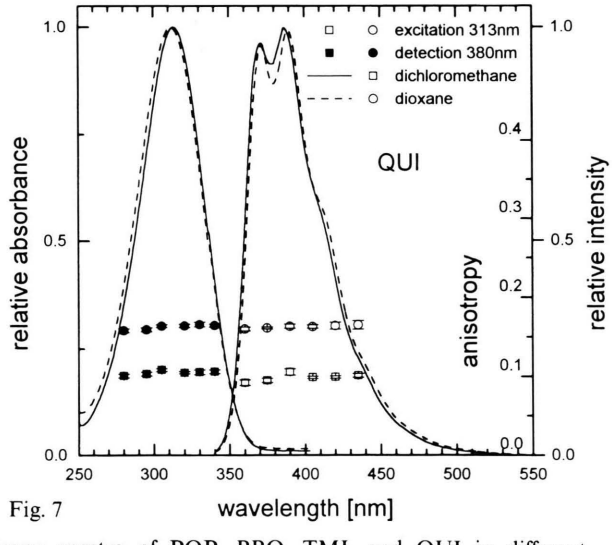

Fig. 7

Fig. 4–Fig. 7. Absorption, fluorescence and emission anisotropy spectra of PQP, BBQ, TMI, and QUI in different solvents at 296 K.

maximum ($\tilde{\nu}_A$) or fluorescence maximum ($\tilde{\nu}_F$) and the function $f' = \dfrac{n^2-1}{2n^2+1}$ (where n is the refractive index of the respective solvent). Such linear dependencies were confirmed for all luminescent molecules investigated. Some conclusions on the quantity related with the differences in the energy of dispersive interactions in the ground and excited state can be drawn based on the solpe of the straight lines.

3.2. *Fluorescence Quantum Yields and Lifetimes*

Table 1 comprises the measured values of quantum yields, Y, lifetimes, τ, and emission anisotropy, r, in three solvents with different polarity and viscosity. Quantum yields, Y, were corrected with respect to the emission anisotropy. For example, $Y = 0.90$ for PQP in cyclohexane, whereas that reported by Berlman [4] was 0.89, and $\tau = 0.8$ ns only slightly differed from the value obtained by the authors (Table 1).

Although the solvents used had low viscosity, the emission anisotropy, r, observed was considerable (Table 1). Furthermore, mean lifetimes, τ, for the four luminescent compounds studied, are distinctly less than 1 ns. In this case the rotational motions of the luminescent molecules do not result in a total depolarization of fluorescence. For example, in the case of PQP, the mean lifetimes of this molecule are almost the same in cyclohexane and dichloromethane, whereas the emission anisotropies differ distinctly, since the difference in the values of solvent viscosities is almost twofold (Table 1).

The radiative lifetime, τ_0, called also the natural fluorescence lifetime, being the inverse probability (per unit time) of fluorescence emission, k_F^{abs}, was determined based on the formula [15, 16]

$$k_F^{abs} = \frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \langle \tilde{\nu}_F^{-3} \rangle^{-1} \int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} \, d\tilde{\nu}, \qquad (1)$$

where n is the sovlent refractive index, $\tilde{\nu}$ the wavenumber in cm^{-1}, $\langle \nu_F^{-3} \rangle$ the mean value of $\tilde{\nu}^{-3}$ over the fluorescence spectrum $F(\tilde{\nu})$, $\varepsilon(\tilde{\nu})$ the decadic molar extinction coefficient, and the integral is over the first absorption band system.

Apart measured fluorescence rate parameters, k_F^{abs}, Table 2 summarizes the values of k_F and k_n calculated from the formulae

$$k_F = Y_F/\tau, \qquad (2)$$

$$k_n = (1 - Y_F)/\tau, \qquad (3)$$

where k_F is the fluorescence rate constant and k_n incorporates all possible radiationless decay processes. The ratio

$$R_F = k_F^{abs}/k_F \qquad (4)$$

is also given in Table 2.

As can be seen, R_F slightly differs from unity for tetraphenyls, whereas in the case of quinquephenyls the difference reaches 1/3. In addition, k_F obtained from the measurements and calculated based on (1) and (2) for PQP and BBQ is independent of the solvent viscosity, similarly as for ω-substituted 4-dimethylamino-*trans*-styrenes [17, 18] (see Table 2). The proba-

Table 1. Fluorescence anisotropies r, mean decay times τ (in ns) and quantum yields Y_F of laser dyes in fluid solvents at 295 K (* at 288 K).

Solvent	Dielectric constant ε	Viscosity $\eta \times 10^3$ [kg·m^{-1}·s^{-1}] at 295 K	PQP			BBQ			TMI			QUI		
			r	Y_F	τ	r	Y_F	τ	r	Y_F	τ	r	Y_F	τ
Cyclohexane	2.02	1.01	0.045	0.90	0.844	–	–	–	–	–	–	–	–	–
Dioxane	2.21	1.45	–	–	–	0.203	0.91	0.815	0.126	0.98	0.450	0.165	0.97	0.433
Dichloromethane	8.93	0.449*	0.027	0.91	0.861	0.113	0.91	0.863	0.113	0.90	0.511	0.106	0.89	0.516

Table 2. Values of rate constants (in 10^9 s^{-1}).

Solvent	PQP				BBQ				TMI				QUI			
	k_F^{abs}	k_F	k_n	R_F	k_F^{abs}	k_F	k_n	R_F	k_F^{abs}	k_F	k_n	R_F	k_F^{abs}	k_F	k_n	R_F
Cyclohexane	0.91	1.07	0.12	0.85	–	–	–	–	–	–	–	–	–	–	–	–
Dioxane	–	–	–	–	0.813	1.117	0.11	0.73	0.649	2.18	0.044	0.30	0.684	2.24	0.07	0.30
Dichloromethane	0.90	1.06	0.10	0.85	0.815	1.06	0.099	0.77	0.703	1.76	0.196	0.40	0.805	1.725	0.213	0.47

bilities (per unit time) of deactivation, k_n, for TMI and QUI are markedly lower than those observed for molecules consisting of tetraphenyls (PQP and BBQ).

4. Conclusions

a) For derivatives of tetra- and quinquephenyls in nonpolar and low-viscosity polar solvents, high fluorescence quantum yields and lifetimes lower than 1 ns are observed. The highest fluorescence quantum yields were obtained for quinquephenyls TMI and QUI in dioxane with the highest viscosity as compared to the viscosity of the other solvents (Table 1).

b) Rotational motions of the terminal phenyl groups only slightly affect the radiationless deactivation of the excitation energy in the singlet state S_1.

c) Strong quenching of the fluorescence of the dyes named in the introduction to the present paper cannot be accounted for solely by the rotations of the phenyl rings about the single bond.

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