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Redox behavior, chromatographic and spectroscopic characterization of some reactive π-conjugated 4`-tricyanovinylhydrazone dyes

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ABSTRACT

A series of π-conjugated nonlinear 4`-tricyanovinylhydrazone (TCH) dyes was synthesized and characterized. The redox behaviors of the TCH dyes were studied by direct current (DC), and derivative polarography (DP), cyclic voltammetry (CV) and controlled potential coulometry (CPC). Excluding the nitro derivatives, the DC and DP polarograms of the compounds at pH < 5 showed two irreversible waves (peaks) corresponding to reduction of the >C=C- and the hydrazone group (>C=N-) groups. The DC and DP polarography of the nitro derivatives at pH<5 showed three waves (peaks). Plots of cathodic peak current ($i_{p,c}$) *vs.* square root of scan rate ($v^{1/2}$) and log $i_{p,c}$ *vs.* log v at -0.59 and -0.93 V at pH 4.46 were linear. The kinetic parameters (log $k^o_{f,h}$, ΔG^* and D) of the compounds were determined. Poor correlations for substituent on the $E_{1/2}$ of the dyes with the Hammett substituent constants were noticed. Based on the chromatographic separation, spectroscopic characterization and molecular weight determination of the end products of the electrolyzed species of 4'-nitrotricyanovinylhydrazone, an electrochemical reduction mechanism is proposed.

Keywords: 4'-Tricyanovinylhydrazone derivatives; Cyclic voltammetry; DC and DP polarography; Kinetic parameters; Chromatographic and spectroscopic characterization; Reduction mechanism.

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1. Introduction

Recent years have seen an upsurge of interest for organic dyes of nonlinear optical media with large nonlinearities [1]. Thus, in recent year's conjugated organic molecules containing both donor and acceptor moieties have received considerable attention [2]. These molecules are crucial components for many advanced technologies e.g. non-linear optical (NLO), electroluminescent, photo-, and photovoltaic devices [2]. These compounds have many advantages over inorganic materials e.g. large nonlinear optical coefficients, simple preparation, cost effectiveness and ease of synthetic design [3, 4]. Thus, great attention has been focused in designing and developing organic nonlinear optical materials, building optoelectronic devices and modern communication technologies [4-14]. Among these compounds, cyanohydrazone derivatives have many applications in electrooptic devices [15-20].

A series of 4`-tricyanovinyl hydrazones has been used as an excellent dyes due to their excellent thermal stability, absorption in the region of 500 nm and electrochemical properties [21-25]. These chemicals contain donor and acceptor groups positioned at either ends of a conjugated system of appropriate length [26-30]. The solvatochromic properties of these compounds originate from donor-acceptor substitution increases their interest [31]. Many applications of 4`-tricyanovinylhydrazone dyes in manufacturing of new materials capable of generating special electro optical effects e.g. frequency doubling or wave mixing have been reported [32-34]. Thus, the redox characteristics of 4`-tricyanovinyl hydrazones organic dyes are of great interest. To the best of our knowledge, the redox characteristics of the title compounds are not reported elsewhere. Thus, the present study is focused on: i) studying the effect of pH on the redox behavior of the title dyes (Fig.1) using DC, DP, CPC and cyclic voltammetry; ii) investigation of the influence of substituent's on the $E_{1/2}$ of >C=C- and >C=N-

NH- groups of studied hydrazones; iii) studying the correlation of Hammett constants (σ_{p-x}) of

the substituents on $E_{1/2}$ of the electrode reactions; iv) calculation of the kinetic parameters (D,

ΔG^*, $K^{\circ}_{f,h}$) of the electrode reactions and finally v) assigning the most probable reduction

mechanism of one of the nitro derivatives. This study helps the scientists in assigning the

semiconducting properties and the feasibility materials or materials with strong non linear

(NLO) properties.

2. Experimental

2.1. Apparatus

A direct current (DC), derivative polarography (DP) and cyclic voltammetry (CV)

measurements were performed on a Metrohm 746 VA trace analyzer and 747 VA stand

(Switzerland).A Metrohm three compartment electrochemical cell (10 mL) configuration

incorporating DME or HMDE, (drop surface area 0.38 mm^2) as working electrode in DC, DP

and CV, respectively. A double-junction Ag/AgCl, (3.0mol dm^{-3} KCl) and Pt wire (MW-1032)

were purchased from Bioanalytical system (BAS) and were used as reference and counter

electrodes, respectively. Controlled potential coulometry (CPC) was performed using Hg (0.38

mm^2) and Pt foil (thickness =0.1 mm; surface 25.4mm× 25.4 mm and 99.95% purity)

electrodes (BAS). DC and DP polarography were carried out at a flow rate of 1.045 mg Hg/s. A

Volac digital-micropipette and a digital pH-meter (model MP220, Mettler Toledo) were used.

2.2. Reagents and materials

 Low-density polyethylene (LDPE) sample bottles, Nalgene and reagent containers were

precleaned by soaking in hot 5% (V/V) micro detergent (DECON, BDH, Poole, England) for

24 h, followed by 50% (v/v) HCl (A.R, Merck) for one week, soaked in HNO$_3$ (2.0 mol dm^{-3}),

rinsed with deionized water and finally dried. Tetra cyanoethylene (TCNE) and hydrazones

were purchased from BDH. A series of Britton-Robinson (BR) buffers (pH 2.2-11.3) was

prepared and stored in LDPE in refrigerator [35]. N, N-dimethylformamide (DMF) at various proportions (40 -60 % v/v) -BR at the required pH was used as supporting electrolyte. Stock solutions of the dyes (1.0×10^{-3} mol dm^{-3}) were prepared in DMF and stored in a refrigerator. Diluted solutions ($1.0 \times 10^{-4} - 8.0 \times 10^4$ mol dm^{-3}) of the dyes were prepared individually and daily. DMF was selected as a proper solvent for the following reasons: i) relatively easy to purify; ii) its function as a better Lewis-base a property that is important for this class of chemicals and finally iii) the dyes have significant solubility in this solvent.

