

Electrochemical Oxidation of p-Phenylenediamine in Aqueous Media: A pH-Dependent Study and Synthesis of a new trimer of p-Phenylenediamine

hadi beiginejad

h.beiginejad@malayeru.ac.ir

malayer university <https://orcid.org/0000-0002-9440-2830>

Fahimeh Varmaghani

Institute for Advanced Studies in Basic Sciences

Zeinab Godini

University of Malayer

Mohammad Moradi

University of Malayer

Research Article

Keywords: p-phenylenediamine, Electrochemical oxidation, p-quinonediimine, Cyclic voltammetry, Controlled-potential coulometry

Posted Date: July 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10288039/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Monatshefte für Chemie - Chemical Monthly on September 17th, 2026. See the published version at <https://doi.org/10.1007/s00706-026-03523-9>.

Electrochemical Oxidation of *p*-Phenylenediamine in Aqueous Media: A pH-Dependent Study and Synthesis of a new trimer of *p*-Phenylenediamine

Hadi Beiginejad • Fahimeh Varmaghani • Zeinab Godini • Mohammad Moradi

Received:/Accepted ...

Abstract The electrochemical oxidation of *p*-phenylenediamine (PPDA) was investigated in aqueous media over a wide pH range using cyclic voltammetry, controlled-potential coulometry, conductometric titration, and spectroscopic techniques. The results demonstrate that PPDA undergoes a two-electron, two-proton oxidation to form *p*-quinonediimine as the primary electroactive intermediate. The subsequent chemical behavior of this intermediate is strongly dependent on the solution pH. It is hydrolyzed in acidic media (pH lower than 4.0) and converted to *p*-benzoquinone via two successive hydrolysis reactions. At intermediate and weakly alkaline pHs, *p*-benzoquinonediimine is trimerized via two successive Michael addition reactions. Moreover, the protonation of *p*-phenylenediamine and the produced *p*-quinonediimine at various pHs was studied using conductometry. This work also provides a facile and one-pot electrochemical method for synthesizing a novel trimer of *p*-phenylenediamine via the

1 electrochemical oxidation of PPDA under green conditions using a carbon
2 electrode.

3 **Keywords** *p*-phenylenediamine, Electrochemical oxidation, *p*-
4 quinonediimine, Cyclic voltammetry, Controlled-potential coulometry.

5
6 Hadi Beiginejad (✉)

7 Department of Applied Chemistry, Faculty of science, Malayer University,
8 65174, Malayer, Iran. e-mail: h.beiginejad@malayeru.ac.ir
9

10 Zeinab Godini

11 Department of Applied Chemistry, Faculty of science, Malayer University,
12 65174, Malayer, Iran

13 Mohammad Moradi

14 Department of Applied Chemistry, Faculty of science, Malayer University,
15 65174, Malayer, Iran

16 Fahimeh Varmaghani

17 Department of Chemistry, Institute for Advanced Studies in Basic Sciences
18 (IASBS), Zanjan 45137-66731, Iran.
19
20
21

1 **Introduction**

2 The electrochemical oxidation of amines has been studied by many
3 researchers, and various products have been reported [1-5]. Published results
4 showed that the electrochemical oxidation of aromatic amines is complex,
5 and the products vary greatly depending on their structure and electrolysis
6 conditions, using aqueous or non-aqueous, and neutral, acidic, or basic
7 conditions [6-8]. Because the conversion of $>\text{C}=\text{N}$ to $>\text{C}=\text{O}$ and vice versa
8 is important in biochemical processes, various researchers have studied the
9 hydrolysis of amines and formation of Schiff bases [9, 10]. The hydrolysis
10 of benzoquinoneimines resulting from the oxidation of amines occurs mainly
11 in acidic solutions, and the hydrolysis rate varies depending on the structure
12 of the species and the pH of the solution [11, 12]. The hydrolysis rate of
13 some amines increases with increasing pH whereas that of others decreases
14 under the same conditions [13]. Owing to the behavioral diversity of para-
15 phenylenediamine (PPDA), various studies have been conducted on its
16 electrochemical oxidation [14-17]. Although various research groups have
17 published their research results on the electrochemical oxidation of PPDA,
18 there are few reports have been published on the product obtained from its
19 electrochemical oxidation. In this study, the electrochemical oxidation of
20 PPDA was investigated using cyclic voltammetry (CV) and controlled
21 potential coulometry methods. Conductometry titration and the potential-pH

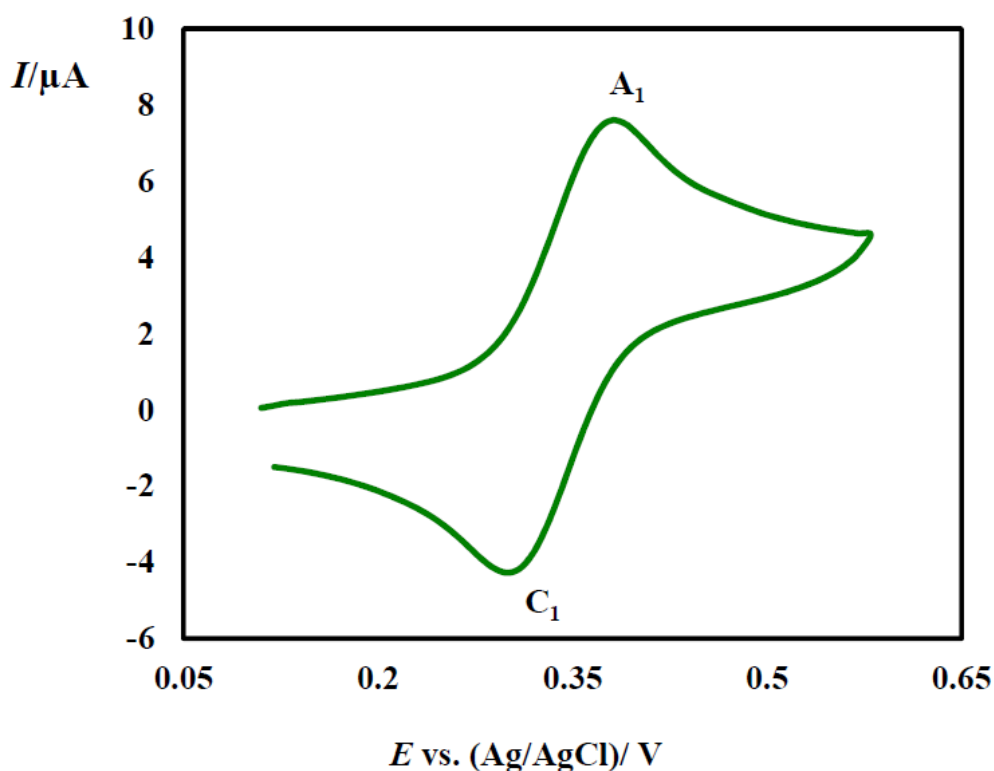
1 diagram of PPDA, were used to study the properties and chemical stability
2 of various kinds of PPDA and p-quinonediimine. Our results show that the
3 hydrolysis rate is high at acidic pH, but it decreases with increasing pH, and
4 the trimerization reaction dominates at intermediate pH. This work also
5 provides a facile and one-pot electrochemical method for synthesizing a
6 novel p-Phenylenediamine derivative via the electrochemical oxidation of
7 PPDA under green conditions, without toxic reagents and solvents using a
8 carbon electrode in a divided cell.

9 10 **Results and Discussion**

11 *Potential-pH study*

12 Figure 1 presents the cyclic voltammogram of 1.0 mM *p*-
13 phenylenediamine (PPDA) recorded in an aqueous acetate buffer solution
14 (0.2 M, pH 4.1). The voltammogram exhibits an anodic peak (A_1) during the
15 forward scan and a corresponding cathodic peak (C_1) on the reverse scan,
16 which are attributed to the interconversion of PPDA ($1H^+$) and *p*-
17 quinonediimine ($1Hox^+$). This redox transformation proceeds through a
18 quasi-reversible two-electron process [18]. Under these experimental
19 conditions, the ratio of the cathodic to anodic peak currents (I_{pC1}/I_{pA1}) is
20 approximately unity, indicating that the electrochemically generated species,

- 1 **1Hox⁺**, remains sufficiently stable on the voltammetric time scale and does
- 2 not undergo significant side reactions during the experiment.



3
 4 Figure 1. Cyclic voltammogram of 1.0 mM PPDA (**1H⁺**) at a glassy carbon
 5 electrode in acetate buffer solution ($c = 0.2 \text{ M}$, $\text{pH} = 4.1$). Scan rate: 25 mV/s ,
 6 $t = 25^\circ\text{C}$.

