ORIGINAL PAPER

Experimental Determination of Ground and Excited State Dipole Moments of N, N-Bis (2, 5-di-tert-butylphenyl)-3, 4:9, 10-perylenebis (dicarboximide) (DBPI) A Photostable Laser Dye

S. A. El-Daly · A. M. Asiri · K. A. Alamry

Abstract In the present work, the absorption, emission spectra and dipole moments(μ_g, μ_e) of N, N-bis (2, 5-di-tert-butylphenyl)-3, 4:9, 10- perylenebis (dicarboximide) (DBPI) have been studied in solvents of various polarities at room temperature. Using the methods of solvatochromism, the difference between the first excited singlet state (μ_e) and ground state (μ_g) dipole moments was estimated from Lippert – Mataga,, Bakhshiev, Kawski – Chamma – Viallet equations. The change in dipole moment ($\Delta\mu$) was also calculated using the variation of the Stokes shift with microscopic solvent polarity parameter (E_T^N). It was observed that the value of excited singlet state dipole moment is higher (3.53 Debye) than the ground state one (1.92Debye), showing that the excited state of DBPI is more polar than the ground state.

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Introduction

It well known that molecular structure determine a activity of the compound [1], and dipole moments of ground and exicted states may afford an insight to reactivity. Solvatochromism is due to a change of electronic distribution and may a higher dipole moment in the excited state [2]. In general, changing solvent polariety is usually accompanied by a change in dielectric constant and a change in polarizability of the environment [3]. Thus, solvent influences the ground and excited state energy differently and a systematic analysis of solvent effect is helpful in understanding the nature of the excited state.
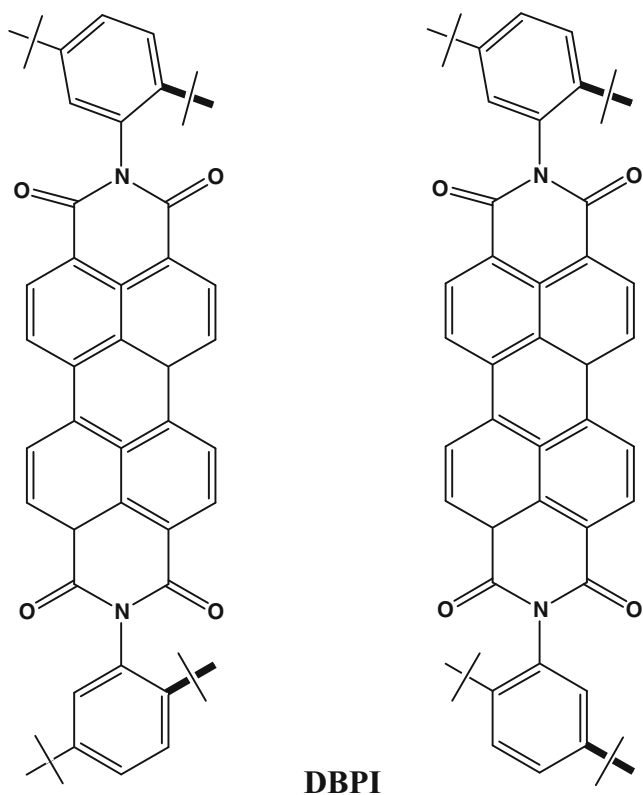
N,N-Bis(2,5-di-tert-butylphenyl)-3,4:9,10-perylenebis(dicarboximide) DBPI is potentially useful in energy and electron transfer reactions [4, 5], site – selective spectroscopy experiments with biological system [6, 7], in p-n hetero-junction solar cells [8] and as laser dye [9]. Certain photophysical characteristics of DBPI found such as fluorescence quenching, excitation energy transfer [10–13], high fluorescence quantum yields, high photostability [14], amplified spontaneous emission and electrochemical properties have been investigated [15]. The morphology effect on the fluorescence of DBPI dissolved in polymer microparticles and its microcrystals has also been reported [16, 17]. Diffraction efficiency of laser induced transient grating and relaxation time of DBPI have been reporetd [18]. DBPI is an important highly photostable probe molecule. To the best of our knowledege the are no reports on the dipole moment of ground and excited states of DBPI. So, in the present manuscript we determine the ground and excited state dipole moments by the solvatochromic method, which depens on a linear correlation between wave numbers of absorbtion and fluorescence maxima

and solvent polarity functions including both dielectric constant (ε) and refractive index (n) of the solvent.