2.3. Synthesis of 4`-tricyanovinylhydrazone and its derivatives

4'-Tricyanovinylhydrazone and its derivatives (Fig.1) have been prepared [20] as dark violet solids as follows: tetra cyanoethylene (10 mmol) was allowed to react with the corresponding hydrazone (10 mmol) in DMF (50 mL) at 50-70$^{\rm o}$ C. The reaction mixtures were stirred for 30 min and the formed violet solid precipitates were separated out and re crystallized from DMF. The produced precipitates (dyes) were fully characterized from their elemental analysis, infrared (IR) and ^{1}H NMR spectral measurements. IR spectra of, the produced dyes exhibited three vibration peaks in the range 3230-3220, 2220-2210 and 1640-1650 *cm^{-1}* and were safely assigned to NH, cyano and *v* (C=N) , respectively. ^{1}H NMR (δ ppm) spectrum of 4-tricyanovinyl-3- nitrohydrazone showed doublet signals of two hydrogen's at δ 8.42 (2 H, d, H-3,s), 8.12 (2 H, d, H -2, 6), 8.1 (1 H, s, H-7), 7.21 (2 H, d, H-3`,5`), 6.61 (d, H 2`,6`) and 4.05 (NH, s) ppm. The purity of the compounds was also confirmed by TLC and HPLC.

Please insert Fig. 1

2.4. General electrochemical procedures of tricyanovinylhydrazone derivatives

An accurate volume (9.0 mL) of DMF (40-60 % v/v) -BR buffer at the required pH (pH 3-10) was placed into the electrochemical cell. The solution was stirred and purged with dry N$_2$ gas for 15 min. The stirring was then stopped after 5s quiescence time and the polarogram was

recorded by applying a negative potential scan (-0.0 to −1.7.0 V) at 20 mVs^{-1} scan rate. An

accurate volume (1.0 mL) of the dye (5.0×10^{-4} mol dm^{-3}) was introduced into the cell and the

solution was stirred under dry N$_2$ gas for 5 min. The stirring was stopped and the polarogram

was recorded after 5s quiescence time at the DME *vs*. Ag/AgCl/V reference electrode. Cyclic

voltammetry of the dyes (5.0×10^{-4} mol dm^{-3}) at HMDE were recorded at various scan rates (*v*

= 1000- 5000 mVs^{-1}) at pH 3-10 under dry N$_2$ gas. No electrochemical study was carried out at

pH>10, since the color of the compounds was disappeared. On the other hand, recording of the

DC, DP and CV in pure aqueous or DMF was not well resolved and the waves and/or peaks are

ill defined. Thus, in the subsequent work DMF (40-60 % v/v) -BR buffer was used as a

supporting electrolyte in all electrochemical experiments.

2.5. Controlled potential coulometry (CPC)

An accurate volume (9.0 mL) of DMF –BR (40-60%v/v) buffer at the required pH (pH <11)

was placed into the cell. The solutions were deaerated by passing N$_2$ gas for 15-20 min, and

then electrolyzed at Pt net electrode at the potential of the limiting current plateau of the

cathodic wave o each compound. The current decreased exponentially with time and the

corresponding numbers of electron transfer were calculated from charge – time curve as

reported [36].

2.6. Characterization of the end products of the electrolyzed species

The end products of the electrolyzed solution were characterized by TLC and GC-MS.

Readymade silica gel plates (60$_{254}$) (E-Merck) company was used. The product was analyzed

by GC-MS, as follows: after preconcentration of the sample from 1.0 mL to 10.0 μL by slow

evaporation, the analyte gets retained on the sorbent and excess solvent was eluted out. Traces

of water were removed by shaking with anhydrous Na$_2$SO$_4$ (100 mg) and the final enriched

sample was stored in vials and1.0μl was injected into GC- chamber. The end products were further subjected to spectroscopic (^{1}HNMR, IR, UV-Visible).

3. Results and discussion

3.1. Influence of pH and substituent on the redox behavior of tricyanovinyljydrazones

The dependence of the limiting current (or peak current) and half-wave (or peak) potentials ($E_{1/2}$) of the parent TCH, and its reactive dye derivatives and the model compound dimethylamino-4,4-tricyanovinyl benzene over a wide range of pH3-11 was investigated. DC and DP polarographic and CV data at pH 4.3-4.66 are summarized in Table 1. Typical DC and DP polarograms of 4`-TCH in DMF-BR (40% v/v) at pH 4.46 *vs.* (Ag/AgCl)/V reference electrode are shown in Fig. 2. In DC polarography, three waves were noticed and the first two waves are very close (~ 0.60 -0.065 ± 0.03 V), while the third wave was at ~ -1.15 ± 0.05 V. CPC of TCH at the potential of the limiting current plateau of the cathodic waves under N_2 atmosphere at Pt net electrode was carried out to calculate the corresponding number of the electron transfer (n) from charge – time curve. At Pt foil as working electrode, the compound TCH was reduced in the potential range -0.2 to -0.9 V and the value of n was calculated employing the following equation [36]:

$$Q_F = Q_t - Q_B = nFVC \tag{1}$$

where Q = charge in columbs. Q_F is the faradic charge required for complete electrolysis of the organic compound in solution. Q_t is the faradic charge required for complete electrolysis of the test solution which was measured by extrapolating the linear region of the curve to zero time, Q_B is the charging current integral within time window required for complete electrolysis of the supporting electrolyte only, V is the sample volume in the electrochemical cell in liter, C is the concentration of the test solution, mol L^{-1} and F is Faraday's constant, 96485 Coul./equiv. When the potential of -0.9 V was applied, the absorbance at λ_{max} and the current of

the compound was decreased systematically with progress of electrolysis and passage of time. The reaction took ≈6 h for complete electrolysis. During electrolysis, reduction in color and in absorbance was occurred while the peak current increased suggesting complete reduction of these electroactive species and the chromophoric groups. Based on the charge-time curve, the value of n involved in the reduction of TCH was found equal 2 electrons. The plot of log $i_{p,c}$. *vs.* time or log absorbance *vs.* time were linear confirming first order kinetic rate equation. Hence, the first two waves (in the range - 0.6 to - 0.65 ± 0.03 V) and the third wave (~ -1.15± 0.06 V) *vs*. (Ag/AgCl/V) electrode in the DC polarogram (Fig. 2) of TCH are most likely assigned to the reduction of the double bond (>C=C<) via two successive H^+/e steps and azomethene >C=N- groups with $4H^+$/4e step [34].

DP polarogram of TCH in DMF-BR (40% v/v) at pH 4.46 (Fig. 2) showed two reduction peaks (42 nA) in the same region of the first two DC waves. Another DP peak (84 nA) close to the region of the third DC wave was also noticed. Based on the charge – time of CPC curves of the reduction waves of TCH and the DP polarogram of the model compound N, N- dimethylamino-4-tricyanovinyl benzene (having no azomethine group), the first two and third waves are safely assigned to the reduction of >C=C and azomethine >CH=N- groups, respectively [36].

