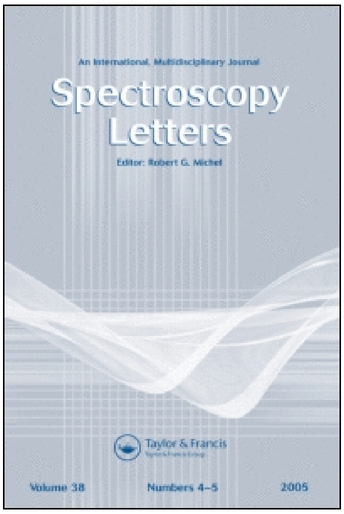

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Energy Transfer Studies with Perylene bis-Diimide Derivatives

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ENERGY TRANSFER STUDIES WITH PERYLENE bis-DIIMIDE DERIVATIVES

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Abstract - Singlet energy transfer between seven derivatives of perylene diimides and cobalt ions are studied. Energy transfer quenching by cobalt ions is observed for all of the perylene diimides. The rate of bimolecular quenching is found to be about, $k_q \cong 10^{10}$ $M^{-1}s^{-1}$, only the N-naphthyl substitution lowered the rates to the range of, $k_q \cong 10^9$ $M^{-1}s^{-1}$. The critical transfer distances, R_o (5.8-10.4 A°), calculated from donor emission and acceptor absorption spectra, are attributed to a Forster resonance energy transfer process.

INTRODUCTION

The thermal[1] and the photostability[2-5] of perylene bisdicarboxyimides are well known in literature. These high stabilities indicate their applicability as laser dyes[4-6], and photosensitizers of energy and electron transfer reactions[2-7]. Wasielewsky[8], has detected electron transfer between perylene diimides and phorphyrin couples, and has demonstrated the molecular switch applications of these systems.

Ford[4] has pointed that the perylene diimides would give photosensitized energy-electron transfer processes from singlet state rather than triplet state due to high difference between singlet to triplet energy levels, 54 kcal/mol to 27.5 kcal/mol, respectively, found for bis(di-*tert*-butylphenyl)diimide. The fluorescence quenching of perylene[11] and of perylene bis(di-*tert*-butylphenyl) diimide[12] by cobalt ions is being reported. At the same time, it is indicated that energy transfer between perylene bis(di-

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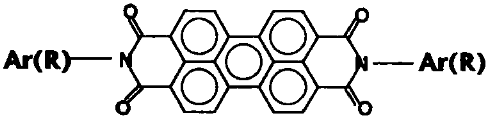
tert-butylphenyl)diimide and cobalt ions occurs with Forster long-range energy transfer mechanism. No other perylene diimide derivatives are studied for comparisons. We have reported the synthesis of the following perylene diimides earlier[5]. In this work we have aimed to investigate the energy transfer from singlet state and calculate the critical transfer distances, rate constants for bimolecular fluorescence quenching for some of the derivatives in order to observe the substituent effects.



	Ar(R)		Ar(R)
1	Ethyl	5	β-Naphthyl
2	Phenyl	6	Acetyl
3	p-Anisyl	7	p-Aminophenyl
4	α-Naphthyl		

MATERIALS AND METHODS

Perylene diimides were synthesized as reported earlier[5]. $CoCl_2.6H_2O$ (Merck) was recrystallised from methanol. All solvents were Analar grade. UV-visible absorption spectra were recorded on a Hewlett-Packard HP 8452A diode array spectrophotometer. Emission spectra were measured on a Spex Fluorolog 2 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

The fluorescence quantum yields calculated in methanol solutions at earlier studies[1-5] have suggested that N-substitution may alter the photophysical and photochemical properties of perylene diimides.

	Substituent	Q_F
1	Ethyl	0.91
2	Phenyl	0.96
3	p-Anisyl	0.11
4	α-Naphthyl	0.04
5	β-Naphthyl	0.67
6	Acetyl	0.17
7	p-Aminophenyl	0.96