DBPI

Fig. 1 Elecronic absorption spectrum of 1×10^{-5} mol.dm^{-3} of DBPI in MeOH, DMSO and cyclohexane

ground state and hence an increase of excited state dipole moment is expected.

Analysis of the solvatochromic offer allows an estimation of the difference in the dipole moment ($\Delta\mu$) between excited singlet and ground state. by application of simplified Lippert – Mataga equation [19–21]

$$\Delta\overline{\nu}_{st} = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3}\Delta f + \Delta\overline{\nu}_0 \qquad (1)$$

$$\Delta f = \frac{\varepsilon-1}{2\varepsilon+2} - \frac{n^2-1}{2n^2+1} \qquad (2)$$

where $\Delta\overline{\nu}_{st}$ is the Stokes shift (in cm^{-1}), h is the Plank, constant, c is the velosity of light in vacuum, and a is the

Experimental

DBPI(Aldrich) was dissolved in a minimum volume of chloroform, 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 and were checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. UV–vis electronic absorption spectra were recorded on a Shimadzu UV–vis 1650-Pc spectrophotometer. Fluorescence measurements were performed using Shimadzu RF 5300 spectrophotometer using a rectangular quartz cell .

Results and Discussion

The electronic absorption and emission spectra of a 1×10^{-5} mol dm^{-3} solution of DBPI were measured in various non-polar, polar aprotic and polar protic solvents at 298 K. It is clear from Figs. 1 and 2 as well as the data presented in Table 1 that the Stokes shift increases with increasing solvent polarity, indicating that singlet excited state is more polar than the
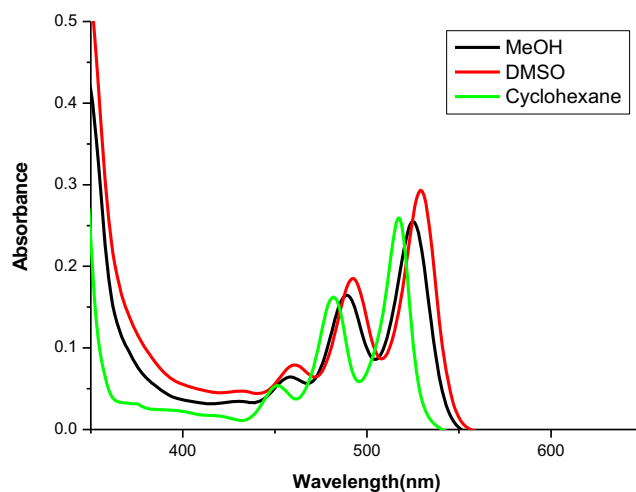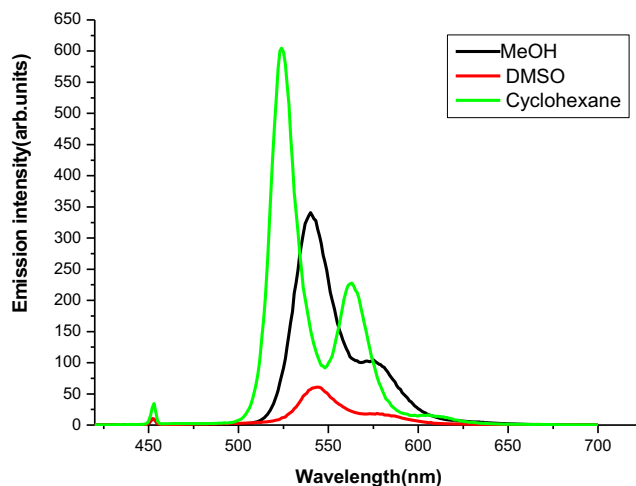