Please insert Fig. 2

The CVs of TCH (5.0×10^{-4} mol dm^{-3}) in DMF-BR buffer (40% v/v) at pH 4.46 at scan rates *v* (0.1 -5 Vs^{-1}) were studied. Representative CV data at 0.5 Vs^{-1} scan rate are summarized in Table 1. The CVs at 1000, 2000 and 3000 mV s^{-1}at HMDE (Fig. 3) showed two cathodic peaks at -0.59 - ± 0.04 V (peak, 1) and -0.93 ± 0.03 V (peak, 2). In the reverse scan, no anodic peaks in were observed revealing the irreversible nature of the electrode processes. On increasing the solution pH and scan rate (*v*) from ν =0.1.0 to 5.0 V s^{-1} , the cathodic peaks were shifted to more negative values adding further support to the involvement of H^+/e and the irreversible nature of the electrode processes [37]. These reduction peaks are most likely assigned to

reduction of the >C=C- and >C=N- groups with the same number of electrons [34]. The plots

of the $i_{p,c}$ at -0.59 ± 0.04 and -0.93 ± 0.03 V *vs.* $v^{1/2}$ were linear , indicating that, the reduction

processes are diffusion-controlled [38, 39]. The plot of log $i_{p,c}$ (*nA*) *vs.* log v (mV s^{-1}) at -0.59 ±

0.04 and -0.93 ± 0.03 V was linear with slope in the range 0.5-0.59 (R^2= 0.98). The current

function ($I_{p,\ c}/v^{\ 1/2}$) of the two peaks *vs.* v increased linearly indicating that, the reduction

processes did not favor electrode coupled chemical reaction of EC type mechanism [39].

<div align="center">**Please insert Figs. 3**</div>

The DC polarogram of TCH at 7 < pH < 8.6, showed one cathodic wave at -0.20 ± 0.04 and

an ill defined wave at -0.85 ± 0.02 V. The possible hydrolysis of the dye may account for the ill

defined wave [26, 36]. The low level of H$^+$ is most likely inhibits the reduction steps and

facilitates formation of negative charge over the molecule [36]. The DP polarography of TCH

exhibited two reduction peaks at -0.16 ± 0.03 and -0.82 ±0.06 V *v s.* (Ag/AgCl)/V electrode.

Thus, the two reduction waves or peaks in the DC and DP were safely assigned to reduction of

>C=C and >C=N- groups, respectively. At pH > 8.6, the DC polarography showed two ill-

defined waves at -0.32 ± 0.02 and -0.9 ± 0.05 V, and the DP also exhibited two ill defined

peaks at - 0.30 ± 0.05, and -0.74 ± 0.06 V indicating the involvement of H$^+$ /e in the electrode

reactions [36].

The dependence of the half-wave potential *($E_{1/2}$)* of the model compound N, N-dimethylamino-

4-tricyanovinylbenzene, parent TCH and its derivatives on pH was critically studied. The plots

of $E_{1/2}$ *vs.* pH of TCH of the first and second DC waves were found linear (Fig. 4) indicating

the involvement of H$^+$ /e on the reduction processes [39, 40]. On raising the solution pH from

pH 3.9 to pH 10.8, the values of $E_{1/2}$ of the first and second waves were shifted from -0.290 ±

0.04 to -0.738 ± 0.02 V and from − 0.588 ± 0.04 to − 0.875 ± 0.06 V, respectively. Direct

exchange of electrons in two successive 2H$^+$/2e$^-$ and 4H$^+$/4e$^-$ steps due to reduction of >C=C-

and >C=N- groups to the corresponding alkyl and amines [27, 36], respectively account for the observed trend.

<div align="center">**Please insert Fig. 4**</div>

The DC and DP polarography of 2-Cl -, 3-Cl, 4-Cl and 2-CH$_3$O, and 4-CH$_3$O derivatives of TCH at $3.04 \leq pH < 5$ showed similar trend, while 2-NO$_2$, 3-NO$_2$ and 4-NO$_2$ derivatives of the parent TCH exhibited different trend. The electrochemical parameters at pH 4.3-4.46 are given in Table 1. Representative DC and DP polarograms of 4-tricyanovinyl-3-nitrohydrazone in DMF-BR (40 %v/v) buffer at pH 4.69 at HMDE are shown in Fig. 5. In the DC, three waves at - 0.33 ± 0.04, - 0.61± 0.08 and - 1.13± 0.03 V were noticed, while in DP four peaks at -0.31, -0.56, - 0.9 and - 1.02 V were observed. The current height of the first two waves in the DC was equal to ½ of the third wave (Fig. 5). Thus, the reduction of >CH=N- group proceeded through two consecutive reduction steps. Similar trend was also noticed in the DP polarogram. Thus, the first and second DP peaks were safely assigned to first and second DC waves at -0.31, -0.56 V, while the third and fourth DP peaks at - 0.9 and - 1.02 V corresponding to the third DC wave (- 1.13± 0.03 V).

<div align="center">**Please insert Table 1 and Fig. 5**</div>

The end product of electrolyzed solution of 3- nitro derivative at pH 4.5 was characterized by ^{1}HNMR (δ ppm). The spectrum showed signals at 8.71 (2 H, br s 2, 6), 6.95 (2 H, d H 3, 5), 6.6 (2 H, d H-7), 4.4 (2 H s -NH$_2$, 4.1 NH s-NH, 2.1 (br.) ppm OH) revealing formation of amino derivative. The purity of the end product was also confirmed by HPLC and TLC. Based upon the DC and DP polarography of the parent TCH in DMF-BR buffer (40% *v/v*) at pH 4.5, (Fig. 2) and the model compound N,N– dimethylamino-4,4`-tricyanovinyl benzene (Fig. 6) (not having nitro and azomethine substituent's) the first DC wave (or DP peak) for 3- nitro derivative was assigned to reduction of NO$_2^-$group by accepting 4H$^+$ /4e$^-$ to form hydroxylamine. The second and third waves (or peaks) in the DC and DP of the 3- nitro

derivative (Fig. 5) are assigned to the reduction of >C=C and >C=N- groups, respectively. Thus, the first and third waves in the DC involved four electrons, while the second wave involved two electrons $2e^-/2H^+$.