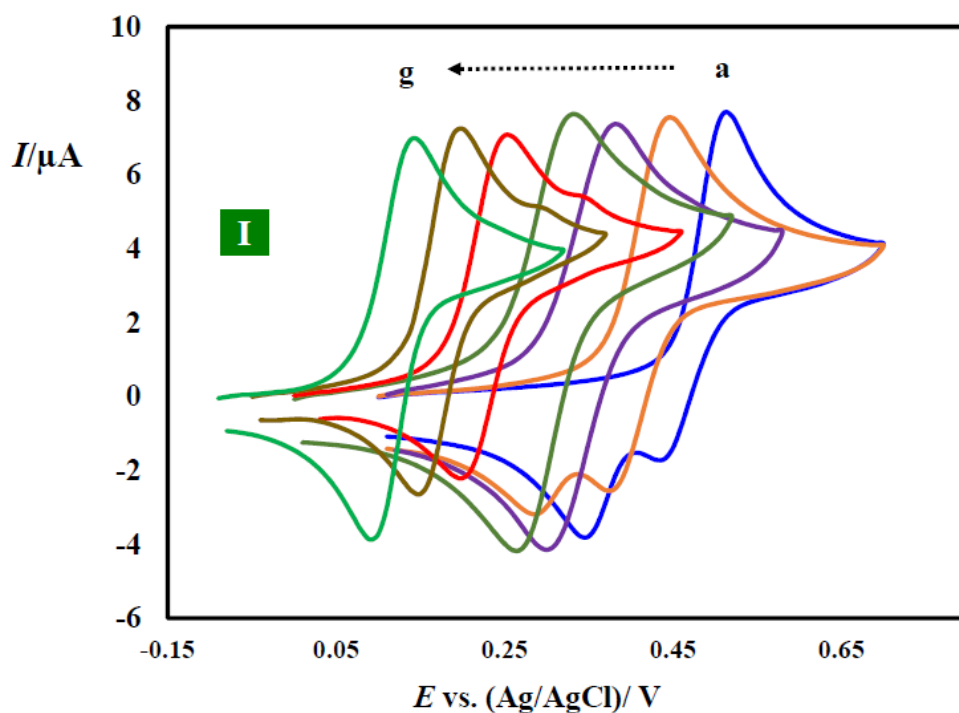
7
 8 Figure 2-I displays the cyclic voltammograms of PPDA (**1**) recorded at
 9 different pH values. Since protons participate in the electrochemical
 10 oxidation of PPDA to its corresponding *p*-quinonediimine species [19],
 11 increasing the pH causes the anodic peak potential (E_{pA1}) to shift toward

more negative values. The dependence of the anodic peak potential on pH can be expressed by the following equation:

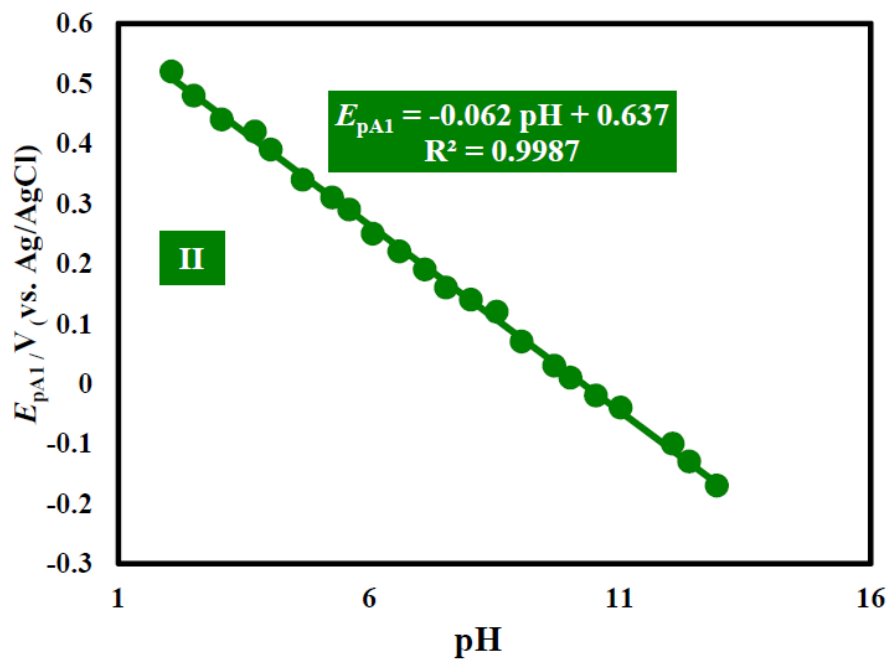
$$E_{pA1} = E_{p0} - 2.303(mRT/2F) \text{ pH}$$

Where m is the number of protons involved in the electrode reaction, E_{p0} is the anodic peak potential at pH 0.0, R is the universal gas constant, T is the absolute temperature, and F is the Faraday constant.

The E -pH plot was constructed by plotting the values of E_{pA1} against pH (Figure 2-II). As shown, E_{pA1} shifts linearly toward more negative potentials with a slope of approximately 62 mV per pH unit. This value is in close agreement with the theoretical slope of 59 mV pH^{-1} for a reaction involving two protons ($m = 2$). Based on this result, it can be concluded that the electrode process proceeds via a two-electron/two-proton mechanism throughout the investigated pH range (Scheme 1).



1



2

3 Figure 2. (I) CVs of 1.0 mM PPDA in buffer solution with various pH values

4 at a glassy carbon electrode. pHs from (a) to (g) are 2.0, 3.0, 4.0, 5.0 , 6.0,

7.0 and 8.0. Scan rate 25 mV s⁻¹, t=25 °C. (II) Potential-pH diagram of PPDA.

Figure 3 presents the cyclic voltammograms obtained at different pH values. The results clearly demonstrate that the electrochemical response is strongly pH-dependent. At pH 3.5 (CV-a), the cathodic-to-anodic peak current ratio (I_{pC1}/I_{pA1}) is smaller than unity, and an additional cathodic peak (C_0) appears at potentials more negative than C_1 . The presence of the additional cathodic peak C_0 indicates that the electrogenerated *p*-quinonediimine is unstable and undergoes a subsequent chemical following reaction, and peak C_0 can be attributed to the electroactive product generated through this follow-up reaction. However, upon increasing the pH by 0.6 unit, peak C_0 disappears and the cathodic-to-anodic peak current ratio (I_{pC1}/I_{pA1}) approaches unity (CV-b). In other words, under these conditions, the rate of the subsequent side reaction decreased, and the stability of the *p*-quinonediimine species increased.

At pH values higher than 5, the electrogenerated *p*-quinonediimine again becomes less stable and undergoes a subsequent chemical reaction. As shown in CV-c (pH 7.0), an additional anodic peak (A_2) appears at potentials more positive than A_1 . Furthermore, the ratio of cathodic to anodic peak currents (I_{pC1}/I_{pA1}) is lower than unity, indicating that the electrogenerated *p*-

1 quinonediimine is unstable on the timescale of the voltammetric experiment
 2 and participates in a follow-up chemical reaction, leading to the appearance
 3 of the anodic peak A_2 . Interestingly, further increases in pH suppress the
 4 follow-up chemical reaction and thereby enhance the stability of the
 5 electrogenerated *p*-quinonediimine species. CV-*d* of this figure, recorded at
 6 pH 8.3, illustrates this behavior. Under these conditions, the ratio of cathodic
 7 to anodic peak currents (I_{pC1}/I_{pA1}) is approximately unity, indicating that the
 8 electrogenerated *p*-quinonediimine remains stable on the voltammetric
 9 timescale and does not undergo significant follow-up reactions.

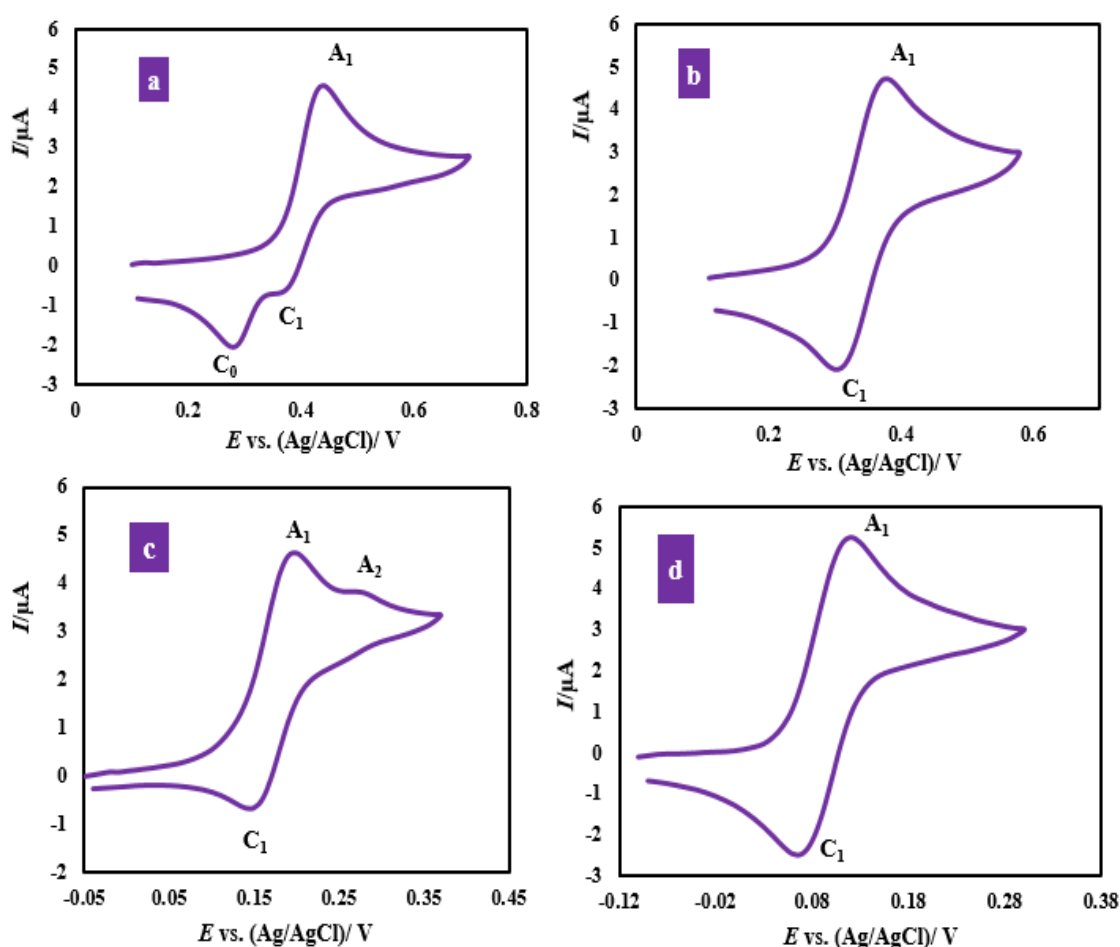


Figure 3. CVs of 1.0 mM PPDA in buffer solution with various pH values at a glassy carbon electrode. pHs: (a) = 3.5, (b) = 4.1, (c) = 7.0 and (d) = 8.3. Scan rate 10 mV s⁻¹, t=25 °C.