Fig. 2 Emission spectrum of 1×10^{-5} mol.dm^{-3} of DBPI in MeOH, DMSO and cyclohexane (λ_{ex}=460 nm)

Table 1 Absorption and fluorescence properties of DBPI in different solvents

Solvent	E_T^N	Δf	f_1	f_2	λ_{ab}(max)	λ_{em}(max)	$\Delta \bar{\upsilon}$	$\frac{\bar{\upsilon}_a + \bar{\upsilon}_b}{2}$
Cyclohexane	0.006	-0.003	-0.003	0.334	517	523	222	19,231
Diethylether	0.117	0.247	0.692	0.586	519	531	425	19,049
Benzene	0.111	0.0026	0.0035	0.3000	527	537	354	19,798
Chloroform	0.259	0.1483	0.371	0.487	529	544	521	19,642
Dioxane	0.164	0.0212	0.042	0.3066	524	545	427	18,869
Acetonitrile	0.472	0.305	0.866	0.666	523	536	464	1,888
Dimethylformamide	0.404	0.275	0.836	0.7102	528	543	523	18,677
Dimethylsulfoxide	0.503	0.263	0.843	0.742	530	548	619	18,557
Methanol	0.762	0.309	0.855	0.649	526	544	6629	18,696
Isopropanol	0.570	0.119	0.894	0.703	527	544	593	18,678
Butanol	0.506	0.264	0.751	0.645	529	545	5521	18,625
Acetone	0.355	0.285	0.792	0.654	520	531	398	19,031

Onsager cavity radius of DBPI. The Onsager cavity radii (a) from molecular volume of molecules is given by Suppan's equation [22]

$$a = \left(\frac{3M}{4\pi\delta N} \right)^{1/3} \qquad (3)$$

where δ is the density of dye, M is the molecular weight of dye and N is Avogadro's number. The value of (a) for DBPI was found to be 6.7A. Figure 3 shows the plot of Stokes shift versus the orientation polarizability (Δf) . The difference in dipole moment $\Delta \mu$ was found to be 2.15 Debye, This result was verified by calculating the change in dipole moment ($\Delta \mu$) using another solvatochromic shift method [23–26] making use of the dimensionless microscopic solvent polarity parameters E_T^N, given by Eqs. (4) and (5)

$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4} \qquad (4)$$

And

$$E_T(solvent) = \frac{28591}{\lambda_{max}(nm)} \qquad (5)$$

where λ_{max} corresponds to maximum absorption in the red region of the intramolecular charge transfer absorption of the betain dye [23, 26]. In this method change in dipole moment is calculated from the plot of Stokes shift versus E_T^N (Fig. 4) according to Eq.(6)

$$\Delta \bar{\upsilon} = 11307.6 \left(\frac{\Delta \mu}{\Delta \mu_D} \right)^2 \left(\frac{a_D}{a} \right)^3 E_T^N + Const. \qquad (6)$$

$\Delta \mu$ is the difference in dipole moment between the excited and ground states of the probe molecule, $\Delta \mu_D$ is the change in the dipole moment of the betain dye, a and a_D is the Onsager cavity radius of the probe molecule and betaine molecule. Since the values of a_D and μ_D are known (6.2 A^o and 9 Debye, respectively,) [25] the change in dipole moment is determined by Eq. (7)

$$\Delta \mu = \left[\frac{81m}{(6.2/a)^3 \times 11307.6} \right]^{1/2} \qquad (7)$$

