

Electrochemical studies of N,N-bis pyrazinyl - 3,4,9,10 - perylenebis (dicarboximide) (PyPD) on Pt electrode

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Abstract: The electrochemical studies of N, N – bis(pyrazinyl) – 3, 4, 9, 10 – perylene bis (dicarboximide) (PyPD) dye has been carried out on Pt electrode using cyclic voltammetry and convolution deconvolution voltammetry combined with digital simulation technique at a platinum electrode in 0.1 mol L⁻¹ tetrabutylammonium perchlorate (TBAP) in acetonitrile solvent (CH₃CN). The compound under consideration was reduced via consumption of two sequential electrons to form radical anion and dianion (EE mechanism). The electrode reaction pathway and the electrochemical parameters of the investigated compound were determined using cyclic voltammetry and convolution – deconvolution transforms. The extracted electrochemical parameters were verified and confirmed via digital simulation method.

Keywords: Perylene derivatives, Cyclic voltammetry on Pt, Convolution voltammetry, Digital simulation

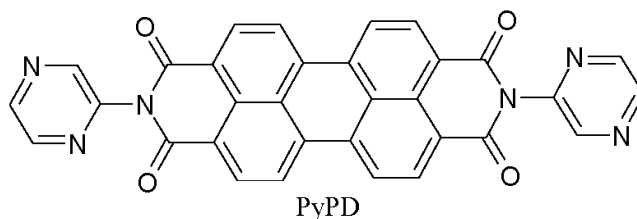
1. INTRODUCTION

The dyes derived from 3, 4, 9, 10 – perylenetetracarboxylic dianhydride have high molar absorptivity in visible region (104 – 105 M⁻¹ cm⁻¹), high fluorescence quantum yield [1-5] and excellent stability to heat and light [6]. These properties make perylene dyes attractive as potential laser dyes [7-11], photosensitizer for electron transfer reactions [12-14], solar concentrators [15,16], some of perylene derivatives serve as liquid crystals [17], organic light emitting diodes [18,19] and light harvesting arrays [20-22] as well as photoreactive thin films [23,24].

To the best of our knowledge there is no report on the electrochemistry of PyPD via cyclic voltammetry and convolution-deconvolution transforms. So, in the present manuscript we investigated the electrochemical behaviour of PyPD dye using cyclic voltammetry and convolution-deconvolution transforms. The electrochemical parameters (standard redox potential, E⁰, standard heterogeneous rate constant, k_s, and diffusion coefficient, D) were determined experimentally and confirmed via digital simulation method.

2. EXPERIMENTAL

N, N – bis (pyrazinyl) -3, 4, 9, 10- perylenebis (dicarboximide) (PyPD) was prepared and purified according to procedure described in detail in ref. [25]. TLC and spectroscopic techniques as well as elemental analysis were used to confirm the purity of the dye. The solvent used in this work was of spectroscopic grade. The prepared dye has the following structure:



Cyclic voltammetry measurements were made using a conventional three electrode cell configuration linked to an EG & G model 170 PAR apparatus. The platinum electrode surface was 7.85×10⁻³ cm² as a working electrode, coiled platinum wire as a counter electrode, saturated Ag/AgCl as a reference electrode. The potential was calculated with relative to the Ag/AgCl reference

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electrode whose potential is at about 0.200 V versus SHE at 25 °C. and 0.1 mol L⁻¹ tetrabutyl ammonium perchlorate (TBAP) as background electrolyte. Cyclic voltammograms were recorded after background subtraction and iR compensation to minimize double-layer charging current and solution resistance.

The working electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric data were obtained at scan rate ranging from 0.02 to 2 V s⁻¹ in non aqueous media at 22 ± 2 °C. Digital simulation of the data for cyclic voltammetric experiments was carried out on a PC computer using EG & G condesim package. Convolution-deconvolution transforms was performed using EG & G condecon software package. All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