<div align="center">**Please insert Fig. 6**</div>

The CVs of 4-tricyanovinyl-4-nitrohydrazone in DMF-BR (60% v/v) buffer of pH 4.3 at various scan rates (1000 -5000 mV s^{-1}) are shown in Fig. 6. Based on the DC and DP polarograms (Fig. of TCH (Figs 2 & 3) and the model compound N,N– dimethylamino-4,4`-tricyanovinylbenzene (Fig. 5) , the first, second and third CV waves (or peaks) are most likely assigned to reduction of NO_2^-, >C=C and >C=N- groups, respectively.

<div align="center">**Please insert Fig. 7**</div>

The influence of dye concentration ($2.0 \times 10^{-4} – 1.2 \times 10^{-3}$ mol dm^{-3}) on the DC and DP polarography of the TCH and its 4-Cl, 4-CH$_3$O, 4-NO$_2$ derivatives at pH 3.04 and pH 9.0 was investigated. Representative DC for 4'-tricyanovinyl-4-hlorohydrazone in DMF-BR (60% *v/v*) at pH 3.05 for >C=N-NH- and >C=C- DC waves and at pH 9.0 for >C=C- DC wave are demonstrated in Fig. 8. Upon increasing the dye concentration, the diffusion currents of the first, second and third DC waves increased linearly (R^2=0.989-0.997) and almost passed through the point of origin (Fig. 8). The slope of the three lines was 0.163, 0.160 and 0.114 for >C=N-NH- and >C=C- DC waves at pH 3 and at pH 9.0, respectively confirming that,the electrode processes are diffusion controlled [27, 36]. At pH 3.04, increasing the dye concentration from 5.0×10^{-4} to 1.0×10^{-3} mol/dm^3 shifted $E_{1/2}$ of the first and second DC waves from -0.24 to -0.28 and from -0. 63 to -0.75 V, respectively adding another support to the irreversible nature and diffusion controlled process of the reduction waves [39, 40].

<div align="center">**Please insert Fig. 8**</div>

The number of protons involved per mole of the reactant at the rate determining step was calculated empolying the following equations [36]:

$$\Delta\, E_{1/2}/\Delta pH = (0.059/\alpha n_\alpha)\, Z_{\mathrm{H}}^{+} \tag{2}$$

$$\alpha n_\alpha = 0.059/\,[\Delta\, E\,/(\Delta log\, i/\, i_d\text{-i})] \tag{3}$$

$$Z_{\mathrm{H}}^{+} = (\Delta E_{1/2}\,/\Delta pH)/\,[\Delta E/(\Delta\, log\, i/i_d\text{ -i})] \tag{4}$$

where, Z_{H}^{+}, α, i_d and n are the number of protons; electron transfer coefficient, the diffusion current (μA) and the number of electron transfer per mole in the reduction process, respectively. Assuming n = 2 and 4 for the first and second DC waves of the dyes, the value of Z_{H}^{+} were in the range 0.4 -0.94 while the value of α was in the range 0.23 - 0.64 and 0.18 – 0.49 for the first and second DC waves, respectively confirming the irreversible nature of the processes. Thus, the DC waves were explained by direct exchange of H^+/e^- transfer in the successive steps forming imine and amine, respectively [36, 40]. A comparison of the limiting current of the reduction processes corresponding to >C=N-NH- and >C=C- groups revealed that, the TCH dye and its derivatives were reduced by the same number of electrons.

In the DC polarography, the plots of $E_{1/2}$ *vs.* pH for >C=N-NH- wave of 2-Cl, 3-Cl, 4-Cl and 4-CH₃O- derivatives were linear with slopes in the range -0.31-0.46 mV/pH. The $E_{1/2}$ values of these derivatives were shifted to more negative values on increasing the solution pH supporting the irreversible nature of the reduction step and reduction of the species by a similar electrochemical mechanism [36, 40]. The plots of $E_{1/2}$ *vs.* pH of the nitro derivatives were also linear with slope in the range -0.08 to -0.06 mV/pH revealing different reduction mechanism of the nitro derivative compared to 2-Cl, 3-Cl; 4-Cl and 4-CH₃O- derivatives.

3.2. Analysis of polarographic waves

Based on the irreversible nature of the tested dyes, the DC polarograms at various pH was studied employing the equation [36]:

$$E_{DMF} = E_{1/2} - [(0.059/ \alpha n_\alpha) (\log i/i_d - i)] \tag{5}$$

where, i_d is the diffusion current. The plots of E_{DME} *vs.* $\log (i/i_d - i)$ n*A* for the reduction waves corresponding to >C=C- and >C=NNH- of 2-Cl, 3-Cl; 4-Cl, 4-CH$_3$O- and nitro derivatives of TCH in DMF-BR of pH 4.46 were critically studied. Representative results for 4'- chloro tricyanovinyl hydrazone derivatives are shown in Fig. 9. The plots were linear with slopes in the range -0.064 to -0.08 and -0.066 to -0.069 V for >C=C- and >C=NNH-, respectively. The slopes were higher than the expected value (-0.059) for reversible electrode reaction adding further support to the irreversible nature of the electrode processes [36] and the species were reduced by similar mechanism [40]. Also in solution of pH 8.7, the slopes of the linear plots of E_{DME} *vs.* $\log i/i_d - i)$ n*A* for >C=C- group were in the range -0.09 to -0.12 V lower than the value expected for reversible electrode process. Thus, the compounds were reduced by similar mechanism [36].

Please insert Fig. 9

3.3. Kinetic parameters

The standard heterogeneous rate constant ($k^o{}_{f,h}$, cms^{-1}), diffusion coefficient (D,cm^{2}s^{-1}) and energy of activation (ΔG^*, *K* cal mol$^{-1)}$ of the first and second reducible species of TCH and its 4-Cl, 4- CH$_3$O and 4-NO$_2$ and N,N-dimethylamino-4-tricyanovinylbenzene were calculated at pH~4.46 and pH = 8.67 using the following equations [36]:

$$i_d = 607 n D^{1/2} C^o m^{2/3} t^{1/6} \tag{6}$$

$$\log k^o{}_{f,h} = \log i/i_{d-1} + \log D^{1/2}(0.87 t^{1/2}) \tag{7}$$

$$\Delta G^* = 5778.8[5.097 - \log k^o{}_{f,h}] \tag{8}$$

where, C^o is the dye concentration (m mole L^{-1}); t = drop time of Hg drop (0.02 s) and m is the rate of flow of Hg from the electrode (1.045 mgs^{-1}). The values of log $k^o_{f,h}$ for the first and second DC waves were calculated from the slopes of the linear plots of log $k^o_{f,h}$ cms^{-1} $vs.$ $E_{1/2}$ with respect to normal hydrogen electrode (NHE). The values of log $k^o_{f,h}$ cm s^{-1} are summarized in Table 2. At pH = 4.46, the values of log $k^0_{f,h}$ $cm.s^{-1}$ were in the range -13.7 ± 0.78 to -8.02 ± 0.66 $cm.s^{-1}$, while at pH 8.67, the values of log $k^o_{f,h}$ cm s^{-1} were in the range -19.5 ± 1.1 to -6.8 ± 0.1cms^{-1}. The values of $k^o_{f,h}$ of the reduction wave of >C=C< group of TCH and its 4-Cl, 4-CH$_3$O and 4-NO$_2$ derivatives and N,N-dimethylamino-4,4-tricyanovinylbenzene decreased on raising pH (Table 2) revealing the irreversible nature of the step and protonation reaction [40].