Amines behave as Brønsted bases in aqueous solutions and are converted into ammonium ions by accepting protons from water molecules. As the pH increases, the protonation equilibrium shifts toward the neutral amine form, and the ammonium ions gradually undergo deprotonation. Consequently, the conductivity of the solution changes. Therefore, monitoring conductivity as a function of pH can be employed to investigate the acid–base behavior of amines and to determine their pK_a values [20].

For this purpose, a 200 mL solution containing 0.006 M HCl and 0.0025 M PPDA (**1**) was titrated with 0.1 M sodium hydroxide, and a conductivity vs. titrant volume plot was constructed. The resulting curve consists of three linear regions with different slopes. Initially, HCl, being the stronger acid, reacts with NaOH, resulting in a decrease in conductivity and hence a negative slope in the conductivity plot. Subsequently, the ammonium ion, which is a weak acid, reacts with NaOH. Since the conductivities of ammonium and sodium ions are relatively similar, the conductivity increases only slightly, giving rise to a region with a small positive slope. Finally, as the concentration of NaOH increases beyond the equivalence point, the

conductivity of the solution increases due to the presence of excess hydroxide ions in the medium (Figure 4). The pH of the solution was measured simultaneously using a pH meter, and a value of 7.91 was obtained at the equivalence point. Accordingly, PPDA is predominantly present in its unprotonated form at pH values higher than 7.91, while protonated species predominate at pH values lower than 7.91.

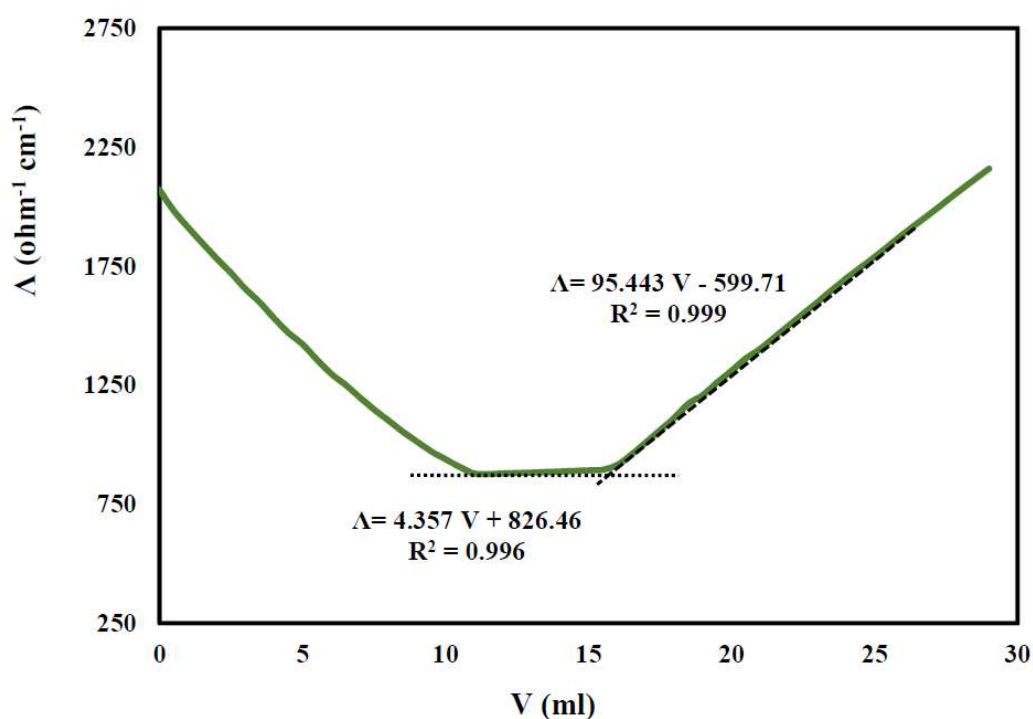
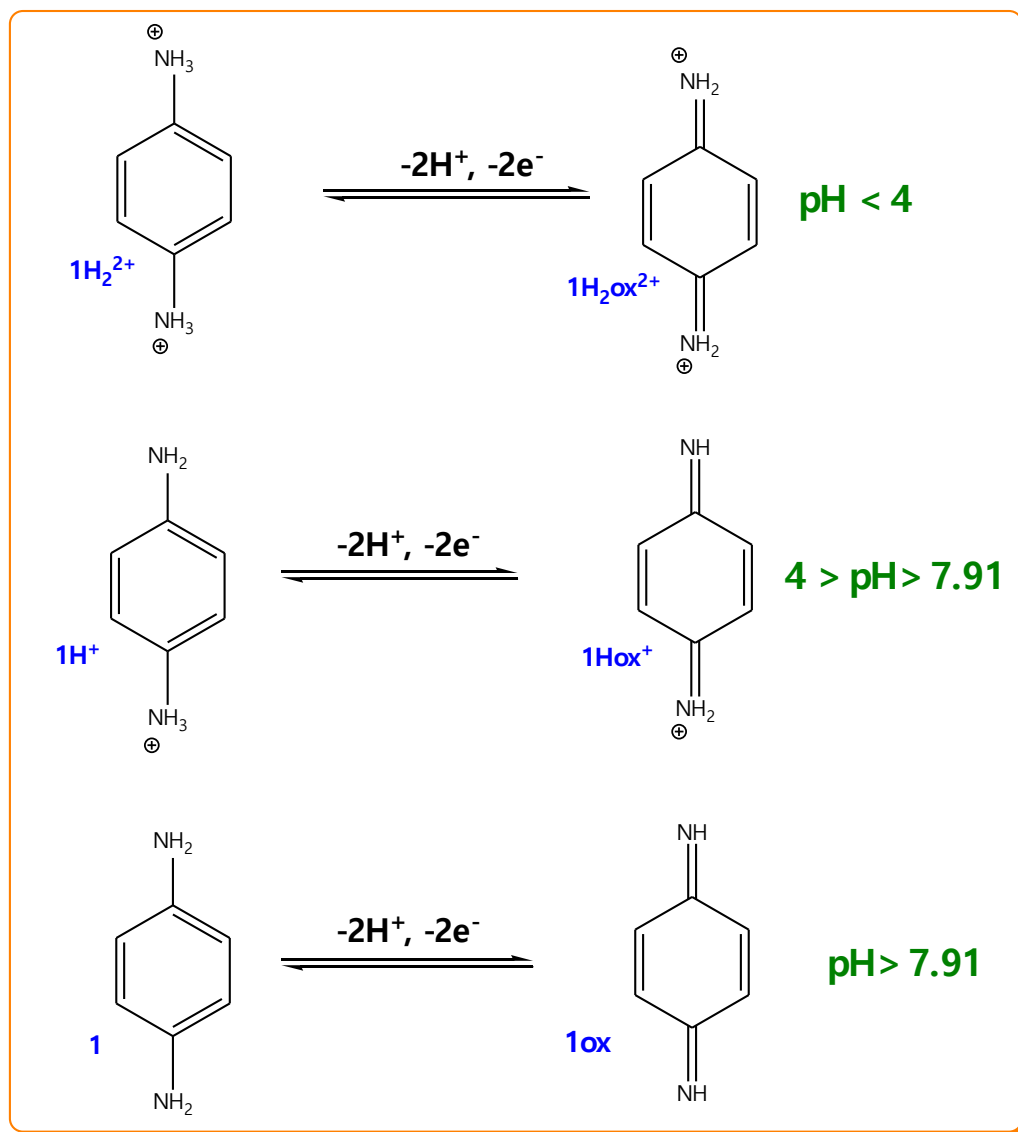


Figure 4. Conductimetry titration 200 ml aqueous solution containing 0.006 M of HCl and 0.0025 M PPDA with sodium hydroxide 0.1 M.



