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Full Length Research Paper

Photochemistry and cyclic voltammetry of N, N-bis(2,5-di-tert-butylphenyl) – 3,4,9,10 perylenebis (dicarboximide) (DBPI)

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The titled dye of DBPI give amplified spontaneous emission (ASE) with maximum at 580 nm upon pumping by nitrogen laser (λex. =337.1 nm). The ground state absorption cross section (σ_A) and emission cross section (σ_E) as well as effective emission cross section(σ^*_E) have been determined. The electronic absorption spectra of DBPI were measured in ethanol and tetrahydrofuran at room and low temperature. DBPI displays molecular aggregation in water. The photochemical reactivity of DBPI was also studied in carbon tetrachloride upon irradiation with 525 nm light. Cyclic voltammetry of DBPI dye was also studied in different solvents at different scan rates. Cyclic voltammograms for reduction of DBPI gives two reversible peaks corresponding to radical anion and dianion formation. The oxidation of DBPI dye give one reversible oxidation peak at 1.4 volt corresponding to radical cation formation.

Keywords: Perylene derivative, amplified spontaneous emission, molecular aggregation, cyclic voltammetry.

INTRODUCTION

The bis(2,5-di-tert-butylphenyl) imide(DBPI) of 3,4,9,10-perylenetetracarboxylic dianhydride is a member of a class of vat dyes that intrinsically are strongly colored and have high fluorescence quantum yield (Luckac and Langhals 1983; Ford 1986).These properties make dyes such as DBPI potentially useful as photo sensitizers in energy and electron transfer reaction (Balzani et al., 1975; Darwent 1982), and in site – selective spectroscopy experiments with biological systems (Kavarnos and Turro 1986; Aubert et al., 1985). Applications of perylene diimides as laser dyes and in p – n heterojunction solar cells have already been demonstrated by Bird and co-workers (Sandra and Bird 1984).

In order to evaluate the potential usefulness of dyes such as DBPI as photosensitizer, it is necessary to determine their photophysical properties and redox potentials. The bulky tert – butyl groups on DBPI dye makes this dye relatively soluble in a number of organic solvents (Wasielewski et al., 1985). DBPI dye was first prepared and studied by Rudemacher et al and its large scale synthesis was more described by (Langhals 1985). The

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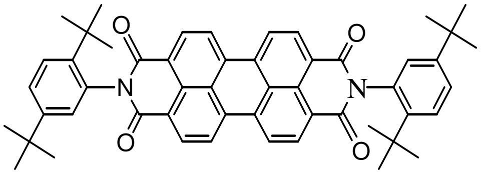
commercial product was probably a mixture of cis and trans a tropic isomers, whose spectral properties are very similar (Langhals 1985). In addition to fluorescence properties of DBPI in solid state, kinetic and energetic properties of the singlet and triplet excited states have been examined (Ford and Komot 1987).

In previous papers (Ebeid et al., 1988; El-Daly 1992; El-Daly et al., 1995; El-Daly and Hirayama 1997; El-Daly 1998), certain photophysical characteristics of DBPI have been reported e. g. a fluorescence quantum yield of unity, high photostability, energy transfer from certain blue laser dyes, fluorescence quenching by cobalt ions and molecular oxygen as well as the effect of re – absorption on fluorescence lifetime has also been studied. In this article we report the electronic absorption spectrum at room and low temperature, amplified spontaneous emission, photoreactivity in carbon tetrachloride of DBPI. The cyclic voltammetry of DBPI are also studied.



DBPI

Experimental

DBPI (Aldrich) was dissolved in a minimum volume of chloroform; the dye was precipitated by adding methanol. The precipitate was collected by filtration and dried in vacuum. All solvents used in this work were of spectroscopic grade.