where m is the slope of linear plot E_T^N versus Stokes shift (Fig. 4). This gives that $\Delta \mu$ = 2.03 Debye which is very close to that obtained by the Lippert – Mataga equation.
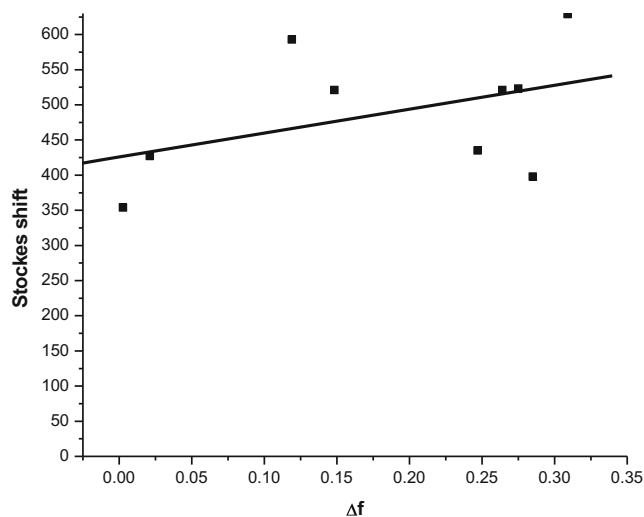

Fig. 3 Plot of E_T^N [normalised E_T (30)] versus Stokes shift(cm^{-1})
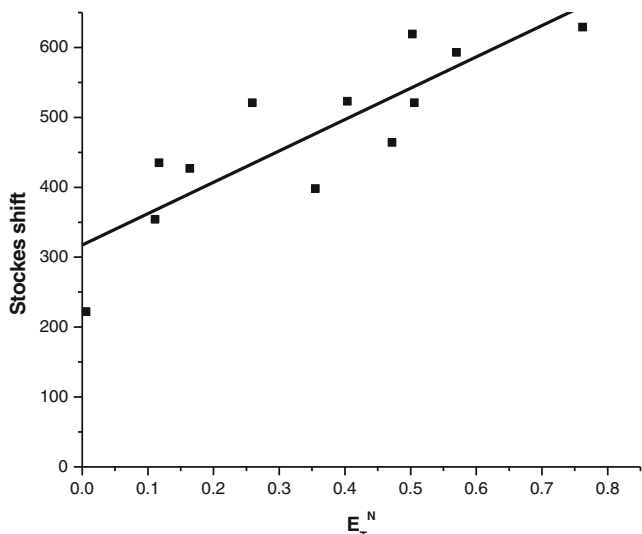
Fig. 4 Plot of $f_1(\varepsilon, n)$ versus Stokes shift(cm^{-1})

Bakshiev's and Kawski – Chamma – Viallet's equations have been used for the treatment of abserved spectral shifts to determine ground and excited state dipole moments of DBPI.

(i) Bakshiev's formula [27] is given by Eq. (8)

$$\overline{\nu}_a - \overline{\nu}_f = S_1 F_1(\varepsilon, n) + Constant \qquad (8)$$

where $\overline{\nu}_a$ and $\overline{\nu}_f$ are the absorption and fluorescence maxima wavenumber in cm^{-1}, respectively; F_1 (solvent polarity function) and S_1 are defined as follows

$$F_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \qquad (9)$$

$$S_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3} \qquad (10)$$

(ii) (Kawski – Chamma – Viallet's formula [28, 29] is given by Eq. (11)

$$\overline{\nu}_a + \overline{\nu}_f / 2 = -S_2 F_2(\varepsilon, n) + Constant \qquad (11)$$