<Scheme 1>

Although conductometric measurements indicated that PPDA (**1**) remains protonated at pH values below 7.91, the compound exhibits two distinct electrochemical behaviors below pH 4.0 (Fig.3- CV-*a*) and above this value (Fig.3- CV-*b*). Moreover, the invariance of the slope of the potential–pH plot (Figure 2-II) suggests that the proton-to-electron ratio in

the redox process remains constant over the entire pH range studied. Therefore, it appears that PPDA (**1**) exists in a diprotonated form (**1H²⁺**) at pH values below 4.0, whereas at pH values 4.0-7.9 it is predominantly present in a monoprotated (**1H⁺**) form. Also, the electrogenerated *p*-quinonediimine is diprotonated form (**1H₂ox²⁺**) at pH values below 4.0, and at pH values 4.0-7.9 it is predominantly present in a monoprotated (**1Hox⁺**) form (Scheme 1).

Electrochemical behavior of PPDA (1**) in acidic media (pH lower than 4)**

Figure 5 shows the first and second cyclic voltammograms of PPDA (**1H₂²⁺**) recorded in an aqueous phosphate buffer solution at pH 2.0. In CV-*a*, one anodic peak, A₁, at 0.49 V and two cathodic peaks, C₁ and C₀, at 0.42 V and 0.33 V versus the Ag/AgCl reference electrode, respectively, are observed. The anodic peak A₁ and the cathodic peak C₁ constitute a redox couple and correspond to the conversion of **1H₂²⁺** to *p*-quinonediimine (**1H₂ox²⁺**) and its subsequent reduction back to **1H₂²⁺** through a quasi-reversible two-electron process. The fact that the peak current ratio (I_{pC1}/I_{pA1}) is smaller than unity indicates that the electrogenerated *p*-quinonediimine species, **1H₂ox²⁺**, is unstable under the experimental conditions and

1 participates in a follow-up chemical reaction. The cathodic peak current, C_1 ,
2 exhibits a significant dependence on the scan rate and increases with
3 increasing scan rate. Furthermore, during the second potential cycle, a new
4 anodic peak (A_0) emerges at less positive potentials. The A_0/C_0 redox couple
5 is associated with a new electroactive species generated on the electrode
6 surface. On the basis of the previously published voltammetric and
7 coulometric studies [18, 21], it is proposed that PPDA ($1H_2^{2+}$) undergoes a
8 two-electron/two-proton oxidation to generate the corresponding *p*-
9 quinonediimine species, $1H_2ox^{2+}$. The resulting *p*-quinonediimine is
10 chemically unstable and is converted into *p*-benzoquinone (BQ) through two
11 successive hydrolysis steps, as depicted in scheme 2.

12 Therefore, peaks A_1/C_1 constitute the redox couple corresponding to the
13 PPDA ($1H_2^{2+}$)/*p*-quinonediimine ($1H_2ox^{2+}$) system, whereas peaks A_0/C_0
14 correspond to the hydroquinone (HQ)/*p*-benzoquinone (BQ) redox couple.

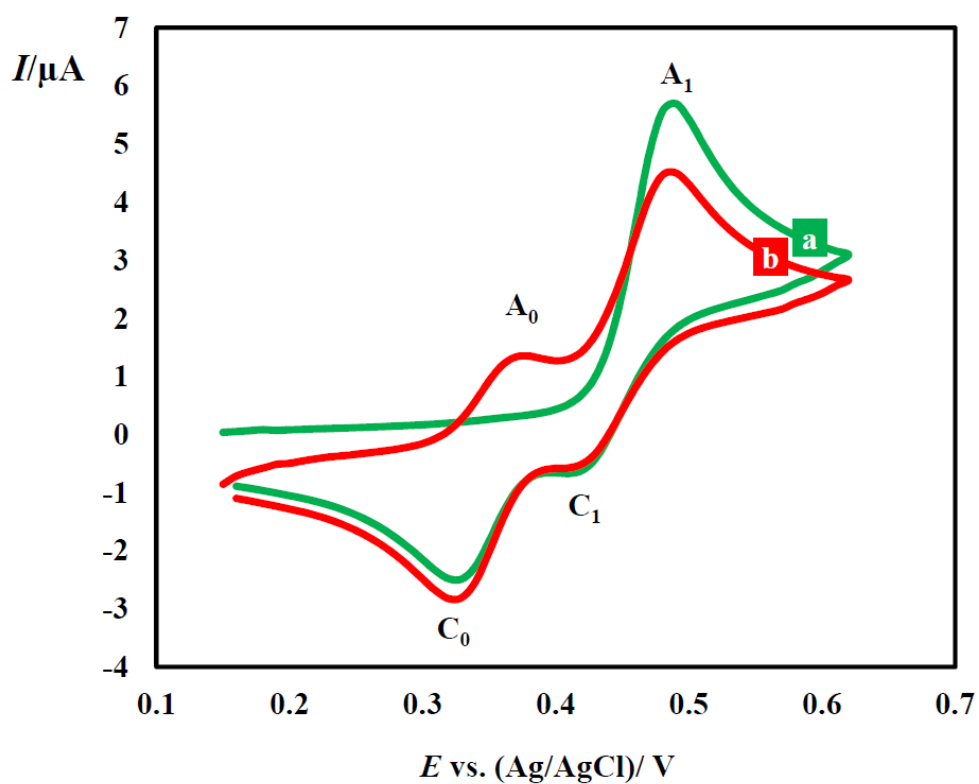
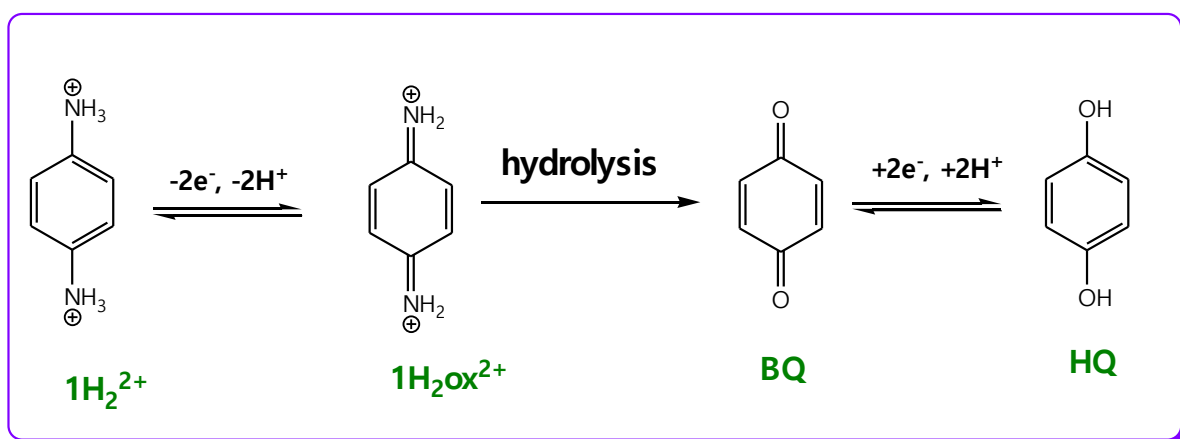


Figure 5. The first (a) and the second (b) CVs of 1.0 mM PPDA (1H_2^{2+}), scan rate: 25 mV s^{-1} , at a glassy carbon electrode, in phosphate buffer solution ($c = 0.2 \text{ M}$, $\text{pH} = 2.0$), $t=25^\circ\text{C}$.



<Scheme 2>

Electrochemical oxidation of PPDA in aqueous solutions at pH 4.0–7.9

Figure 7 shows the cyclic voltammogram of 1.0 mM PPDA recorded in an aqueous phosphate buffer solution (0.2 M, pH 6.0) at a scan rate of 100 mV s⁻¹. In this voltammogram, an anodic peak (A₁) is observed during the forward scan together with a corresponding cathodic peak (C₁) in the reverse scan. These peaks are attributed to the conversion of PPDA (**1H**⁺) to p-quinonediimine (**1Hox**⁺) and its subsequent reduction back to PPDA through a quasi-reversible two-electron process. The peak current ratio (I_{pC1}/I_{pA1}) is smaller than unity, indicating that the electrogenerated species **1Hox**⁺ is unstable under these conditions and undergoes a subsequent chemical reaction. The anodic peak A₂ corresponds to the oxidation of a product formed at the electrode surface.