Low temperature electronic absorption spectra were taken on a shimadzu double beam spectrophotometer UV – 200 connected with cooling unit (DN 1704 variable temperature liquid nitrogen cryostat) oxford instruments. UV-Visible absorption spectra were measured using a Shimadzu UV-1200S spectrophotometer. Fluorescence lifetime were measured by the single photon counting technique using an air lash lamp operating between 20 and 40 K Hz. Excitation wavelengths were selected using a band – pass filter, the emission wavelengths were selected by appropriate filter (Schott, Mainz, Germany). The data were registered in a 1000 channels analyzer with a resolution of 24 channels/ns. The decay profiles were analyzed by iterative convolution using autocorrelation and residual criteria (Demas 1993). Amplified spontaneous emission (ASE) was measured using a nitrogen laser (type 1M 50 A Lambda physics, λ_{ex} =337.1 nm, pulse duration = 5 ns) as excitation source and an optical multichannel analyzer (type OMA II. Princeton Applied Research Corp.) as. detector (Klink 1995). The dye cuvett was placed in the focus of a cylinder lens, which concentrate the nitrogen laser beam to a narrow line. The dye concentration was 5×10^{-5} M in DMF. Eight ASE spectra were recorded for different pulse energies between 0.1 and 1.5 mJ. All spectra were measured in the unsaturated light amplification region. Within the model used (Klink 1995)., the relation between ASE intensity I and excitation pulse intensity P is given by equation 1-3:

$$I(L,\lambda,p) = F(\lambda)N_1(p) \int_0^l \exp[N_1(p)\sigma_E^*(\lambda) - N_o(p)\sigma_A(\lambda)]dx \quad (1)$$

$$N_1 = N\frac{\sigma_{ex}k_\tau p}{\sigma_{ex}k_\tau p + \frac{1}{\tau}} \quad (2)$$

$$N = N_o + N_1$$

Where N are the total dye concentration in molecules / cm^3, $N_o$and N_1 are the populations of the ground state (s_o) and the excited state (s_1) respectively, σ_A is the absorption cross section of the s_o, σ_{ex} is σ_A at 337.1 nm. , σ^*_E is the effective emission cross section. L is the length of the excited region within the cuvette (16 -19 mm), τ is the lifetime of s1 state, k_τ is a correction factor and F is a factor depending on fluorescence intensity, detector sensitivity and geometrical conditions. The factor k_τ gives state conditions and depends on the ratio of excitation pulse duration to s1 lifetime (τ). The difference between emission cross section σ_E and effective emission cross section σ^*_E we interpret as the absorption cross sections σ^*_A of $s_1 \rightarrow s_n$ transitions. F as well as σ^*_E are determined from the ASE spectra by curve fitting. The emission cross section σ_E is calculated from equation(4), where E means the normalized fluorescence line shape function, which is correlated with fluorescence quantum yield ϕ_f by equation(5).

$$\sigma_E(\lambda) = \frac{E(\lambda)\lambda^4}{8\pi\tau c n^2} \quad (4)$$

$$\int E(\lambda)\, d\lambda = \phi_f \quad (5)$$

Where n is the refractive index of the dye solution, c is the velocity of light in vacuum, E (λ) is obtained from solutions whose absorptivities are low at avoid reabsorption processes (optical density at absorption maximum ≤ 0.1). The excited state absorption cross – section σ^*_A is calculated from the difference (σ_E – σ^*_E) (Klink 1995). Absolute light intensities were measured using ferrioxalate actinometry as described by (Hatchard and Parker 1965; Steven 1973).

Cyclic voltammetry measurements were taken on a PAR 170 electrochemistry system with this specification: scan rates 0.1 mV to 500mV /s, pulse duration 1m sec to 500 sec. Initial and final potentials between ± volts, potentiostate range ± 100 volts at 1 ampere, ±20 volts at 5 ampere. Input impedance 10^{14} ohm and current supply up to ± 5 ampere. The apparatus has 11 × 17 x-y recorder with built-in time base. Zero – offset and scale expansion to 10 times full scale included. The cell used has three necks and is heated over night at 110 °c. The measurements were taken by using platinum electrode (EDI 40410) as working electrode, silver – silver nitrate as a reference electrode, coiled platinum wire as counter electrode, and 0.1 M tetrabutyl ammonium perchlorate (TBAP) a conduction salt. The working electrode was polished on a polisher Ecomet Grinder.