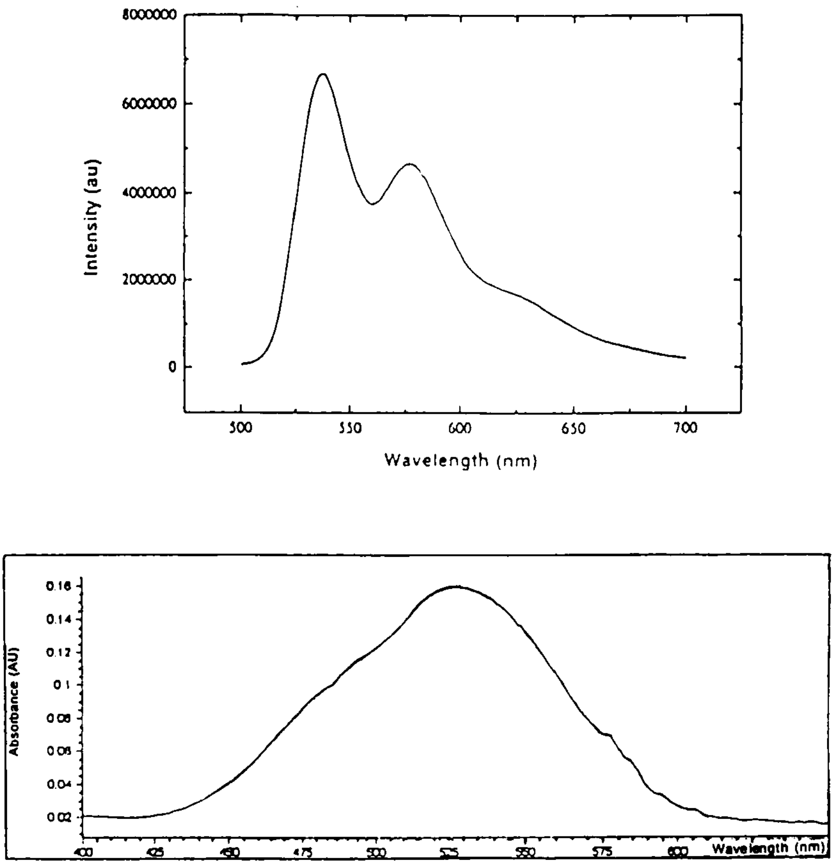


Figure 1. Emission spectrum (λ_{exc} = 485 nm) of 1 x 10^{-5} M perylene 3,4,9,10-tetracarboxylic acid-bis-N,N'-phenyl diimide, 2, in methanol and absorption spectrum of 0.02 M Co^{2+} ions in methanol.

Langhals[13] reports a fluorescence quantum yield of unity for majority of diimides. Considering the extreme low solubilities of perylene diimides even in acetonitrile and methanol solutions which gives the highest concentrations (about 10^{-5} M), the low Q_F values for *p*-anisyl, *3*, α-naphthyl, *4*, and acetyl, *6*, derivatives as 0.11, 0.04, and 0.17, respectively, may be attributed to aggregate formations. The transfer of energy from singlet energy level to triplet would be prevented by dominant fluorescence. It is expected that perylene diimides would not give any triplet sensitized reactions. In accordance with, it is found that no singlet oxygen formations were detected for any of

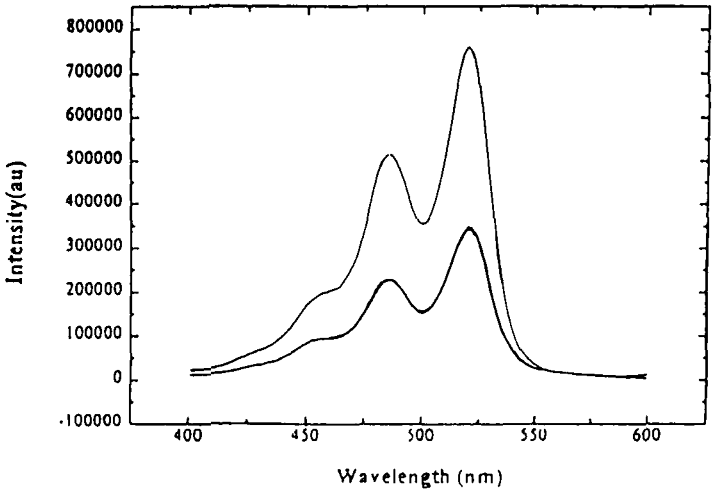
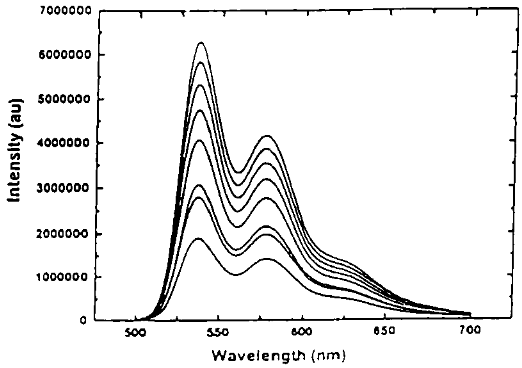


Figure 2. Excitation spectra (λ_{emi}= 620 nm) of 1x10^{-5} M perylene 3,4,9,10-tetracarboxylic acid-bis-N,N'-phenyl diimide, 2, in presence of varying cobalt concentrations in methanol. Co^{2+} concentrations, in the order of decreasing excitation intensities are; 0.001 M, and 0.020 M.