3. RESULTS AND DISCUSSIONS

3.1. Cyclic voltammetry measurements

The electrochemical properties of 2.5 × 10⁻³ mol L⁻¹ of the PyPD dye were studied in detail using cyclic voltammetry and convolutive voltammetry in solvent, CH₃CN at scan rates ranging from 0.02 - 5 V s⁻¹. In CH₃CN solvent, the first reductive peak (I) was coupled with the oxidative peak (II) while the second reductive peak (III) was coupled with the oxidative peak (IV). It was found that the height of the first and the second peaks increased with scan rate, while the position of the forward and the reverse peaks of the first and the second reduction processes were independent of scan rate. The constancy of peaks separation ($\Delta E_p = 59$ mV) with variation of scan rate give evidence that, the first and the second reduction processes of the investigated PyPD dye proceed as fast charge transfer [26]. This behaviour demonstrates that the first charge transfer produces a radical anion that gains another electron to form a dianion. Figure 1 gives an example of the cyclic voltammogram at sweep rate of 0.2 V s⁻¹ of the PyPD dye in 0.1 mol L⁻¹ TBAP/CH₃CN solvent. The ratio of the anodic to cathodic peak current demonstrates the rapidity of the charge transfer. The measured values of peak width of two waves, $E_p - E_{p/2} = 56.5/n$ mV ± 2 mV, demonstrate the reversibility behaviour of the investigated system, where E_p , $E_{p/2}$ and n are the peak potential, the half- peak potential and the number of electrons consumed in electrode reaction respectively.

The peak separation ΔE_p of the first and second charge transfers were found to be 60 mV confirming the rapidity of charge transfer in 0.1 mol L⁻¹ TBAP/CH₃CN. The redox potential (E^\ominus)

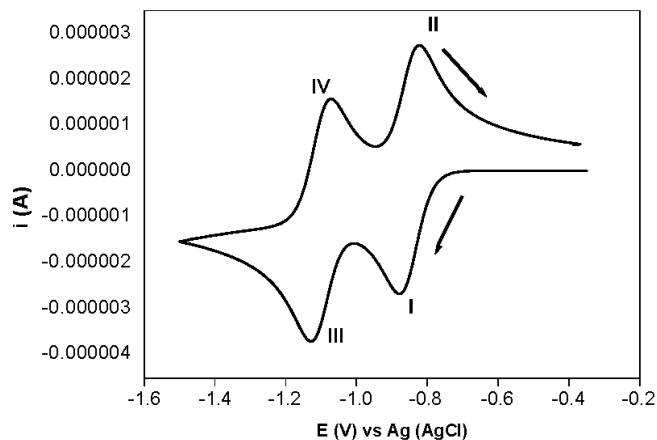


Figure 1. Reductive cyclic voltammogram of 2.5 × 10⁻³ M of PyPD in CH₃CN / 0.1 M TBAP at scan rate of 0.2 V s⁻¹.

was determined from the mean position of the peak potentials (Table 1). Based on the above discussion the given redox reaction might be confirmed as reversible faradaic processes. The standard heterogeneous rate constant (k_s) was determined from the generated cyclic voltammograms [27]. From the plot of i_p vs. \sqrt{v} , the diffusion coefficient (D) of the electroactive species is determined and cited in Table 1. The results given in Figure 2 employ the experimental and theoretical values of the electrochemical parameters of the PyPD dye, which demonstrate excellent agreement between the captured and the simulated data.

3.2. Convolution transforms

In cases of straight forward electron transfer or subsequent chemical reaction, the I_t convolution which is defined as [28-35]:

$$I_t = \frac{1}{\sqrt{\pi}} \int_0^t \frac{i(u)}{\sqrt{t-u}} du \quad (1)$$

allows to determine the diffusion coefficient of the bulk species from the Eq. (2) [29]:

$$I_{lim} = nFAC\sqrt{D} \quad (2)$$

where I_{lim} is the limiting value achieved for I_t when the potential is driven to a sufficiently extreme value past the wave; the other terms have their usual significance.

