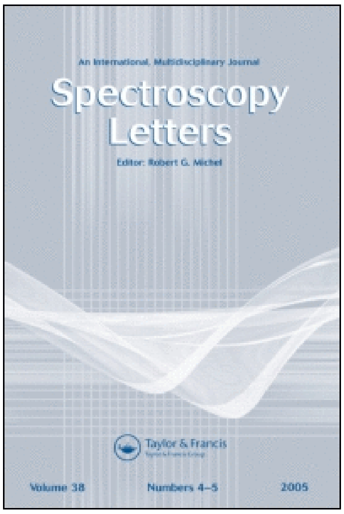

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Fluorescence Quantum Yields of Perylene 3,4,9,10-Tetracarboxylic Acid-*bis*-N,N'-aryl(alkyl) Diimides

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FLUORESCENCE QUANTUM YIELDS OF PERYLENE 3,4,9,10-TETRACARBOXYLIC ACID-BIS-N,N'-ARYL(ALKYL) DIIMIDES

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ABSTRACT

The synthesized perylenes 3,4,9,10-tetracarboxylic acid N,N'-ethyl, phenyl, ρ-anisyl, α-naphthyl and acetyl diimides have shown great variations in absorption and emission spectra. The variation in molar extinction coefficients and fluorescence quantum yields have indicated that steric and electronic effects, caused by N-substitution, alters emission characteristics of perylene diimides significantly.

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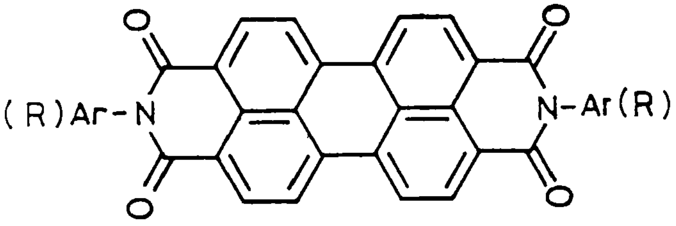
INTRODUCTION

Bis-imides of perylene tetracarboxylic acid are known as highly fluorescent solid pigments which are very stable to photochemical reactions. They are potentially suitable as photosensitizers, photon counters and laser dyes. The high stability of these compounds to heat and light proves them to be useful for plastics and synthetic textile materials [2–4]. Furthermore, perylene diimides may be highly advantageous for applications in the field of solar energy conversion [1–7].

Some bis-N,N'-aryl and alkyl diimides of perylene have been first synthesized as red pigments by Kardos and Friedlander [1]. Langhals et al. [2] have synthesized a number of diimides and measured the fluorescence quantum yields with solubility tests in DMF. Among the perylene diimides, the 2,5-di-t-butylphenyl derivative has attracted attention of researchers as a result of its high fluorescence quantum yield (>0.95) and enhanced solubility. Perylene bis-N,N'-aryl (alkyl) diimides have low solubilities in organic solvents (<10–20 mg/lt). Photostability, emission characteristics, and laser dye capacities have been studied by Bird [3], Ford [4] and Ebeid [5]. Electron transfer reactions of perylene diimides have been observed by El-Daly [6] and Wasielewski [7]. All the later investigations were done on a single aryl derivative of perylene diimide. The high fluorescence quantum yield of this compound led to the conclusion that perylene diimides are good photosensitizers via singlet excited states and excellent laser dyes due to favorable location of triplet-triplet absorption and low probability of intersystem crossings. The photo-sensitized generation of singlet oxygen is thought to be useful with perylene diimides, because of low lying triplet states [4].

In the present work we have synthesized various alkyl and aryl, perylene diimides, as shown below, for studying the emission characteristics as a function of the substitution pattern. UV and emission spectra are discussed in relation to literature data and substituent effects for these compounds.