Where, F_2 and S_2 are defined as

$$F_2(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] + \frac{3}{2}\left[\frac{n^4 - 1}{(n^2 + 2)^2}\right] \qquad (12)$$
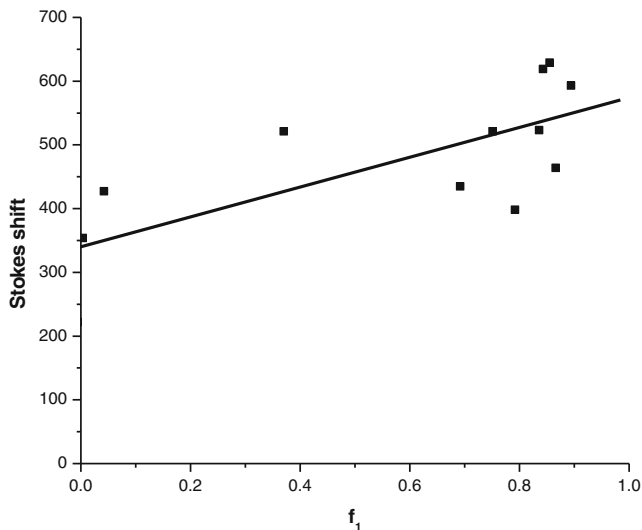
$$S_2 = \frac{2\left(\mu_e^2 - \mu_g^2\right)^2}{hca^3} \qquad (13)$$

and the symbols have the usual meaning given in Eqs. 1 and 2. The parameters S_1 and S_2 can be determined from absorption and fluorescence band shifts (Eqs. 8 and 11, Figs. 5 and 6). If the ground and excited states are parellel, the values of μ_g and μ_e can be obtained using Eqs. 10 and 13 [29]

$$\mu_g = \frac{S_2 - S_1}{2}\left[\frac{hca^3}{2S_1}\right]^{1/2} \qquad (14)$$

$$\mu_e = \frac{S_2 + S_1}{2}\left[\frac{hca^3}{2S_1}\right]^{1/2} \qquad (15)$$
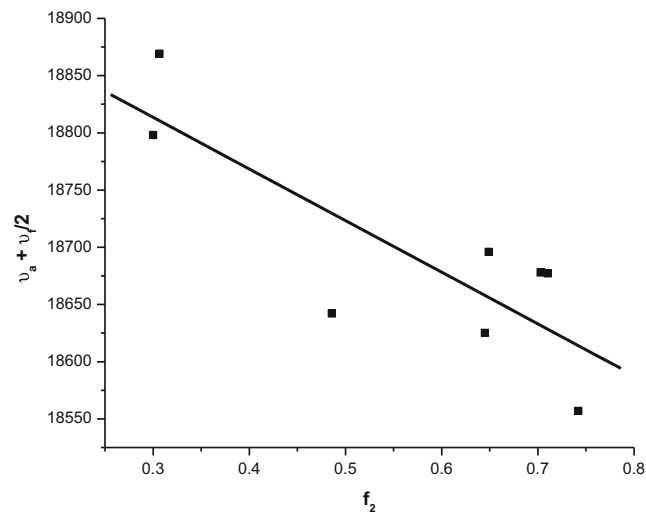

Fig. 5 Plot of $f_1(\varepsilon, n)$ versus Stoker shift

Fig. 6 Plot of $f_2(\varepsilon, n)$ versus $\frac{\overline{\nu}_a + \overline{\nu}_b}{2}$

And

$$\mu_e = \frac{S_1 + S_2}{S_2 - S_1} \mu_g \left(S_2 \rangle S_1 \right) \tag{16}$$

The calculated values of μ_g and μ_e were found to be 1.92 and 3.35 Debye, respectively showing that the excited state of DBPI is more polar than the ground state due to re-distribution of charge and change of geometry in DBPI upon excitation. Apparently, the planarity of DBPI is lost in the singlet excited state as confirmed by the UV-Visiable spectrum which is more structured than the fluorescence spectrum.

Conclusion

The absorption and fluorescence spectra of DBPI exhibits a red shift in the solvents used, consistent with a of π-π^* transition. The solvatochromic shift of absorption and emission spectra were used to calculate ground and excited state dipole moments.

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