Please insert Table 2

The values of D (Table 2) were in the range (0.27 -0.73) × 10^{-6} $cm^2.s^{-1}$ close to the values computed from CV (0.23 -0.83) ×10^{-6} cm^2. s^{-1} using the following equation [40, 41]:

$$i_{p,c} = 2.72x10^5 n^{3/2} D^{1/2} C^0 \boldsymbol{v}^{1/2} \qquad (9)$$

where, $i_{p,c}$ = cathodic peak current, $\boldsymbol{v}$ scan rate Vs^{-1}. Increasing the dye concentrations, didn't lead significant variations in the values of D which are strongly-related to the dye aggregation in the solution. Low aggregation and fast diffusion of the analyte towards electrode surface may account for the higher values of D [41]. On raising the solution pH, the D values decreased. Protonation reaction hampers charge transfer process, thereby causing aggregation and hydrolysis of the dye at high pH [35, 36].

The ΔG* values for the first and second reduction waves of some of the parent TCH and selected derivatives (*4*-Cl; *4*-OCH$_3$; 4-NO$_2$) and N,N`–dimethylamino-4,4`-tricyanovinyl benzene at pH~4.46 and pH 8.67 are given in Table 2. The ΔG* values at pH 4.46 and pH 8.67 of the first wave were in the range 75.8 -108.4 ± 3.8 and 68.7 -85.3 ± 6.6 $Kcal.mol^{-1}$, while at

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pH~4.46 and pH 8.67, the ΔG^* values of the second wave were in the range 97.8 – 154.1± 0.99

and 75.2 -142.1 Kcal.mol^{-1}, respectively. Significant variation on the values of ΔG^* was

noticed on raising the pH for *4*-OCH$_3$; *4*-NO$_2$ except 4-Cl derivatives. The decrease on ΔG^* of

4-OCH$_3$ and *4*-NO$_2$ derivatives on raising the solution pH was attributed to the aggregation and

difficulties in the protonation of the electrolyzed species [41, 42]. The charge transfer process

and D values at high pH are limited; thereby lowering the ΔG^* values. On raising the solution

pH of the dye, non significant variation in $\Delta G^*$was noticed. The ease of protonation and poor

aggregation of the dye are most likely account for the observed trend [41, 42]. The kinetic

parameters ($K^{\circ}_{f,h}$,D, ΔG^*, K°) of the electrode reactions suggest the semiconducting properties

and the feasibility materials or materials with strong non linear (NLO) properties.

The plots of the Hammett constants (σ_{p-x}) of the substituent's 2 - Cl, 3- Cl, 4 –Cl, 3-CH$_3$O and

4- CH$_3$O *vs.*$E_{1/2}$ of the reduction waves corresponding to >C=N-NH- (1) and >C=C- (2) groups

at pH 3.04 were linear (Fig. 10) with a slope of 0.1.46×10^{-3} and 3.69×10^{-4}, respectively. The

substituent's appear to have no significant effect. At pH 9.0, the slope of the linear plot

corresponds to reduction step of >C=N-NH (3) group was - 0.014 ± 0.004 (Fig. 10) indicating

poor influence of 2 -, 3- and 4–Cl and 3-CH$_3$O and 4-CH$_3$O substituent's [43]. The reduction

step of –C=N-NH group is controlled by nucleophilic attack of the electron. Thus, the overall

shifts in $E_{1/2}$ of the parent compound due to the substituent's effects of 2 -, 3- and 4 –Cl and 3-

and 4- CH$_3$O - groups are poorly correlated with the Hammett constants σ_{p-x}.

Please insert Fig. 10

3.4. Characterization of the end products of 4'- nitrotricyanovinylhydrazone

3.4.1. Chromatographic characterization

The electrolyzed solution of 4-nitro TCH was first tested by TLC using different solvent

systems e.g. dioxane-water, acetone-water and petroleum ether at various compositions. Good

results were achieved with petroleum ether where well –separated spots were noticed. The sample solution was preconcentrated from 1.0 mL to 10 µL fractions for injection in gas chamber of GC-MS. The products were identified by GC-MS. Total ion chromatogram of the electrolyzed species showed significant peak fragments at m/z 224.11, 164.09 and 138.08 which are most likely corresponding to 2-(4-(dimethylamino)) phenyl)ethane-1, 1, 2-tricarbonitrile ($C_{13}H_{12}N_4$) **(IV)**, (E)-N-(1-(4-hydroxyamine)phenylethylidene)methamine ($C_9H_{12}N_2O$) **(V)** and (4-hydroxyamino) phenyl) - methamine ($C_7H_{10}N_2O$) **(VI)** formation, respectively.

3.4.2. Spectroscopic characterization

IR spectrum of the end products showed characteristics vibrations at 3400-3485, 3321, 3043 and 1512 cm^{-1} due to OH, NH_2, >CH=C- and >C=C- groups, respectively. With progress of electrolysis and passage of time, the absorbance at λ_{max} (390 nm) and the current systematically decreased at potential of -1.2V using Pt foil as working electrode. The absorbance at λ_{max} became close to zero after ≈6 h of electrolysis showing complete reduction of the chromophoric groups in the compound. The influence of the initial dye concentration on the kinetics and diffusion current was also investigated. On increasing the dye concentration, the diffusion current decreased and the kinetics of the reduction step changed. The plots of log absorbance *vs.* time and log $i_{p,c}$ *vs.* time of the end products were linear suggesting first order rate equation. IR spectrum of the end products showed vibration at 3400-3450$_{br}$ cm^{-1} corresponding to NH_2 group suggesting formation of amine as an end product.^{1}H NMR spectrum of **IV** ($C_{11}H_8N_4$) recorded signals δ at 3.8 -4.05, 6.3, 6.6- 7.07 ppm due to methine, aromatic C-NH and benzene protons, respectively confirming formation of **IV** and m/z=196.2 (Scheme I). ^{1}H NMR spectrum of **VI** ($C_7H_{10}N_2O$) recorded signals δ at 2.06, 4.06, 8.7, 6.5-7.05 and 4.4 ppm corresponding to OH, aromatic C-NH, NH_2 and benzene and methylene protons, respectively

demonstrating formation of compound **VI** (Scheme I). Molecular weight determination of **IV** and **VI** were 196.2 and 138.3, respectively.