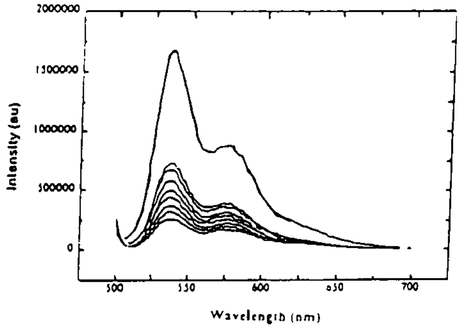
the above derivatives[14]. All energy and electron transfer processes of perylene diimides would proceed via singlet energy levels.

We have studied the singlet energy transfer of perylene diimide derivatives with cobalt ions. The cobalt ion has absorption at 530 nm, which overlaps with emission bands of diimides (Fig. 1). A long- range energy transfer mechanism is suggested for N,N'-bis(2,5-di-tert-butylphenyl) perylene diimide derivative[11,12]. The perylene diimides, 1-7, had shown no changes in shape of the absorption spectra when $CoCl_2.H_2O$ is added. The absence of ground state complexation between cobalt ions and perylene diimides is evident. The similar observation at excitation spectra (Fig.2) and emission spectra (Fig.3) at varying cobalt ion concentrations, prove that exciplex formation do not occur at any of the perylene diimides in methanol solutions. We have not detected any exciplex formation even with very soluble perylene derivatives[15]. Quenching of emission bands were observed for all of the derivatives (Fig.3). A long-range energy transfer causes the quenching, appear to be present at all of the perylene diimides.

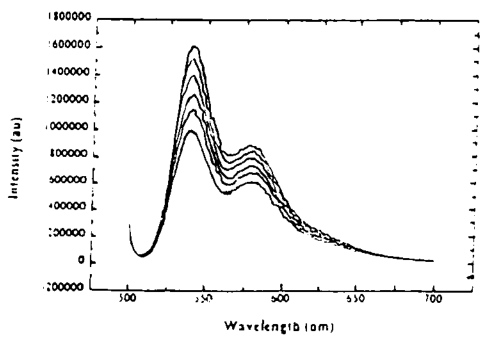
The critical transfer distances, R_o, calculated from donor emission and acceptor absorption spectra using Förster formula[12], are shown in Table 1. The critical distances are seen to vary between 5.8-10.4 A°. Alkyl (ethyl) substitution shows the largest critical distance (10.4 A°), but in general overall values are low. In addition, the reason of the low R_o values is the applied high quencher concentration due to the low molar



Co^{2+} concentrations, in the order of decreasing emission intensities are; 0 M, 0.001 M, 0.002 M, 0.004 M, 0.005 M, 0.007 M, 0.010 M, 0.020 M.



Co^{2+} concentrations, in the order of decreasing emission intensities are; 0 M, 0.002 M, 0.005 M, 0.009 M, 0.013 M, 0.019 M, 0.030 M, 0.040 M.



Co^{2+} concentrations, in the order of decreasing emission intensities are; 0 M, 0.005 M, 0.007 M, 0.009 M, 0.010 M, 0.015 M, 0.020 M.

Figure 3. Emission spectra (λ_{exc} = 485 nm) of 1x10^{-5} M phenyl, *2*, *p*-anisyl, *3* and α-naphthyl, *4*, derivatives in presence of varying cobalt concentrations in methanol.

Table 1. Critical transfer distances of perylene 3,4,9,10-tetracarboxylic acid-bis-N,N'-aryl(alkyl) diimides. Calculated from Förster formula, in methanol solutions.

$$R_o{}^6 = \left[\left(9000\,(\ln 10)\,K^2 \phi_D\right) / \left(128\,\pi^5 n^4 N\right) \right] \int_0^{\infty} \left[\left(F_D(\bar{v})\varepsilon_A(\bar{v}) \right) / \bar{v}^4 \right] d\bar{v}$$

ϕ_D is the emission quantum yield of the donor in the absence of the acceptor.

K is the orientation factor ($K^2 = 0.67$ for randomly distributed molecules).

N is the Avogadro's number.

n is the refractive index of the solvent.

$F_D(\bar{v})$ is normalized fluorescence spectrum of the donor.

$\varepsilon_A(\bar{v})$ is the extinction coefficient of the acceptor at the wavenumber $\bar{v}$.