The important parameters of a cyclic voltammogram are the magnitude of anodic peak current (i_{pa}), and anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}) and cathodic peak potential (E_{pc}). For a reversible reactions (Greef et al., 1985; Kissinger and Heineman 1983).

$$Ox + ne \longleftrightarrow Red \qquad (6)$$

A redox couple in which both species rapidly exchange electrons with working electrode is termed an electrochemically reversible couple. The formal reduction potential (E_o) for a reversible couple is centered between E_{pa} and E_{pc}

$$E_o = \frac{Epa + Epc}{2} \qquad (7)$$

The number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation between the potentials (Greef et al., 1985; Kissinger and Heineman 1983).

$$\Delta E_p = E_{pa} - E_{pc} = 57 /n \quad mV \quad (8)$$

Where

$$E_{pa} = E_{1/2} + 1.109 \frac{RT}{nf} = E_{1/2} + 28.5/n$$

$$E_{pc} = E_{1/2} - 1.109 \frac{RT}{nf} = E_{1/2} - 28.5/n$$

$$E_{1/2} = E_{0.85ip}$$

$E_{1/2}$ is the potential when the current equals85.1 % of its maximum value.

For reversible multistep charge transfer (Polcyn and Shain 1966), which fellow the reactions

$A + n_1e \leftrightarrow B$

$B + n_2e \leftrightarrow C$

When both charge transfers are reversible and when the two electroactive species are reduced at sufficiently different potentials, the cathodic stationary electrode polarogram exhibits two waves. Each of individual waves has the shape and peak height of uncomplicated reversible charge transfer, provided the descending branch of the first wave is used as the base line for the second wave. In order that the polarograms behave as independent reversible waves a certain minimum potential separation of about 118/n mV is required between the formal reduction potentials.

RESULTS AND DISCUSSION

Spectral behavior of DBPI

5 ×10^{-4} M of DBPI in DMF give amplified spontaneous emission (ASE) with maximum at 580 nm upon excitation by nitrogen laser (λ_{ex} = 337.1 nm). The ground state absorption cross section (σ_A), the emission cross section (σ_E) as well as effective emission cross section is shown in Figure. 1. The excited state absorption cross section (σ^*_A) is given from the difference ($\sigma_E - \sigma^*_{E)}$ .we interpret this difference as the first excited singlet state absorption band which reduces the dye laser efficiency. The low intensity of amplified spontaneous emission (ASE) could be interpreted to the $s_1 \rightarrow s_n$ transition and reabsorption of emitted photons by ground state molecules due to the strong overlap between emission and absorption spectra (overlap area was calculated as 8.6 × 10^{-13} mol dm^{-3} cm^3 from the relation (Langhals et al., 1998).

$$\mathbf{J = \int \varepsilon(\acute{u})f(\acute{u})\acute{u}^{-4}\, d\acute{u}}$$

Where f (ú) is the emission intensity normalized to unity and ε (ú) is the

molar absorptivity of DBPI in DMF. The populations of DBPI triplet state via intersystem crossing also play a role in decreasing the intensity of ASE, the triplet state energy and lifetime of DBPI were 27.5±2 kcal.mol^{-1} 100 μs (Ford and Komot 1987), whears the energy and lifetime of excited singlet state are 54 kcal mol^{-1} and 3.7 ns. The photophysical properties of DBPI in solution are probably representative of perylene diimides in general. The high fluorescence quantum yield (ϕ_f = 0.96) and low triplet state energy of perylene diimides make them more likely to be useful as photosensitizer via the singlet rather than triplet excited state. On other hand, the fact that the triplet state is low – laying in energy but readily quenched by oxygen molecule (Ford and Komot 1987), make these dyes useful as energy traps in antennae systems for photosensitizer generation of singlet oxygen.