3.5. Proposed reduction pathway mechanism for 4-nitro derivative

Based on DC and DP (Fig. 7), CV and CPC, chromatographic (TLC, GC-MS) and spectral (^{1}HNMR, IR and UV-Visible) data of the end products of the electrogenerated reduced species of 4'-nitro tricyanovinylhydrazone at pH < 5.1, a possible mechanism describing the overall reduction processes is proposed in scheme I. On raising the solution pH the observed shift of $E_{1/2}$ indicated that, the overall electrode processes involve proton transfer and the sequence of H^+/e addition preceded as H^+, e^-, H^+, e^- after proton uptake and adding one electron. These data add further support to the proposed mechanism (scheme I). Thus, radical **(I)** would accept proton to form a protonated radical **(II)** (scheme I)**. T**his radical was further cleavage after taking one electron to form hydroxylamine derivative **(III).** Compound **III was** further converted to 2-(4-(dimethylamino) phenyl) ethane-1, 1, 2-tricarbonitrile ($C_{13}H_{12}N_4$) **(IV)** and (E)-N-(1-(4-hydroxyamine)phenyl ethylidene) methamine ($C_9H_{12}N_2O$) **(V).** Compound **V** was finally reduced to form (4-hydroxyamino)phenyl)methamine ($C_7H_{10}N_2O$) **(VI)** via $2e^-/2H^+$.

Please insert Scheme 1 here

4. Conclusion

 The redox behavior and spectroscopic characteristics of some tricyanovinylhydrozone chromophores and some of its conjugated dyes were studied. The study helps in assigning the semiconductor and non linear (NLO) properties of the dyes. The electrode processes of the dyes were irreversible and the shifts in $E_{1/2}$ of the azomethine group (>C=N-NH) of the parent compound were correlated with the Hammett constants σ_{p-x} whereas, the values of $E_{1/2}$ corresponding to >C=C- group were poorly correlated. Work is continuing to study the non linear refractive index, nonlinear absorption coefficient by the z-scan technique and third- order

susceptibility of the dyes. Spectroelectrochemical characteristics of the dyes at gold mesh (100 w/ inch, 82% transparency) transparent thin layer electrode will be carried out to participate in assigning their non linear (NLO) properties. Such compounds may be of use in developing photonic devices like optical limiters for eye and equipment safety.

Acknowledgment

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Figure caption

Fig.1. Chemical structures of 4'-tricyanovinyl-hydrazone and its derivatives. X= *2*-chloro; *3*-chloro; *4*-chloro; *2*-methoxy; *2*-nitro; *3*-nitro or *4*-nitro group.

Fig.**2**. DC (1) and DP (2) polarograms of TCH (5.0×10^{-4} mol dm^{-3}) in DMF-BR (40 %v/v) buffer at pH 4.46 *vs.* (Ag/AgCl)/V reference electrode.

Fig.3. Cyclic voltammograms of TCH (5.0×10^{-4} mol dm^{-3}) at 1000 (1), 2000 (3) and 3000 (2) mV s^{-1} at HMDE electrode in aqueous acidic solution of pH 4.46 *vs.* (Ag/AgCl)/V electrode.

Fig. 4 Plots of $E_{1/2}$ of the first (1) and second (2) waves of TCH (5.0×10^{-4} mol dm^{-3}) *vs.* pH.

Fig.**5**. DC (1) and DP (2) polarography of 4'- tricyanovinyl -3- nitrohydrazone (5.0×10^{-4} mol dm^{-3}) in DMF-BR (40 %v/v) buffer of pH 4.69 at HMDE *vs.* (Ag/AgCl)/V electrode.

Fig.**6**. DC (1) and DP (2) polarography of the model compound N,N –dimethylamino -4-4- tricyanovinyl benzene (5.0×10^{-4} mol dm^{-3}) in DMF-BR (40% v/v) buffer of pH 4.5 *vs.* (Ag/AgCl)/V electrode.

Fig.**7**. Cyclic voltammetry of 4'- tricyanovinyl -4- nitrohydrazone (5×10^{-4} mol dm^{-3}) in DMF-BR (60% v/v) buffer of pH 4.3 at various scan rates 1000 (1), 2000 (2) and 3000(3) mV s^{-1} *vs.* (Ag/AgCl)/V electrode.

Fig.8. Plots of $i_{p,c}$ *vs.* concentrations (2.0×10^{-4}-1.2×10^{-3} mol dm^{-3}) of the dye 4'- tri -cyanovinyl- 4- chlorohydrazone at DMF-BR (60% v/v) buffer of >C=N-NH- (**1**) and >C=C- (**2**) DC waves at pH 3.04 and >C=C wave (3) at pH 9.

Fig.9. Plots of potential (E_{DME}) of the second wave (>C=C-) *vs.* log i/i_{d-i} of 2-, 3- and 4'- chloro tricyanovinylhydrazone derivatives (5.0×10^{-4} mol dm^{-3}) in DMF-BR (40 %v/v) buffer at pH 4.46 *vs.* (Ag/AgCl)/V electrode.

Fig.10. Plots of $E_{1/2}$ of >C=N-NH (**1**) and >C=C- (**2**) groups of TCH (5.0×10^{-4} mol dm^{-3}) in DMF-BR (40 %v/v) *vs.* Hammett constant (σ_{p-x}) of the substituent's 2 - Cl, 3- Cl, 4 –Cl, 3- CH$_3$O and 4- CH$_3$O at pH 3.04 and >C=N-NH (3) at pH 9.