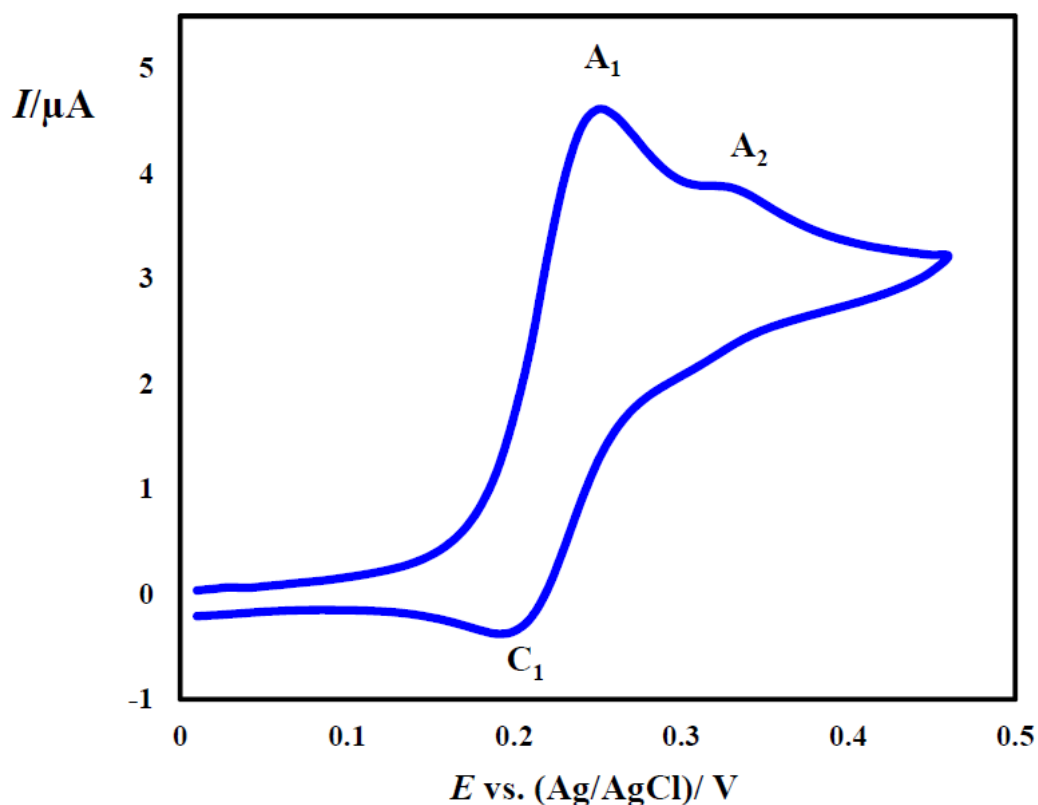
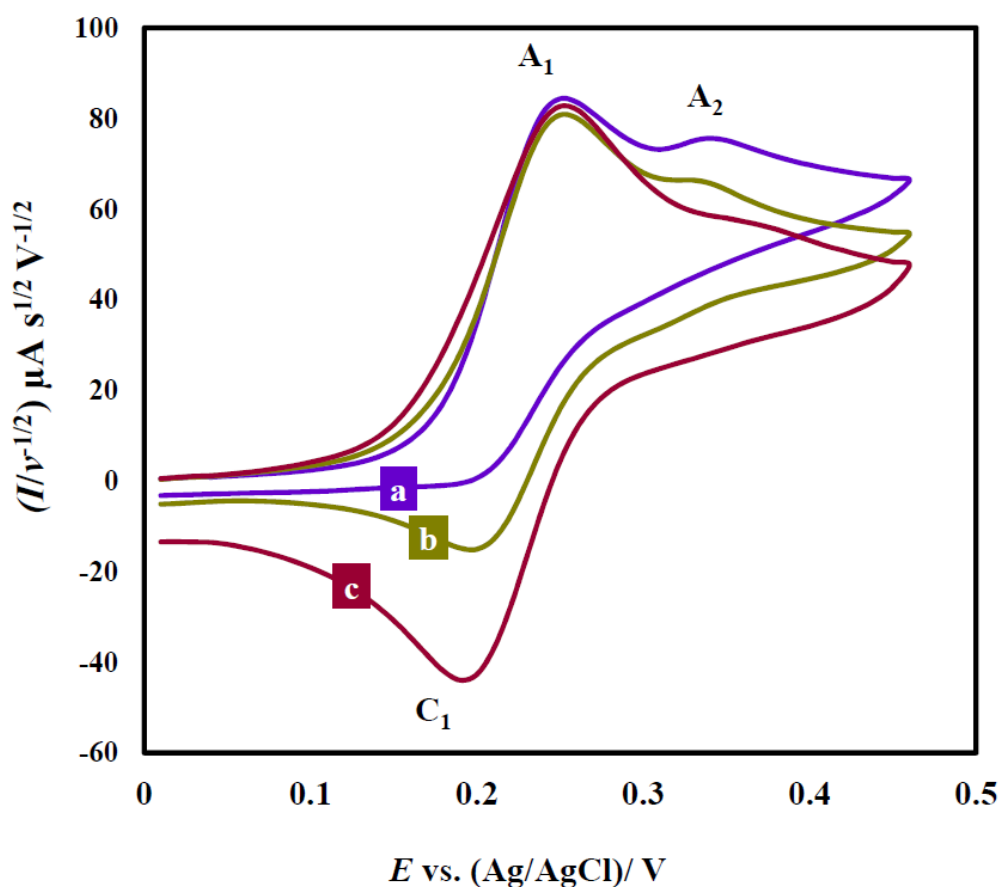


Figure 6. Cyclic voltammogram of 1.0 mM PPDA (1H^+) at a glassy carbon electrode in phosphate buffer solution ($c = 0.2 \text{ M}$, $\text{pH} = 6.0$). Scan rate: 10 mV/s, $t=25 \text{ }^\circ\text{C}$.

The effects of both the potential scan rate and the concentration of PPDA (1H^+) were investigated, and the results demonstrated that the peak current ratio ($I_{\text{pC1}}/I_{\text{pA1}}$) depends on both of these parameters. Figure 7 shows the normalized cyclic voltammograms of 1.0 mM PPDA (1H^+) in aqueous phosphate buffer (0.2 M, pH 6.0) recorded at various scan rates. The normalized CVs are obtained by dividing the current by the square root of

1 the scan rate ($I/v^{1/2}$). With decreasing scan rate, the peak current ratio
 2 (I_{pC1}/I_{pA1}) decreases, while a new anodic peak (A_2) emerges at more positive
 3 potentials. These results indicate that at lower scan rates, the
 4 electrogenerated species has a longer lifetime and therefore a greater
 5 opportunity to participate in subsequent chemical reactions, leading to the
 6 formation of a new product.



7
 8 Fig. 7. Normalized CVs 2.0 mM of PPDA ($1H^+$) at glassy carbon electrode
 9 in phosphate buffer solution ($c = 0.2M$, $pH = 6.0$), at various scan rates. Scan
 10 rates from (a) to (c) are 10, 25 and 100 $mV s^{-1}$.

11

1 The obtained voltammograms also revealed that increasing the concentration
2 of PPDA ($\mathbf{1H}^+$) has an effect similar to that of decreasing the potential scan
3 rate. Figure 8 illustrates the influence of PPDA ($\mathbf{1H}^+$) concentration on the
4 normalized cyclic voltammograms recorded at pH 6.0. These normalized
5 voltammograms were obtained by dividing the current by the concentration
6 (I/c). As shown in this figure, increasing the concentration of PPDA leads to
7 a decrease in the peak current ratio (I_{pC1}/I_{pA1}), while the ratio (I_{pA2}/I_{pA1})
8 increases. The dependence of the peak current ratio (I_{pC1}/I_{pA1}) on PPDA
9 concentration is indicative of a dimerization reaction occurring subsequent
10 to the electron-transfer process [22 p. 498]. Furthermore, the appearance of
11 the anodic peak A_2 indicates that the product formed at the electrode surface
12 is oxidized at a more positive potential than PPDA [23].