	Ar (R)		Ar (R)
1	Ethyl	4	α–Naphthyl
2	Phenyl	5	β–Naphthyl
3	p–Anisyl	6	Acetyl

EXPERIMENTAL

General

The perylene N,N'–disubstituted imides were synthesized by condensation of perylene–3,4,9,10–tetracarboxylic dianhydride and aryl (alkyl) primary amines neatly. $Zn(OAc)_2$ was used to catalyse the imide formation [2]. The perylene N,N'–disubstituted imides were purified by washing of the reaction mixture with acetone to remove unreacted material, and by crystallization from nitrobenzene. The imides have very low solubility (about 1 mg in 100 ml of acetonitrile or dimethyl formamide) and a high melting point (about 450 °C). They were identified by IR and elemental analysis.

The perylene diimides **1–6** are obtained in nearly quantitative yields in the absence of solvents. Synthetic trials in the solvents chinoline and nitrobenzene gave lower yields. Identification of these compounds by NMR spectroscopy was found to be unpractical due to low solubility. All the perylene diimides give characteristic carbonyl–I and carbonyl–II bands, as well as imide–I and imide–II bands (CONRCO) (Table 1).

TABLE 1. Characteristic IR absorptions of **1** - **6**.

Perylene	Carbonyl-I[a]	Carbonyl-II[a]	Imide-I[a]	Imide-II[a]
1	1693	1654	1592	1578
2	1703	1667	1594	1577
3	1705	1671	1595	1578
4	1706	1672	1594	1578
5	1696	1656	1593	1578
6	1687		1590	1576

[a] Wavenumber, cm^{-1}

Perylene 3,4,9,10–tetracarboxylic acid–bis–N,N'–α–naphthyl diimide **4.**

A mixture of perylene–3,4,9,10–tetracarboxylic acid dianhydride (1 g, 2.55 x 10^{-3} mole), α–naphthylamine (7.30 g, 51 x 10^{-3} mole) and $Zn(OAc)_2$ as catalyst (0.559 g, 2.55 x 10^{-3} mole), were refluxed for 2 h at 100 °C, 3 h at 140 °C, and 3 h at 180 °C neatly. Ethanol (90 ml) was added to the mixture which was stirred for 1 h at 40 °C and filtered while hot. The filtrate color was dark violet. The wet cake was dried in vacuum and refluxed for 30 minutes with 2% NaOH (100 ml) in order to convert amides to imides. The filtrate which showed green fluorescence, was washed with 2% hot NaOH until the green fluorescence disappeared. The wet product was treated with 10% HCl (100 ml), heated to 90 °C and filtered hot and dried in vacuum to give a brown–red powder with a yield of 95%.

The IR spectra were taken with KBr pellets using an IFS 66 spectrophotometer. Elemental analyses were obtained from a Carlo Erba–1106 C, H, N analyzer. The UV absorption spectra were recorded with a Perkin Elmer–320 spectrophotometer and the emission spectra with a Spex Fluorolog. Rhodamine 101 was used as reference probe for fluorescence quantum yield measurements.

TABLE 2 .The UV absorption data of perylene bis-N,N'-aryl (alkyl) diimides in dimethyl formamide.^{a}

Perylene	$\lambda_1{}^b$	$\epsilon_1{}^c$	$\lambda_2{}^b$	$\epsilon_2{}^c$	$\lambda_3{}^b$	$\epsilon_3{}^c$
1	524	3070	488	1940	457	580
2	525	22000	488	11500	457	3770
3	524	2150	488	1790	457	1250
4	526	87300	490	31800	458	8650
5	525	1570	488	1170	456	860
6	519	8340	484	5940	453	2780

^{a} At concentrations of $(1.1\text{-}1.8)\text{x}10^{-5}$ M; ^{b} λ (nm); ^{c} ϵ ($M^{-1}cm^{-1}$) .

RESULTS AND DISCUSSION

Bird [3], Langhals [2], Ford [4], Ebeid [5] and El–Daly [6] have reported high photostability of perylene diimides and photosensitizer capacities in energy and electron transfer reactions. They have concluded that in general perylene diimides have very high fluorescence quantum yields. However our work shows that both, the fluorescence quantum yields and the molar absorption coefficients are extremely N–substitution dependent. Previous investigations have focused attention only on one diimide, bis–2,5–di–tert–butylphenyl, due to advantageous solubility in alcohol in which shows a high fluorescence quantum yield of 0.99^4.