Table 1. Electrochemical parameters of the cathodic reduction process of PyPD dye in 0.1 mol L⁻¹ tetrabutyl ammonium perchlorate (TBAP)

$-E^{01}$ V	$-E^{02}$ V	$k_{s1} \times 10^3$ m s ⁻¹	$k_{s2} \times 10^3$ m s ⁻¹	$D_1 \times 10^9$ m ² s ⁻¹	$D_2 \times 10^9$ m ² s ⁻¹	α	K_c
0.850 ^a	1.102	3.0	2.80	4.50	4.85	0.49	4.36 × 10 ⁹
0.852 ^b	1.105	3.1	2.71	4.60	4.75	0.48	-
----- ^c	-	-	-	4.46	4.65	-	-
0.853 ^d	1.103	-	-	4.32	4.21	-	-
----- ^e	-	-	-	4.80	4.29	-	-

a) Experimental values, b) Simulated values, c) Values of D calculated via Eq. (2), d) Values calculated from convolutive voltammetry, e) Values calculated via Cottrell plot

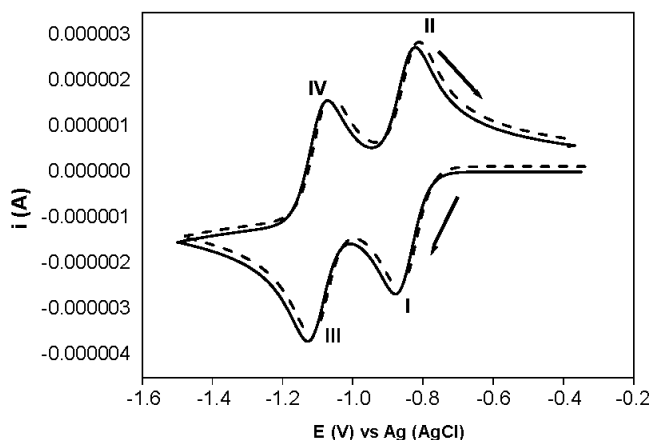


Figure 2. Matching between reductive experimental voltammogram of PyPD dye (—) and simulated voltammogram (.....) at a sweep rate of 0.2 V s^{-1} .

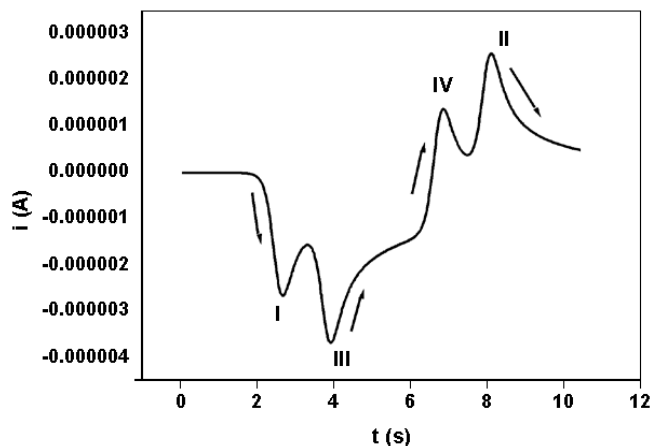


Figure 4. Plot of i versus t corresponding to a reductive cyclic voltammogram at sweep rate of 0.2 V s^{-1} . The point $t = 5.4 \text{ s}$ is the time at which the potential scan is switched to the reverse direction.

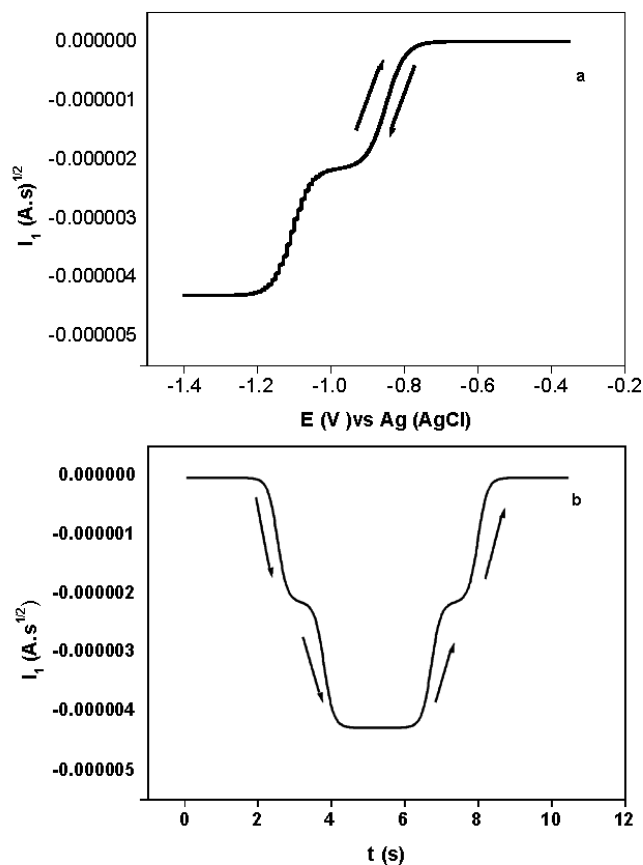


Figure 3. Convolution voltammetry (I_t) of the reductive process of PyPD dye at sweep rate of 0.5 V s^{-1} (a) and I_t of PyPD vs time (b).