	-Ar (R)	**R_o**
1	**Ethyl**	**10.4**
2	**Phenyl**	**9.7**
3	**p-Anisyl**	**6.5**
4	**α-Naphthyl**	**5.8**
5	**β- Naphthyl**	**8.9**
6	**Acetyl**	**8.0**
7	**p-Aminophenyl**	**7.7**

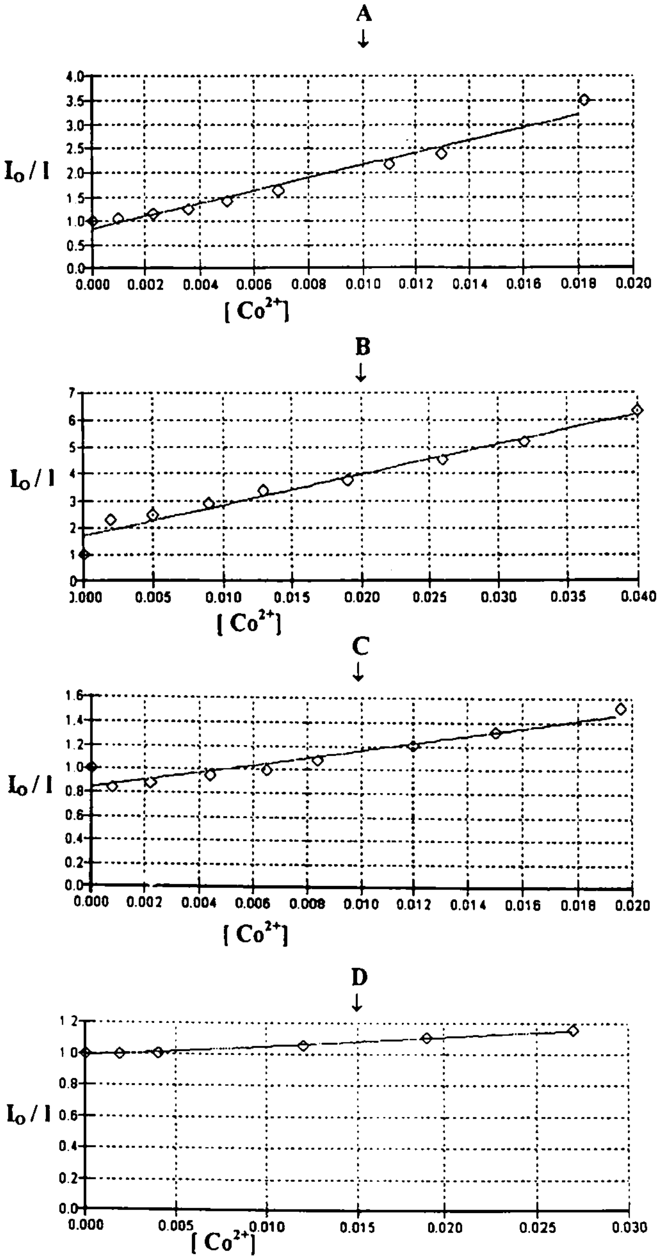


Figure 4. Stern-Volmer plots of fluorescence quenching of phenyl, 2 (A), p-anisyl, 3 (B), α-naphthyl, 4 (C) and β-naphthyl, 5 (D) derivatives(1×10^{-5} M) using Co^{2+} ions in methanol at 25 °C.

Table 2. Rate constants for bimolecular fluorescence quenching of perylene diimides in methanol, calculated from the slopes ($k_q\tau_o$) of Stern-Volmer plots.

Ar(R)	$k_q\tau_o$	k_q (x 10^9 M^{-1} s^{-1})
2 Phenyl	132	30.0
3 p-Anisyl	113	25.7
4 α-Naphthyl	32	7.3
5 β-Naphthyl	6	1.4

obsorptivity of Co^{2+}(10 L mol^{-1} cm^{-1} in methanol). These results indicate that the energy transfer would occur by a long-range energy transfer. The R_o values reported earlier for perylene (13 A°)[11] and N,N'-bis(di-*tert*-butylphenyl) perylene diimide (14 A°)[12] are in proximity to our results, but higher than 10 A°.

Figure 4 shows the Stern-Volmer plot drawn from emission intensities of perylene diimide versus to quencher cobalt ion concentrations. Bimolecular quenching rate constants (k_q), calculated from the slopes of plots and inserting the solution lifetime of the donor as 4.4 ns[5] (for all the derivatives in methanol), give values between 10^9 - 10^{10} M^{-1} s^{-1} (Table 2). These rate constants are in the range of photosensitized bimolecular rate constants of quenching by energy transfer[7], in agreement with, El-Daly 's report (0.99 x 10^{10} M^{-1} s^{-1} rate of quenching by cobalt ions for N,N'-bis(2,5-di-*tert*-butylphenyl) perylene diimide in methanol solution)[12]. The N-substitution of α- and β- naphthyl groups appears to lower the fluorescence quenching about tenfold compared to N-phenyl, *2* and N-anisyl, *3* derivatives (Table 2).

Above results prove that bimolecular quenching with cobalt ions vary significantly only on N-naphthyl substitutions for perylene bis diimides. This may possibly due to some another quenching mechanism. The critical transfer distances (5.8-10.4 A°) indicates that a Förster resonance energy transfer mechanism is dominant in energy transfer from all perylene diimides to cobalt ions.

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