The UV spectra of all six perylene diimides investigated in this work show the typical three bands around 525 nm (λ_1), 490 nm (λ_2) and 455 nm (λ_3). Only the N,N'–diacetyl derivative 6 blue shifts of the bands of about 3–6 nm. The absorption intensities of the three bands are declining in the order of

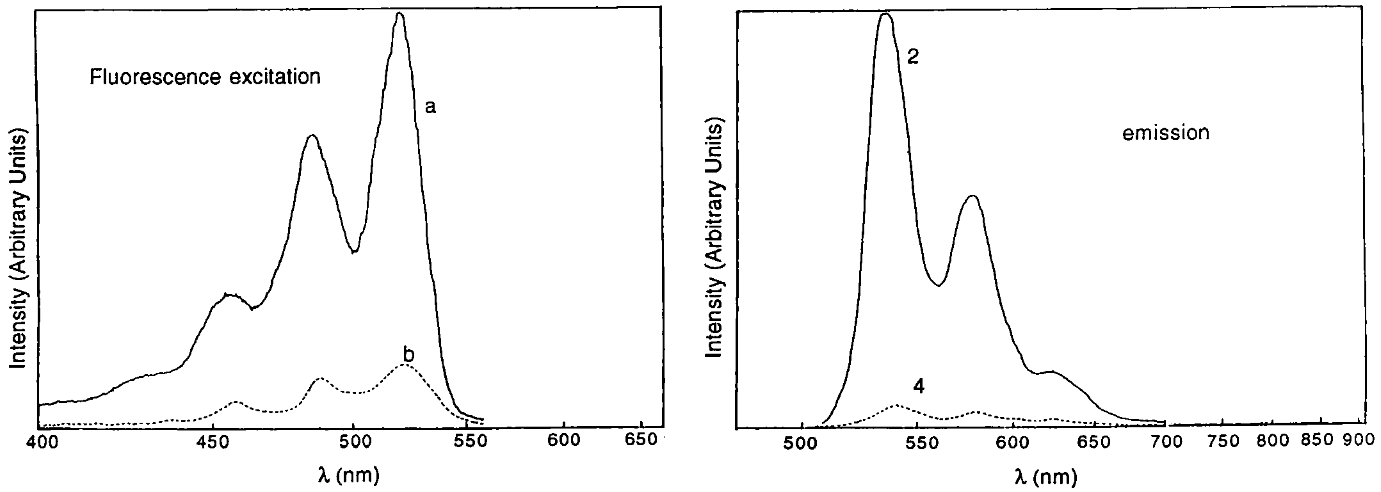


Fig. 1. Fluorescence excitation spectra of perylene bis-N,N'-phenyl diimide 2 in acetonitrile; a) at λ_{ems} = 570 nm, and b) at λ_{ems} = 620 nm, and emission spectra of 2 and perylene bis-N,N'-α-naphthyl diimide 4 in acetonitrile at λ_{exc} = 485 nm.

$\lambda_1 - \lambda_2 - \lambda_3$ in agreement with literature data (Table 2, Figure 1). However, there are drastic variations of the molar extinction coefficients. The highest absorbance is observed for the α-naphthyl derivative **4** with $\varepsilon_{max}^{526} = 87300$, being close to the value reported by Langhals[2] for bis-2,5-di-tert-butylphenyl perylene diimide ($\varepsilon_{max}^{526} = 95000$). The β-naphthyl derivative **5** has a much lower absorbance ($\varepsilon_{max}^{525} = 1570$), as compared to **4**. Another striking difference in absorbance is seen for the phenyl derivative **2** and the p-anisyl derivative **3**. p-Methoxy substitution at the phenyl ring seems to cause a hypochromic shift together with a lower extinction coefficient at 525 nm ($\varepsilon_{max}^{524} = 2150$). The difference in absorption intensity between **4** and **5** may be attributed to changes of the dihedral angle of the aryl C-N bond which is expected to be larger in **4** due to steric hindrance. On the other hand the notable absorption intensity change from **2** to **3** may only be attributed to inductive influence of the p-methoxy group. However these steric and inductive variations can not be attributed as primary causes for absorption parameter variations.