The electronic absorption spectrum of 1× 10^{-5} M of DBPI was measured in ethanol, 1 N sodium hydroxide ethanolic solution and 50% aqueous ethanol. As shown in Figure 2, the spectral pattern of DBPI changes upon addition of sodium hydroxide and water to ethanol. It seems that the addition of water and sodium hydroxide favors the aggregation of DBPI dye and the tendency of dye to aggregate is higher in polar solvent. The spectral changes shown in Figure 2, (the extinction coefficients were reduced, the bands were red shifted and broadened and relative intensities of maximum were shifted to highest energy band near 485 nm). These differences are

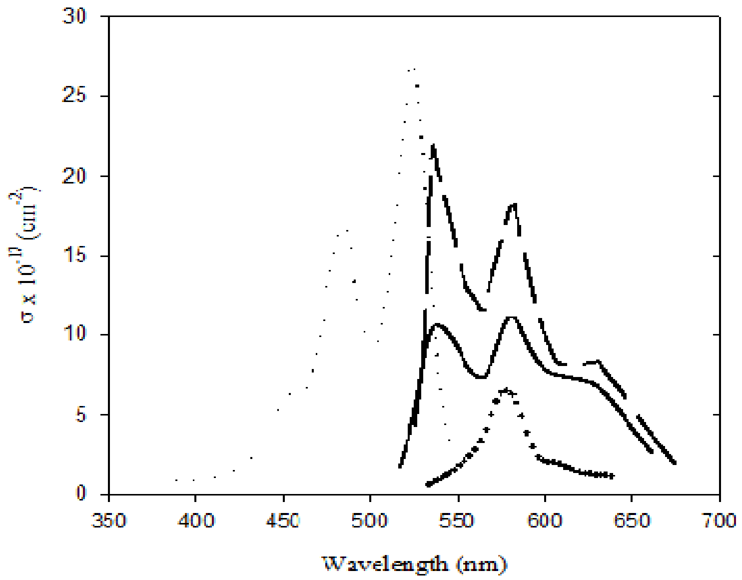


Figure 1. Electronic absorption spectrum (----), emission Spectrum (….), excited state absorption spectrum (—) and (xxxx) ASE spectrum of DBPI in DMF.

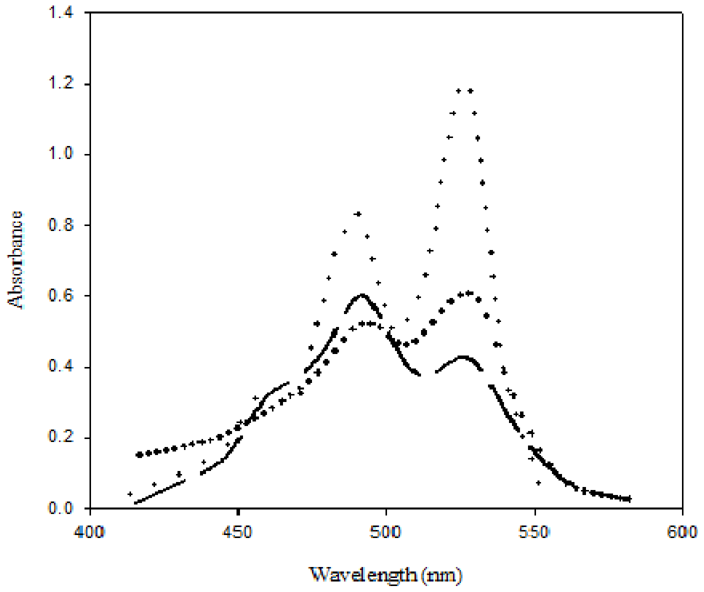


Figure 2. Absorption spectra of 1× 10^{-5} M of DBPI in (….) ethanol, (xxx) 1 N NaOH ethanolic solution and (---) 50 % aqueous ethanol.

indicative of the presence of aggregates higher than dimmer. The aggregation also occurs in frozen sample (at 77 K) in ethanol at concentration of 1×10^{-5}M but it is not in tetrahydrofuran (THF) as shown in Figure 3. This indicates that the polarity of solvent plays more important role in enhancing the aggregation of DBPI dye. It seems that the electrostatic repulsion between DBPI dye molecules decreases in polar solvents.