The values of the diffusion coefficient (D) corresponding to the reduction steps were calculated via Eq. (2) and are listed in Table 1. The I_t convolution of the reductive voltammogram of PyPD at a scan rate of 0.5 V s^{-1} is indicated in Figure 3. As shown in Fig. 3a

the I_t convolution of the backward scan are completely overlay on the forward one and return to zero, confirming the simple electron transfer and the rapidity of the two charge transfer between the electrode and the electroactive dye compound PyPD, *i.e.* fast EE mechanism.

In the case of fast electron transfer, the following equation is applied [33]:

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{(I_{lim} - I_t)}{I_t} \quad (3)$$

The plot of $\ln \frac{(I_{lim} - I_t)}{I_t}$ versus E exhibits two slope lines for the two consecutive charge transfer with slope = $1/0.025$ for each line, confirming the rapidity of both charge transfer and also provide overall n value equals two.

Fig. 3b shows I_t convolution vs time for the voltammogram plotted in Fig. 1. For $t < 4.8 \text{ s}$, I_t convolution decreases with time leading to minimum, I_M , which equivalent to the limiting convoluted current, I_{lim} . The average value of I_M obtained for a set of five different experiments with several values of v , between 0.05 and 1 V s^{-1} is $I_M = -4.2 \pm 0.1 \times 10^{-6} \text{ A.s}^{1/2}$. For $t > 5.5 \text{ s}$, I_t increases with time, due to the oxidation process of the investigated compound. When the electrode reaction is completely reversible, the I_t must return to zero as observed in Fig. 3b.

The presentation of i vs t of the voltammogram at sweep rate of 0.2 V s^{-1} is shown in Fig. 4. The plot produces discontinuity Δi_c at $t = 5.4 \text{ s}$ due to the reversibility of the scan. By selecting the data points a Cottrel plot is obtained as current versus the reciprocal square root of time. The slope of Cottrel plot yields a diffusion coefficient $D = 4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Inspection of Fig.4 revealed that, the height of the forward and reverse peaks are the same, *i.e.* the height of peak I is equals to the height of peak II and the height of peak III is equaled to the height of peak IV confirming the rapidity of the simple charge transfer process of PyPD.

3.3. Deconvolution transforms

The deconvolution transforms of the current (dI_t/dt) as a function of E of reversible process is defined as [31]:

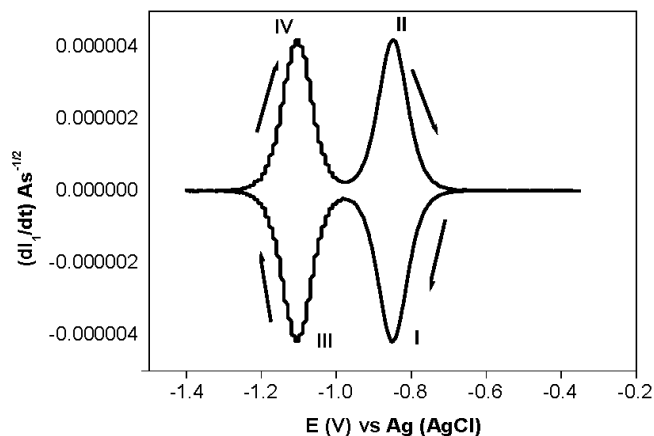


Figure 5. Deconvolution voltammetry (dI_1/dt) of the reductive cyclic voltammogram of PyPD at a sweep rate of 0.2 V s^{-1} .

$$(d^{1/2} i/dt^{1/2}) = (dI_1/dt) = nFAC\sqrt{D} a\zeta / (1+\zeta)^2 \quad (4)$$

where

$$a = nvF/RT \quad (5)$$

and

$$\zeta = \exp [nF/RT (E - E^0)] \quad (6)$$

and the representation of this equation at $v = 0.2 \text{ V s}^{-1}$ in $0.1 \text{ M TBAP/CH}_3\text{CN}$ is indicated in Fig. 5. It was found that the width of deconvoluted peak $w_{p/2}$ at half peak height of two deconvoluted current peaks are equal to $90 \pm 2 \text{ mV}$ confirming the rapidity of both charge transfer.