13

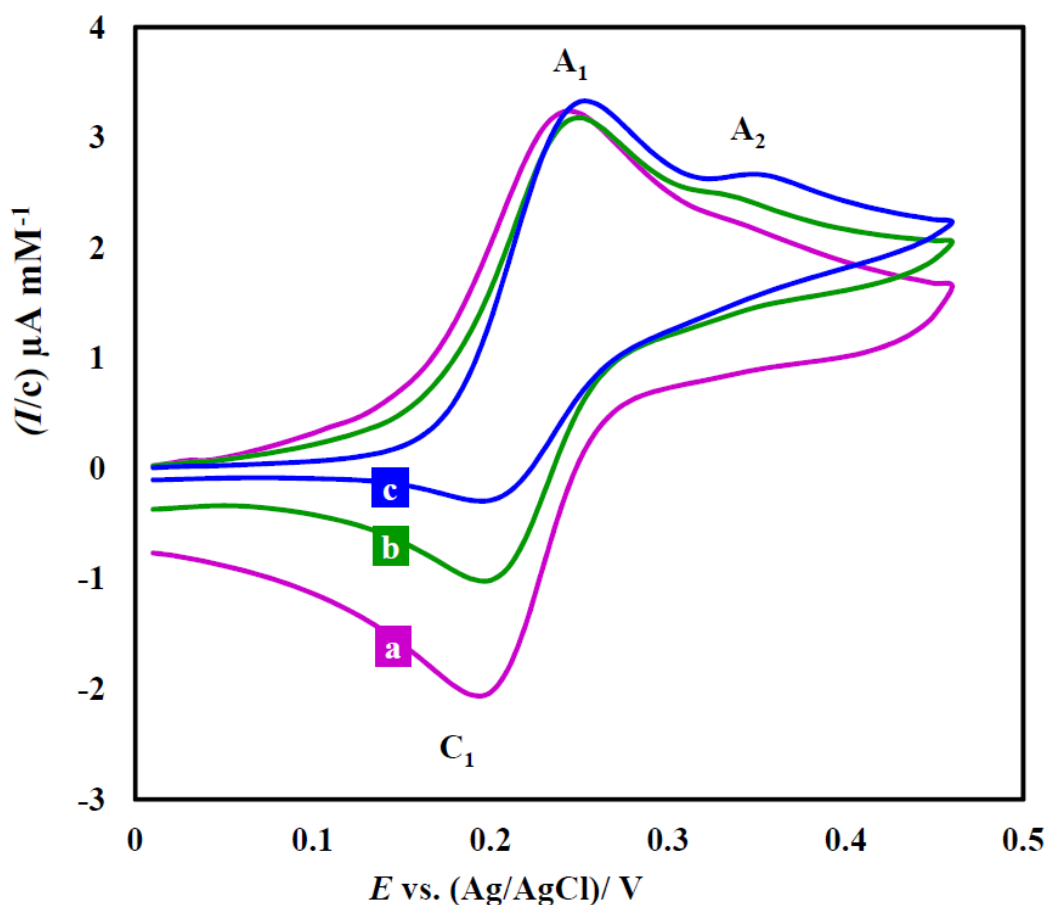
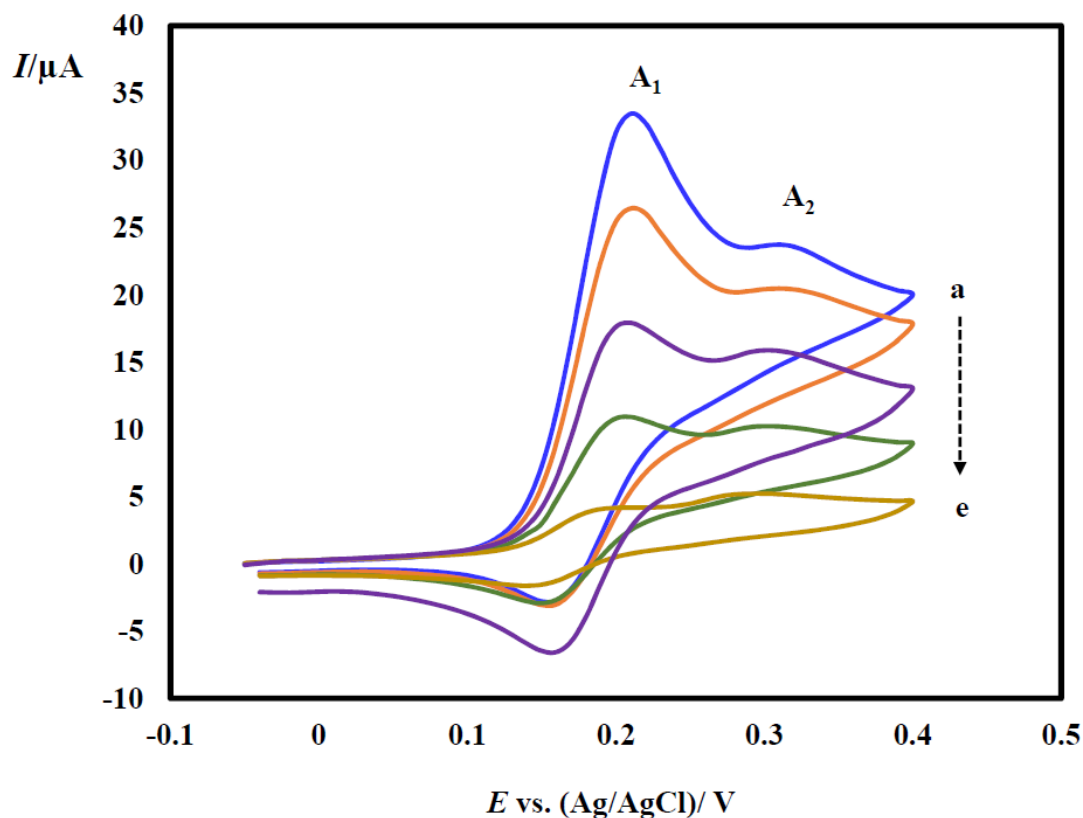


Figure 8. Normalized CVs of PPDA (1H⁺) at glassy carbon electrode, in phosphate buffer solution ($c = 0.2 \text{ M}$, pH 6.0) at various concentrations. (a) 0.5 mM, (b) 1.0 mM and (c) 2.0 mM. Scan rate = 10 mV s^{-1} , $t = 25 \pm 1^\circ\text{C}$.

Controlled-potential coulometry was carried out in an aqueous phosphate buffer solution (0.2 M , pH 6.5) containing 0.32 mmol of PPDA at a potential of 0.21 V versus Ag/AgCl. The progress of the electrolysis was monitored by cyclic voltammetry (Figure 9). The results showed that the anodic peak A₁ gradually decreased in intensity during electrolysis and disappeared completely when the charge consumed reached approximately 2 electrons

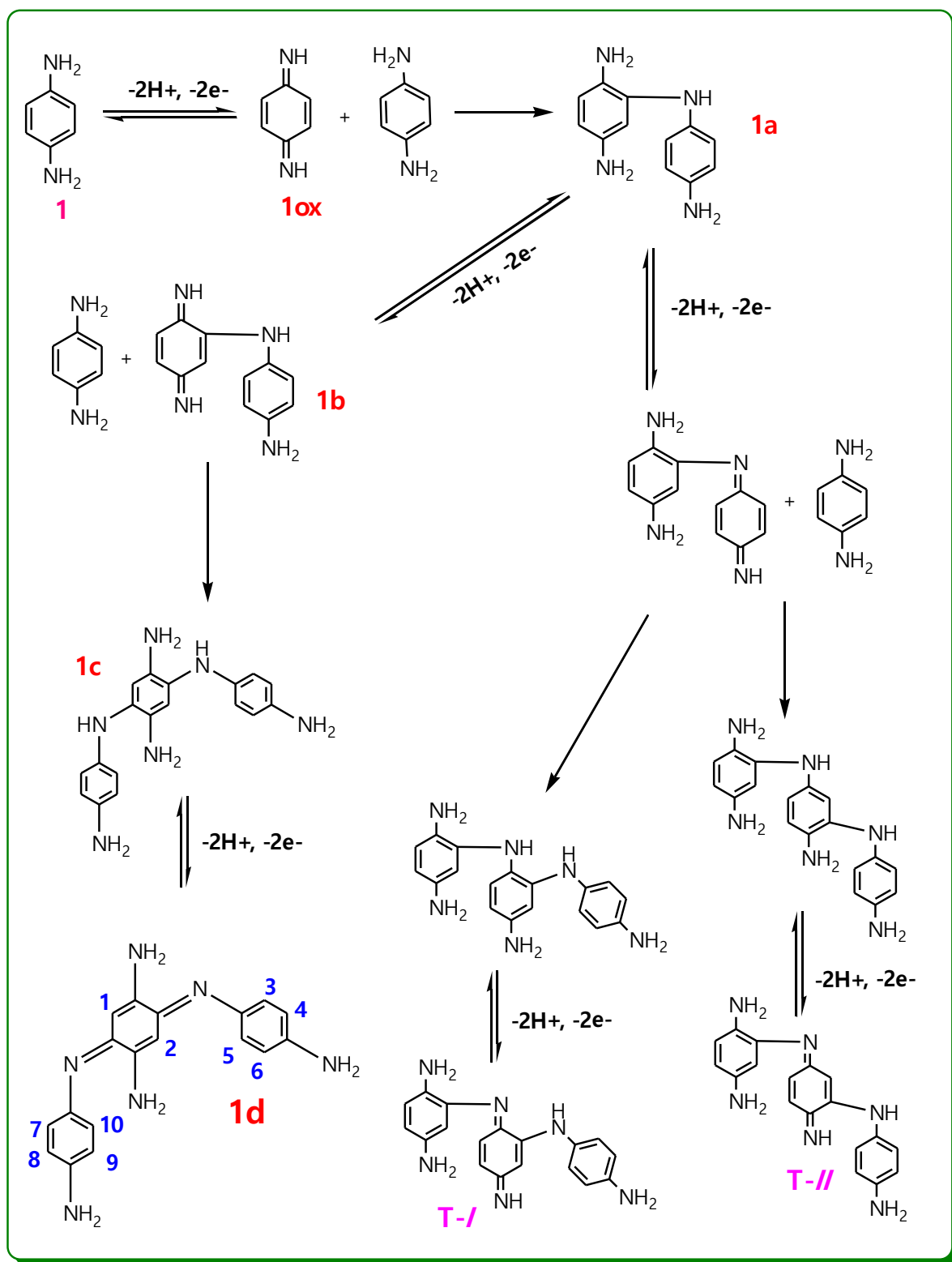
1 per PPDA molecule. The resulting product was extracted with ethyl acetate
 2 and characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy.



3
 4 Figure 9. CVs of 0.32 mmol PPDA (1H^+) during controlled potential
 5 coulometry at 0.21 V vs. Ag/AgCl in aqueous solution containing phosphate
 6 buffer (pH 6.5, $c = 0.2$ M), after the consumption of: (a) 0 C, (b) 15 C, (c) 30
 7 C, (d) 45 C and (d) 65 C. Scan rate: 50 mV s^{-1} , $t=25^\circ\text{C}$.

8
 9 On the basis of the voltammetric and coulometric findings, as well as the
 10 spectroscopic characterization of the isolated product, the reaction
 11 mechanism shown in scheme 3 is proposed for the electrochemical oxidation
 12 of PPDA at pH 6.0. Initially, *p*-quinonediimine **1ox** is generated through the

1 electrochemical oxidation of PPDA. Subsequently, a Michael-type addition
2 reaction takes place between PPDA and *p*-quinonediimine **1ox**, leading to
3 the formation of intermediate **1a**. Since the oxidation of **1a** is
4 thermodynamically more favorable than that of PPDA (**1**), **1a** is readily
5 oxidized under the applied potential to give intermediate **1b**. In the next step,
6 intermediate **1b** reacts with compound **1**, and the resulting adduct undergoes
7 aromatization to afford intermediate **1c**. Finally, **1c** is oxidized to form the
8 final product **1d**. Because the oxidation of **1d** requires a more positive
9 potential than the oxidation of PPDA (**1**), the final product **1d** is not further
10 oxidized under the experimental conditions. As illustrated in scheme 3, three
11 different trimeric products (**T-I**, **T-II**, and **1d**) could be formed. However,
12 the experimental ¹HNMR data for the aromatic protons revealed the presence
13 of a doublet integrating for eight protons and a singlet integrating for two
14 protons. The singlet signal was assigned to protons H₁ and H₂, whereas the
15 doublet was attributed to protons H₃–H₁₀ in trimer **1d**. These spectral features
16 are inconsistent with the proposed structures **T-I** and **T-II** and provide
17 evidence in support of structure **1d** as the isolated product.