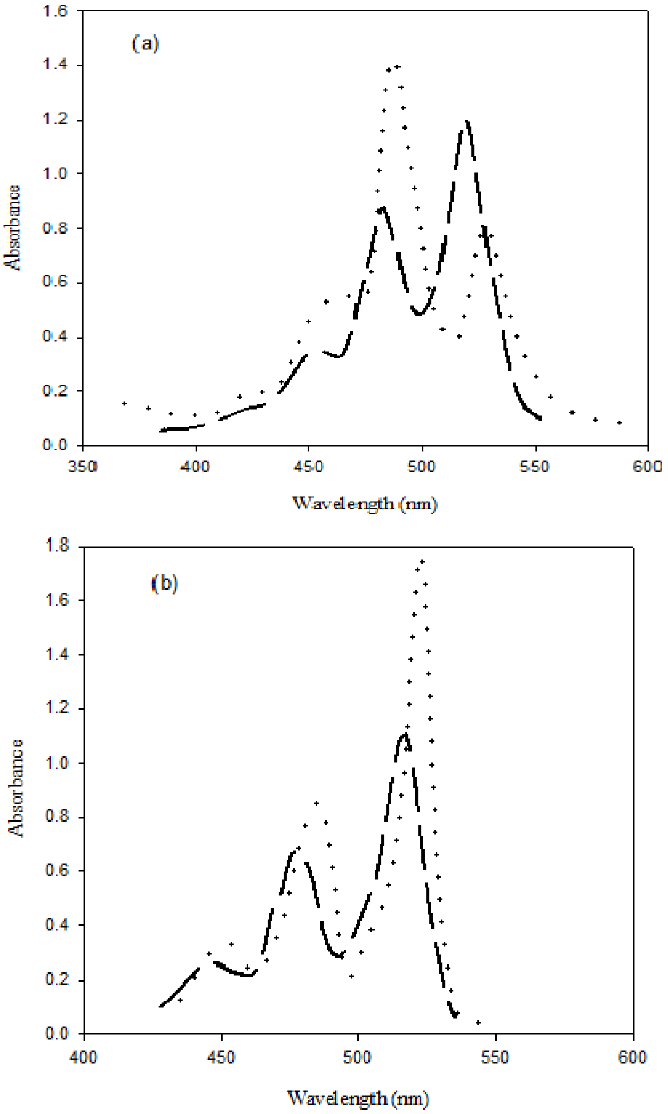


Figure 3. Absorption spectra of 1× 10^{-5} M DBPI in (a) ethanol and (b) in THF at (---) 300 k and (…) 77 K.

Study of contact ion pair

A compound formed when a cation and a negative ion interact with each other by coulomb attraction to get close together, but with both charges still separated, is called a contact ion pair. Since the charge separation is complete, a large dipole moment can be expected. The formation of a contact ion pair usually occurs by electron transfer from excited donor to the acceptor. In order for such a compound to be formed a low ionization potential of the donor and high electron affinity of acceptor are necessary. A direct observation of a contact ion pair $DBPI^{\cdot+}Cl^{-}$ in CCl_4 solvent was studied by UV-Visible absorption technique. Photoirradiation of 8 10-6M of DBPI by 525 nm light (I_o =5× 10^{-6} Ein / min) in CCl_4 (E_A = 2.12 eV) causes a decrease in absorbance and a new absorption peak appears at 570 nm with isobestic point at 540 nm (Figure 4). The photochemical quantum yield (ϕ_c) of ion pair formation was calculated using a method described elsewhere (Ebeid et al., 1986), and was found to be $\phi_c = 0.018$, the formation of ion pair is a one photon process as represented by reaction 1 and 2

$$DBPI + h\upsilon \rightarrow DBPI^{*} \qquad (1)$$

$$DBPI^{*} + CCl_4 \rightarrow DBPI^{\cdot+}Cl^{-} + {}^{\cdot}CCl3 \qquad (2)$$

We propose that the electron transfer from the excited singlet state of DBPI to CCl_4 in the transient excited charge transfer complex 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 solvent cage. The photoionozation of some aromatic and