Table 1. DC and DP polarographic and CV data of the parent compound tricyanovinyl-hydrazone and its derivatives (5×10^{-4} mol dm^{-3}) at pH 4.3-4.46 [a]

Compound	DC-Polarographic Data		CV data,
	$-E_{1/2}$ (V)	$-i_d$ (nA)	Ep,c (V)
Tricyanovinyl hydrazone	0.58± 0.05 (0.53)	130.8 ±6.9	0.59±0.04
	0.66 ±0.03 (0.62)	78 ±6.7	
	1.01 ± 0.03 (0.95)	238 ± 9.4	0.93± 0.03
4-Cl	0.69± 0.03 (0.64)	117± 7.9	0.6± 0.05
	-	-	0.66± 0.04
	1.2±0.05 (1.1)	199± 5.7	0.95 ± 0.08
3-Cl	0.73± 0.03 (0.63)	41± 2.3	0.6± 0.03
	-	-	0.67± 0.04
	1.08 ± 0.05(1.02)	71.6	0.95± 0.06
2-Cl	0.66 ± 0.04 (0.65)	86.2± 3.8	0.6± 0.04
	-	-	0.67± 0.06
	1.05± 0.06 (1.98)	123 ± 5.9	0.93± 0.05
4-OCH$_3$	0.66 ± 0.04 (0.62) (0.65)	133.7± 6.3	0.63± 0.06
	1.29± 0.03 (1.17)	195.7± 4.1	1.1± 0.07
2-OCH$_3$	0.66± 0.06 (0.61)	146.3± 9.9	0.66± 0.04
	1.1± 0.03 (1.02)	234.6± 12.6	0.98± 0.08
4-NO$_2$	0.29± 0.06 (0.20)	264.4± 6.8	0.38± 0.04
	0.59± 0.05 (0.53)	320.0± 8.4	0.68± 0.08
	1.08 ± 0.03 (1.02)	263.5± 8.5	1.19± 0.03
3-NO$_2$	0.33 ± 0.04 (0.31)	231.6± 9.9	0.44± 0.05
	0.61± 0.08 (0.56)	188.5± 9.56	0.67± 0.06
	1.13± 0.03 (0.9, 1.02)	240.6±8.8	1.18± 0.04
2-NO$_2$	0.29± 0.03 (0.23)	287.3± 11.8	0.44± 0.04
	0.61± 0.04 (0.59)	121.9± 10.4	0.69± 0.05
	1.2± 0.05 (1.13)	267.4± 8.9	1.23± 0.09
3,4-OCH$_3$	0.64± 0.05 (0.59)	144.6± 5.5	0.64± 0.06
	-	-	0.72± 0.05
	1.22± 0.05 (1.19)	225.8± 12.3	1.13± 0.03
2-Napthyl	0.71± 0.03 (0.68)	109.8± 6.7	0.65± 0.07
	-	-	0.72± 0.07
	1.2 ± 0.05(1.04)	196.7± 11.3	1.03± 0.05
Y[b]	0.59± 0.04 (0.54)	193.7± 4.9	-

[a] DP polarographic data are given in parentheses.

[a] CV data are given at 0.50 V s^{-1} scan rate *vs.* (Ag/AgCl)/V reference electrode.

[b] **Y** = N,N –dimethylamino-4-4- tricyanovinyl benzene.

Table 2. Kinetic parameters (log $k^o_{f,h}$ $\Delta G*$ *and D*) of the first (>C=C<) and the second (azomethine ->C=N<) waves of tricyanovinyl-hydrazone, N,N` –dimethylamino – 4,4`- tricyanovinyl benzene and its derivatives (5×10^{-4} mol dm^{-3}) in DMF-BR (40 %v/v) buffer at pH 4.46 [a]

Compound	DC-Polarographic Data		
	log $k^o_{f,h}$	$\Delta G*$ K(cal mol $^{-1}$)	D cm^2 s^{-1} ×10^{-6}
Tricyanovinyl hydrazone	12.3 ± 0.55 (6.8)	100.7 ± 7.5 (68.7)	0.27 ± 0.03 (0.18)
	11.8± 0.13 (13.5)	97.8± 4.5 (107.3)	0.34± 0.05 (0.21)
	9.5 ± 0.44 (9.7)	84.4± 3.8 (85.3)	0.56± 0.05 (0.46)
4-Cl	16.3± 1.0 (15.46)	123.4± 3.7 (119.4)	0. 34± 0.04(0.23)
4-OCH$_3$	8.0± 0.83 (7.9)	75.8± 3.6	0.69± 0.06 (0.54)
	21.6± 0.75 (19.87)	154.1± 0.99 (75.2)	0.72± 0.03 (0.51)
4-NO$_2$	8.3 ± 0.66 (19.5)	77.3± 1.1	0.65± 0.04 (0.49)
	15.7± 0.97 (15.4)		
		120.4± 2.2 (142.1)	0.54± 0.02 (0.39)
			0.66± 0.06 (0.51)
		108.4± 3.3	
	13.7± 1.3 (9.2)	(82.8)	
Y [b]	(12.18)	(99.8)	0.73± 0.04 (0.52)

[a] Data in parentheses were obtained at pH 8.67.

[b] Y = N,N –Dimethylamino 4, 4'- tricyanovinyl benzene.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