<Scheme 3>

Electrochemical Oxidation of PPDA at pH > 8.0

The cyclic voltammogram of a 1.0 mM PPDA solution at pH 8.2 is shown in Figure 10. As can be seen, the cathodic-to-anodic peak current ratio (I_{pC1}/I_{pA1}) is approximately unity, indicating that the electrogenerated *p*-quinonediimine is stable under these conditions and does not undergo any significant follow-up chemical reaction on the voltammetric time scale. This behavior demonstrates that the rate of trimerization is pH-dependent. At pH values above 8.0, the trimerization reaction becomes sufficiently slow that it cannot be detected within the voltammetric time scale of the experiment.

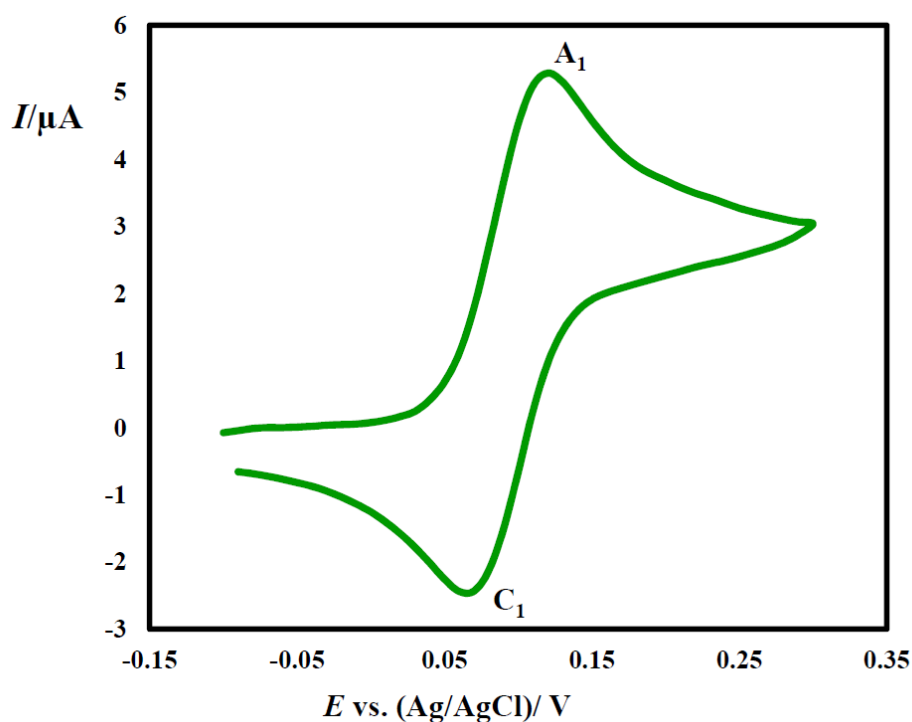
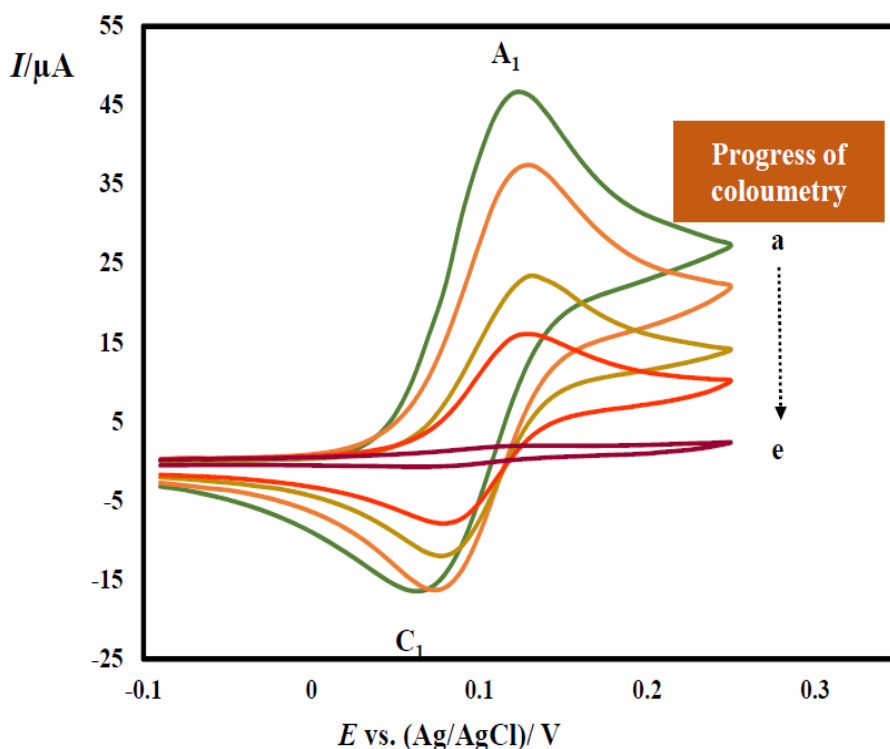


Figure 10. Cyclic voltammogram of 1.0 mM PPDA (**1**) at a glassy carbon electrode in phosphate buffer solution ($c = 0.2$ M, $\text{pH} = 8.3$). Scan rate: 10 mV/s, $t = 25$ °C.

1 To further investigate the electrochemical behavior, controlled-potential
 2 coulometry was performed in an aqueous phosphate buffer solution (0.2 M,
 3 pH 8.3) containing 0.52 mmol of PPDA at a potential of 0.12 V versus
 4 Ag/AgCl. The progress of electrolysis was monitored by cyclic
 5 voltammetry. The results showed that the anodic peak A_1 gradually
 6 decreased during electrolysis and disappeared completely when the
 7 consumed charge corresponded to approximately two electrons per PPDA
 8 molecule. The resulting product was extracted with ethyl acetate and
 9 analyzed by ^1H NMR spectroscopy. The obtained results were found to be
 10 consistent with those obtained for the electrolysis performed at pH 6.5.



11

Figure 11. CVs of 0.5 mmol PPDA (**1**) during controlled potential coulometry at 0.12 V vs. Ag/AgCl in aqueous solution containing phosphate buffer (pH 8.5, c = 0.2 M), after the consumption of: (a) 0 C, (b) 25 C, (c) 50 C, (d) 71 C and (d) 98 C. Scan rate: 50 mV s⁻¹, t=25 °C.

Conclusion

Electrochemical oxidation of para-diaminephenyl (PPDA) investigated in aqueous solutions with different pH values. The results of this study show that PPDA is oxidized to *p*-quinonediimine. In the next step, the produced *p*-quinonediimine participates in hydrolysis (scheme 2) and trimerization (Scheme 3) reactions based on the pH of the solution. Conductometry titration and the potential-pH diagram of PPDA were used to study the properties and chemical stability of various kinds of PPDA and *p*-quinonediimines. Under these conditions, *p*-quinonediimine produced via trimerization and electrochemical oxidation is converted to (E)-N1-((E)-2,5-diamino-4-(4-aminophenylimino)cyclohexa-2,5-dienylidene)benzene-1,4-diamine (**1d**).

Experimental

Apparatus and reagents

An Ivium potentiostat/galvanostat (model vertex) was used for the voltammetric study. A glassy carbon disc (1.8mm diameter) and a platinum wire were used as the working electrode and counter electrode, respectively, in the voltammetry experiments. The working electrode used in controlled-potential coulometry was an assembly of four carbon rods (28 cm²), and a large platinum gauze constituted the counter electrode. The working electrode's potential was measured versus standard Ag/AgCl (all electrodes from AZAR Electrode). Controlled-potential coulometry experiments were performed using coulometry BHP 2050 potentiostat/galvanostat (Iran) equipped with a digital coulometer. All chemicals were reagent-grade materials, from Aldrich and E. Merck. These chemicals were used without further purification. The phosphate buffer solution (H₃PO₄/NaH₂PO₄) was prepared by dissolving appropriate amounts of phosphoric acid (H₃PO₄). The pH was then adjusted to 2.0 using concentrated sodium hydroxide and the volume was completed to 0.5 L with deionized water (c = 0.2 M). The same procedure was used to prepare acetate (pH 4–5), H₃PO₄/ NaH₂PO₄ (pH 3) and NaH₂PO₄/Na₂HPO₄ (pH 6–8.5) buffers. All experiments were conducted at room temperature.