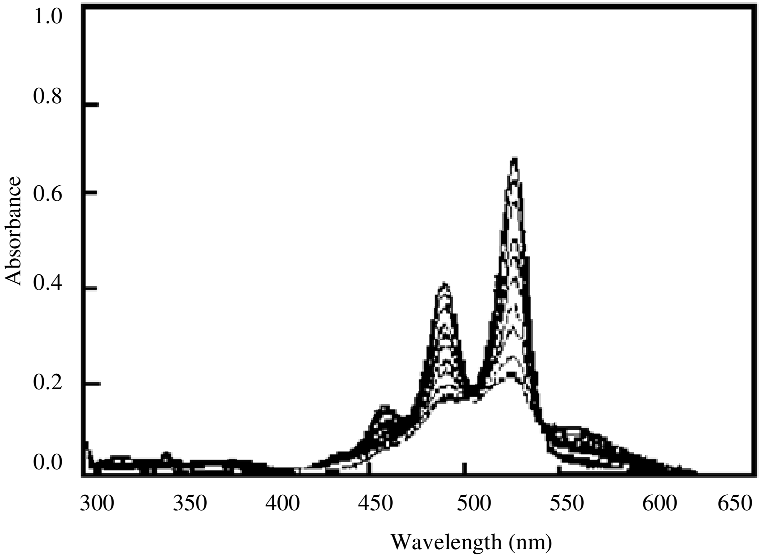


Figure 4. Effect of irradiation on the electronic absorption spectrum of 8× 10^{-6} M of DBPI in CCl4 (λ_{irr} = 525 nm) the irradiation times at decreasing absorbance are 0.0, 5, 9, 16, 30, 40, 65, 75, 100 and 125 min.