2

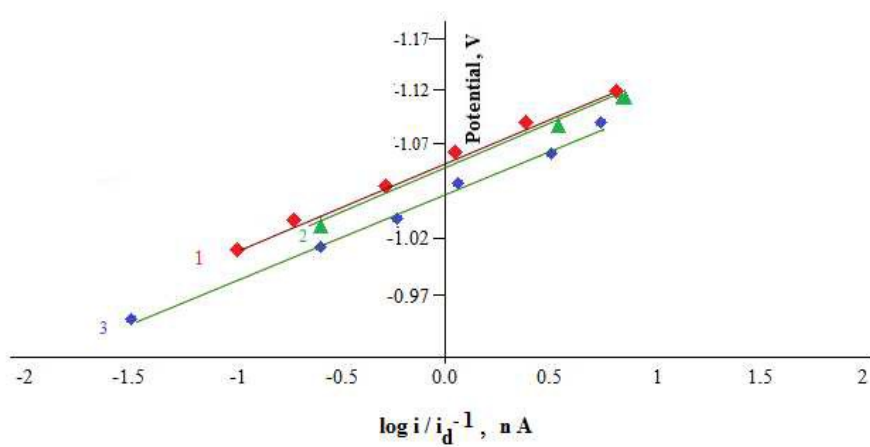**Fig.5**

Fig. 6
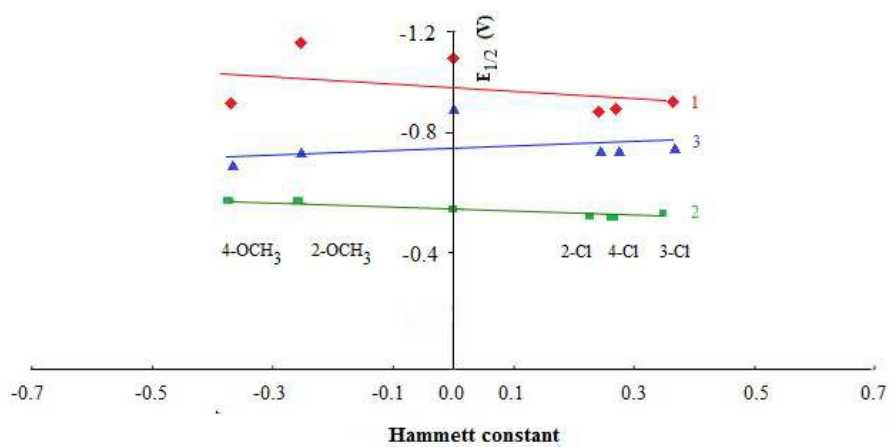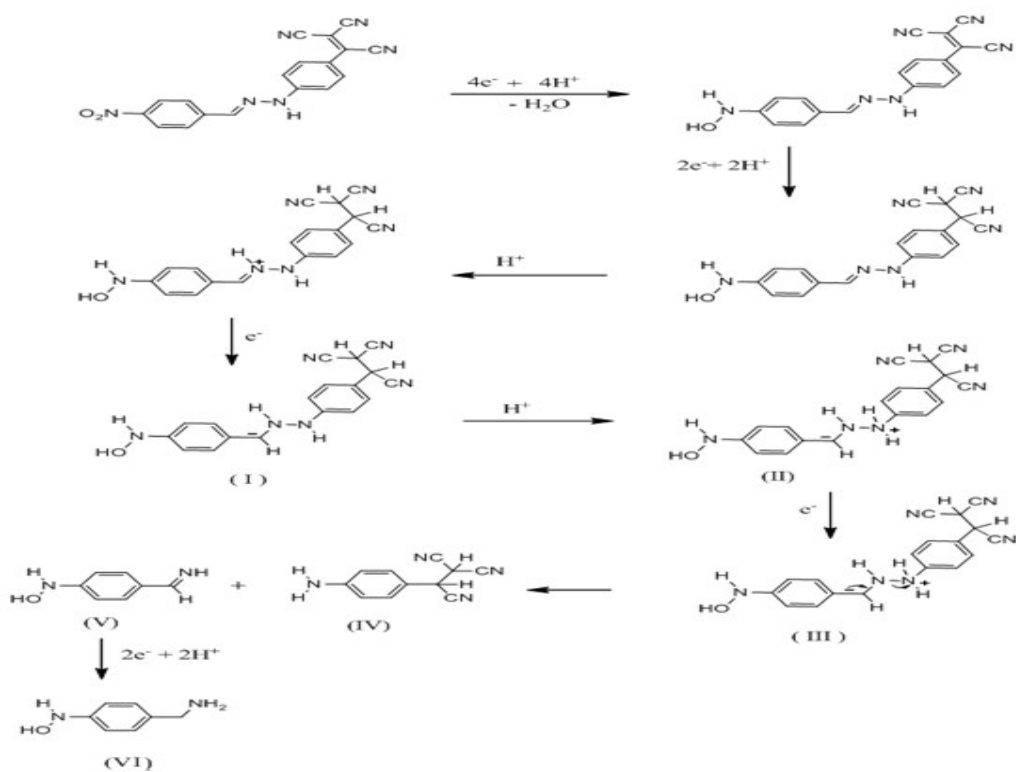
3
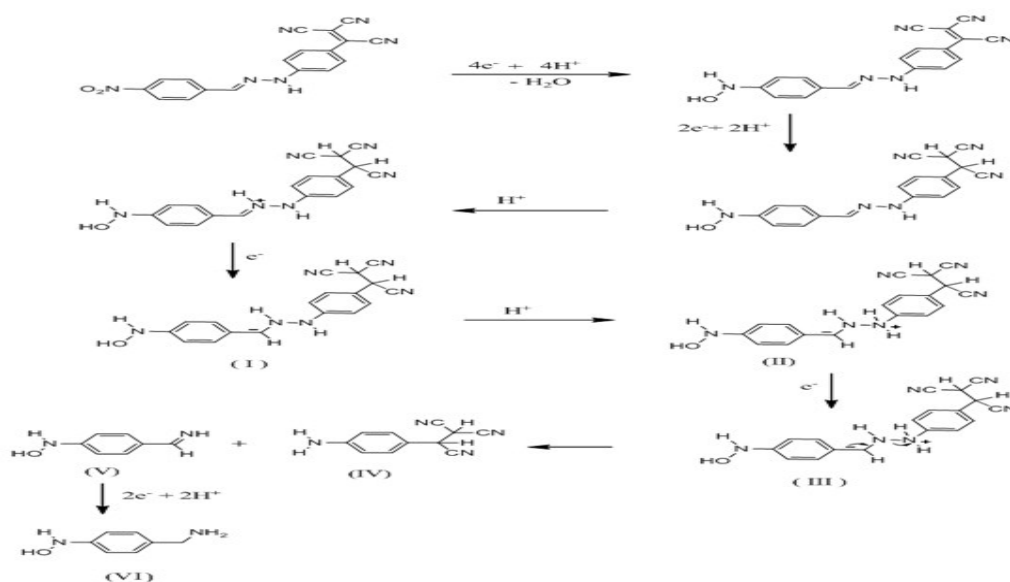
Fig. 7

Fig. 8

Fig. 9

Fig. 10

5

Scheme1. Proposed scheme for the electrochemical reduction of 4-nitrotricyanovinylhydrazone.

Graphical Abstract

The redox behavior of π-conjugated reactive 2-(4-(2-benzylidenehydrazinyl)phenyl)ethane-1,1,2

tricarbonitrile dye derivatives (Fig. 1) in DMF-Britton Robinson buffer-DMF at various pH were

studied. The most probable electrochemical reduction mechanism of 4'-nitrotricyanovinylhydra-

zone to the corresponding (4-hydroxyamino)phenyl)- methamine ($C_7H_{10}N_2O$) via $2H^+/2e^-$

reduction of the produced (E)-N-(1-(4-hydroxyamine)phenyl -ethylidene)methamine ($C_9H_{12}N_2O$)

is proposed.

Scheme1. Proposed scheme for the electrochemical reduction of 4-

nitrotricyanovinylhydrazone.

Fig. 1