The fluorescence excitation spectra of perylene diimides in dimethyl formamide are identical to the absorption spectra indicating molecular rigidness [2,4]. Figure 1 shows the change of fluorescence excitation spectra of the diphenyl derivative **2** at 570 and 620 nm emission wavelengths. The fluorescence emission spectra of perylene diimides were taken at (1-2) x 10^{-5} molar concentrations in nitrogen-saturated acetonitrile at 485 nm excitation wavelength. Excitation at 520 nm have caused the observation of incomplete spectra. The reference rhodamine-101 fluorescence was recorded at 485 nm in ethanol solution. The refractive index corrections of solvents were included in the calculations. The UV spectra of all perylene diimides were recorded for the samples in acetonitrile solutions, for fluorescence quantum yield calculations, in order to avoid errors from concentration variations and solvent effects on absorption. The fluorescence spectra of perylene diimides are seen as nearly mirror images of the corresponding absorption spectra, in agreement with earlier results.

Table 3 lists the calculated fluorescence quantum yields of perylene diimides. Langhals [2] reported a quantum yield of 0.93 for perylene bis

Table 3. Fluorescence quantum yields of perylene diimides in acetonitrile.[a,b,c]

Perylene	Q_F
1	0.91
2	0.96
3	0.11
4	0.04
5	0.67
6	0.17

[a] At concentrations of (1–2) x 10^{-5} M. [b] Samples were nitrogen purged
[c] Error limits are ± 5%.

diphenyl imide, **2**, in DMF. Our result is 0.96 in acetonitrile. The difference, although within error limits, may be attributed to solvent change. Acetonitrile appears to give better fluorescence quantum yields as compared to other solvents. Langhals [2] reports lower quantum yields in cyclohexanol and methyliodide, whereas Ford [4] reports as high as 0.98 and 0.99 quantum yields for perylene bis–(2,5–di–tert––butylphenyl) diimide in acetonitrile and chloroform, respectively, in comparison to benzene, acetone, ethanol and bromobenzene, 0.97, 0.95, 0.93, 0.97, respectively.

The most striking feature of Table 3 is that fluorescence quantum yields vary between 0.04 to 0.96. Other than diethyl derivative, **1**, (Q_F = 0.91) and diphenyl derivative, **2**, (Q_F = 0.96) the only derivative with appreciable fluorescence quantum yield is β = naphthyl derivative, **5**, (Q_F = 0.67). Although this compound has the lowest absorption intensity among the six diimides, ε^{525}_{max} = 1570.

The drastic change in fluorescence quantum yields from α–naphthyl, **4**, (Q_F = 0.04) to β–naphthyl may be explained by the change in dihedral angle between the naphthyl moiety and perylene tetra–carboxylic acid diimide moiety, that results in radiationless deactivation of the first excited singlet state (S_1).

In compound 3, which has the electron donating substituent, p-methoxy group, a fluorescence quantum yield of 0.11 was obtained, again a serious decline compared to diphenyl diimide, 2, (Q_F = 0.96). The electron donation to the aryl group appears to enhance radiationless deactivation. A similar observation was reported by Langhals [2], for perylene 2-hydroxyphenyl and 4-methoxy-2-methylphenyl diimides, with fluorescence quantum yields of 0.03 and 0.02, respectively, in DMF.

CONCLUSION

Our results show that the emission characteristics of perylene N,N'-disubstituted imides are strongly dependent on steric and electronic effects of the substituents at the imide nitrogen. Thus, it is dangerous to claim that perylene diimides, in general, may have high fluorescence quantum yields and hence are useful as laser dyes and for some photochemical uses. So far there exists just one example, the perylene di-t-butylphenyl diimide, fulfilling the latter requirement of a high Q_F (0.99) [4]. By comparing the fluorescence quantum yields of diethyl imide **2** (Q_F = 0.91) and the diacetyl imide **6** (Q_F = 0.17), it appears that also an electron withdrawing substituent on the imide nitrogen lowers the emission capacity of the perylenes significantly, as found for electron donating substitution on aryl ring of imide nitrogen, between 2 and 3. These results indicate that substituent effects on emission characteristics are not of primary origin.

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