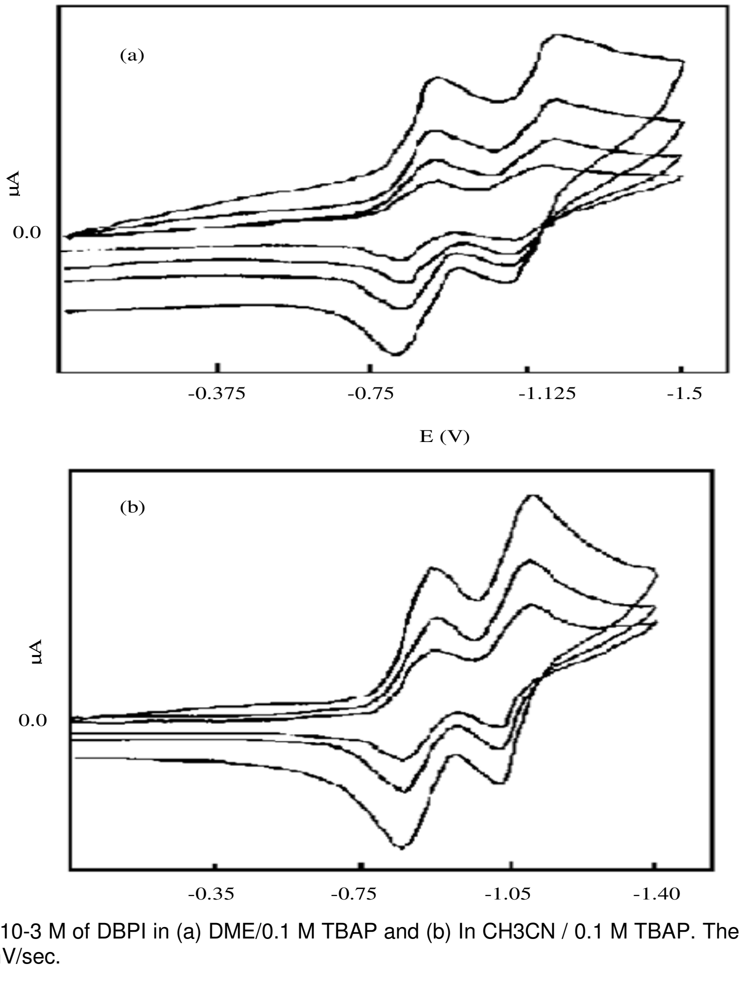


Figure 5. Cyclic voltammogram of 1× 10-3 M of DBPI in (a) DME/0.1 M TBAP and (b) In CH3CN / 0.1 M TBAP. The scan rates at increasing peak current intensities are 50, 100, 200 and 500 mV/sec.

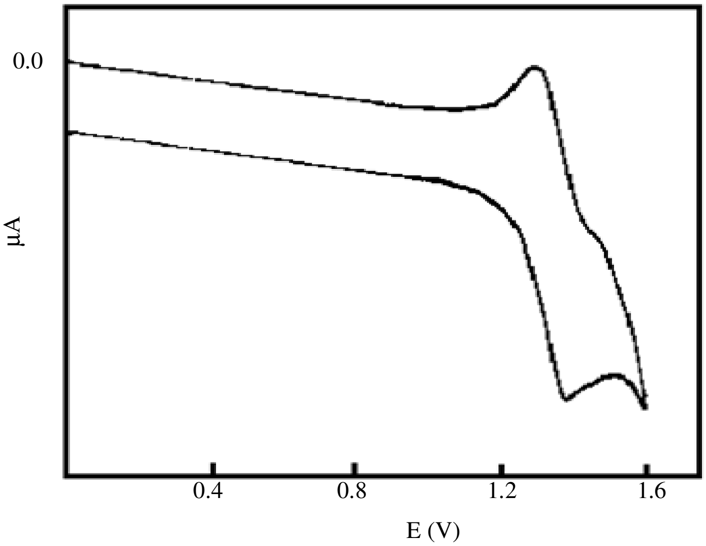


Figure 6. Oxidation of 1× 10^{-3} M DBPI dye in CH_3CN / 0.1M TBAP

Table 1. Cyclic voltammetry data of DBPI in different solvents

	CH_3CN	DMF	CH_2Cl – CH_2Cl
E_{pc1}	- 0.85 v	- 0.88V	- 0.86 V
E_{pc2}	- 1.07 v	- 1.15 V	- 1.10 V
ΔE_{pc}	220 mV	270 mV	240 mV
ΔE_{p1}	60 mV	60 mV	60 mV
ΔE_{p2}	60 mV	80 mV	60 mV

aliphatic amines in chloromethane solvents has been reported (Bord et al., 1971; Shimamon 1992). Photoreactivity of some anthracene and perylene derivatives are recently reported (Azim et al., 1996; El-Daly 1999; El-Daly and Fayed 2000).

Cyclic volatmmetry of DBPI

Cyclic voltammetry of DBPI dye was measured in different solvents at different scan rates 50, 100,200 and 500mV/s. It is found that the peak current density increases with scan rate, and the cathodic and anodic peak potentials independent on scan rate. Cyclic voltammograms for reduction of DBPI gives two reversible peaks(Figure. 5) corresponding to radical anion and dianion formation even at low voltage sweep rate of 50 mV/s. the reduction peak potentials are slightly solvent dependent as shown in Table 1. This is because the charges of dianions of DBPI dye are dispersed over much larger framework and the reversibility of the anion – dianion couple is unaffected by the size of counter – ion and this decreases the ion – pair formation with electrolyte. The reduction of DBPI dye follows EE mechanism as shown below

$DBPI + e \leftrightarrow DBPI^{\cdot -}$ First reduction peak
$DBPI^{\cdot -} + e \leftrightarrow DBPI^{-2}$ second reduction peak

The oxidation of DBPI dye is also unaffected by solvent changes and give one reversible oxidation peak (Figure.6) at 1.4 volt corresponding to radical cation formation as
$DBPI \leftrightarrow DBPI^{\cdot +} + e$

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