The symmetry and alignment of the forward and reverse sweep of figure 5, further confirming the rapidity of both charge transfer of the reduction process of PyPD dye. The standard reduction potential was determined from the deconvoluted peak current of the two peaks (Table 1). It was found that, the values of E^0_1 & E^0_2 determined from deconvolution voltammetry via Figure 5 compare well with the values calculated from cyclic voltammetry (Table 1). The peak height of fast electron transfer is predicted to be proportional to the concentration of the reducible species, to the electrode surface area, and to the scan rate v . The peak potential for reversible process is a constant equal to the polarographic half wave potential. The peak shape is very dependent on n , the number of transferred electrons, as n increase, the peak is predicted to become narrower and much higher. It was observed that, the I_1 vs E and (dI_1/dt) vs E curves were easier to interpret more than i vs E curve.

Also, the values of diffusion coefficient were calculated from deduced convoluted current (I_{limd}) via the following relationship [26,29]:

$$I_{limd} = \frac{i_{prev}}{2.788\sqrt{(nv)}} \quad (7)$$

where I_{limd} is the deduced limiting convoluted current, which is defined as the limiting convoluted current, i_{prev} is the peak current

of reversible electrode reaction, n is the number of electrons consumed in electrode reaction and v is the scan rate. The values of diffusion coefficient calculated from I_{limd} agree well with the values calculated from convolutive and deconvolutive voltammetry of the experimental voltammograms (Table 1).

Also, the number of electrons consumed in electrode reaction can be calculated from the following equation [26]:

$$n = 0.103 ep / v I_{limd} \quad (8)$$

which is found to be equals to 2 for the overall reduction process.

From the obtained result, it can be seen that the redox potential of the second reduction process is more negative than that of the first one, which indicates that the second process requires more energy than the first one. As the degree of interaction increases, ΔE^0 and K_c also increase. The separation of the peak potentials for systems with two redox centers is in terms of the comproportionation equilibrium constant of the intermediate (*i.e.* the product of the first electron transfer reaction). This is given by the following equation [26]:

$$K_c = \exp\left[\frac{(E_1^0 - E_2^0)F}{RT}\right] \quad (9)$$

which gives 4.36×10^9 for K_c value, indicating extensive delocalization of charge between the centers of PyPD dye ($K_c > 10^6$) [26]. The magnitude of K_c confirm that the reduction process are characterized by successive reversible reductions to the corresponding radical anion and dianion species which support the extended conjugation [36]. Additionally it was established that, perylene-3,4:9,10-bis(dicarboximide)s (PDIs) compound is slightly easier to oxidize (by ca. 0.06 V) and to reduce (by ca. 0.06 V) which again is presumably due to the more delocalized nature of the HOMO and LUMO [36].

Based on the above electrochemical studies the reductive electrode behavior of PyPD dye can be proposed to proceed as follows:



i.e. EE mechanism

4. CONCLUSION

Based on the results obtained in this work, it could be concluded that:

- 1) The cathodic reduction of PyPD dye in $0.1 \text{ M TBAP/CH}_3\text{CN}$ at a platinum electrode involved a two reduction peaks (I & II) and (III & IV);
- 2) The first and the second reduction processes of the investigated PyPD dye proceed as fast charge transfer;
- 3) The electrode reaction is suggested to proceed as EE mechanism;
- 4) The rate of the first and the second charge transfer were calculated and found to proceed as fast charge transfer;
- 5) Convolutive – deconvolutive voltammetry is a more powerful technique in determination of the electrochemical parameters as well as identification of the nature of electrode mechanism;
- 6) The experimental kinetic parameters were determined experimentally and verified via a digital simulation method by comparing the generated theoretical cyclic voltammograms with the experimental cyclic voltammograms.

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