Synthetic procedures

An aqueous solution (120 mL) of phosphate buffer (0.2 M, pH 6.5), containing 0.5 mmol of diaminephenyl (**1**), was electrolyzed at 0.21 V vs. Ag/AgCl electrode in a divided cell. The electrolysis progress was monitored using cyclic voltammetry on the glassy carbon electrode. Electrolysis was performed for 5 h. The electrolysis was terminated when the monitoring current (measured on the glassy carbon electrode) decreased by >95%. At the end of the electrolysis, the pH of the solution was adjusted to 8.2 by adding 2 M aqueous NaOH and then extracted with ethyl acetate (2× 30 mL). The separated organic layer was dried over Na₂SO₄ and filtered. The crude product was collected after the evaporation of the solvent, and the product was characterized by spectroscopic techniques including FT-IR (Fourier Transform Infrared Spectroscopy), ¹H NMR and ¹³C NMR. The isolated yield of **1d** is 56%.

Characteristic of Product (1d). IR(KBr) 499.36, 554.87, 603.09, 831.91, 1147.23, 1168.05, 1237.46, 1279.75, 1360.88, 1430.49, 1503.11, 1513.83, 1566.46, 1605.79, 1703.55, 2926.19, 2975.67, 3034.50, 3215.76, 3336.72, 3418.68 cm⁻¹; ¹H NMR, d(300 MHz DMSO-d₆) 5.74 (s, 2H (H-1, H-2)), 6.06 (br, NH₂), 6.64 (d, 8H (H-3, H-10)). ¹³C NMR, d (75 MHz, acetone-d₆) 91.21, 114.89, 122.77, 140.54, 145.37, 148.79, 135.75.

1 **References**

2 13. Beiginejad H, Nematollahi D (2016) *Monatsh. Chem.* 147: 329.

3 **References**

4 [1] Gennaro A, Vianello E (1997) *Electrochim. Acta* 42: 2065.

5 [2] Kádár M, Nagy Z, Karancsi T, Farsang G (2001) *Electrochim. Acta* 46:
6 3405.

7 [3] LARGERON M (2009) *Electrochim. Acta* 54: 5109.

8 [4] Andrieux C P, Gallardo I, Junca M (1993) *J. Electroanal. Chem.* 354:
9 231.

10 [5] Otero L, Vettorazzi N, Barbero C, Miras M C, Silber J J, Sereno L (1993)
11 *J. Electroanal. Chem.* 350: 251.

12 [6] Varmaghani F, Nemati V (2022) *J. Electroanal. Chem.* 918: 116447.

13 [7] Beiginejad H, Nematollahi D (2013) *Electrochim. Acta* 114: 242.

14 [8] Esmaili R, Nematollahi D (2011) *Electrochim. Acta* 56: 3899.

15 [9] Ohmori H, Matsumoto A, Masui M, Sayo H (1977) *J. Electrochem. Soc.*
16 124: 1849.

17 [10] Thota A, Boga K, Arukula R, Narayan R, Rao C R K (2019) *Synth. Met.*
18 247: 240.

19 [11] Beiginejad H, Nematollahi D, Khazalpour S, (2016) *J. Electrochem.*
20 *Soc.* 163: H234.

- 1 [12] Beiginejad H, Nematollahi D, Khazalpour S (2015) J. Electrochem. Soc.
2 162: H877.
- 3 [13] Beiginejad H, Nematollahi D, Varmaghani F, Bayat M (2013) J.
4 Electrochem. Soc. 160: H469.
- 5 [14] Li X, He J, Xie B, He Y, Lai C, Wang W, Zeng J, Yao B, Zhao W, Long
6 T (2024) J. Electroanal. Chem. 955: 118052.
- 7 [15] Jamshidi M, Nematollahi D, Amiri Rudbari H (2016) J. Electrochem.
8 Soc. 163: G145.
- 9 [16] Ernst S, Baltruschat H, Hönes J, Lungu M (2009) Electrochim. Acta
10 54: 3129.
- 11 [17] Jamshidi M, Amani A, Khazalpour S, Torabi S, Nematollahi D (2021)
12 New J. Chem. 45: 18246.
- 13 [18] Fernandez-Merino A, del Caño R, Chávez M, Sánchez-Obrero G,
14 Madueño R, Blázquez M, Pineda T (2024) J. Electroanal. Chem. 969:
15 118547.
- 16 [19] Beiginejad H, Amani A, Nematollahi D, Khazalpour S (2015)
17 Electrochim. Acta 154: 235.
- 18 [20] Coelho L H G, Gutz I G R (2006) Talanta 69: 204.
- 19 [21] Amani A, Khazalpour S, Nematollahi D (2013) J. Electrochem. Soc.
20 160: H33.

[22] Bard A J (2001) Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, 2nd ed.; Wiley: New York.

[23] Beiginejad H, Nematollahi D, Bayat M, Varmaghani F, Nazaripou, A (2013) J. Electrochem. Soc. 160: H693.

Figure Captions:

Figure 1. Cyclic voltammogram of 1.0 mM PPDA ($\mathbf{1H}^+$) at a glassy carbon electrode in acetate buffer solution ($c = 0.2$ M, $\text{pH} = 4.1$). Scan rate: 25 mV/s, $t=25$ °C.

Figure 2. (I) CVs of 1.0 mM PPDA in buffer solution with various pH values at a glassy carbon electrode. pHs from (a) to (g) are 2.0, 3.0, 4.0, 5.0 , 6.0, 7.0 and 8.0. Scan rate 25 mV s⁻¹, $t=25$ °C. (II) Potential-pH diagram of PPDA.

Figure 3. CVs of 1.0 mM PPDA in buffer solution with various pH values at a glassy carbon electrode. pHs: (a) = 3.5, (b) = 4.1, (c) = 7.0 and (d) = 8.3. Scan rate 10 mV s⁻¹, $t=25$ °C.

Figure 4. Conductometry titration 200 ml aqueous solution containing 0.006 M of HCl and 0.0025 M PPDA with sodium hydroxide 0.1 M.

Figure 5. The first (a) and the second (b) CVs of 1.0 mM PPDA ($1H_2^{2+}$), scan rate: 25 mV s⁻¹, at a glassy carbon electrode, in phosphate buffer solution (c = 0.2 M, pH = 2.0), t=25 °C.

Figure 6. Cyclic voltammogram of 1.0 mM PPDA ($1H^+$) at a glassy carbon electrode in phosphate buffer solution (c = 0.2 M, pH = 6.0). Scan rate: 10 mV/s, t=25 °C.

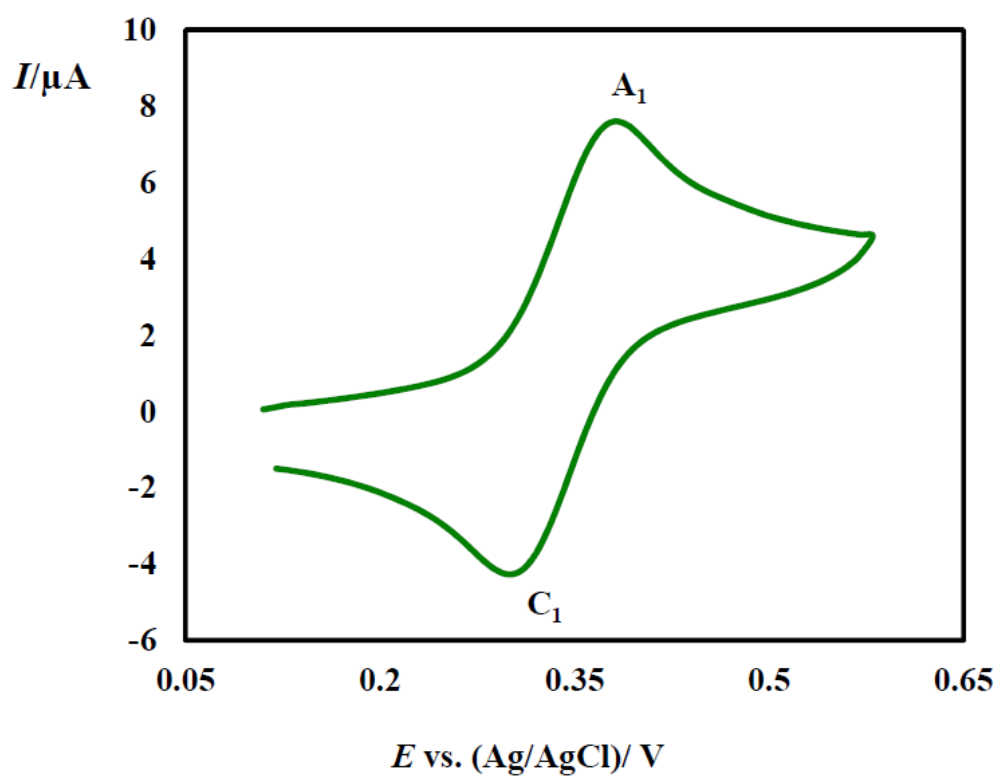
Fig. 7. Normalized CVs 2.0 mM of PPDA ($1H^+$) at glassy carbon electrode in phosphate buffer solution (c = 0.2M, pH = 6.0), at various scan rates. Scan rates from (a) to (c) are 10, 25 and 100 mV s⁻¹.

Figure 8. Normalized CVs of PPDA ($1H^+$) at glassy carbon electrode, in phosphate buffer solution (c = 0.2 M, pH 6.0) at various concentrations.(a) 0.5 mM, (b) 1.0 mM and (c) 2.0 mM. Scan rate = 10 mV s⁻¹, t = 25 ± 1°C.

Figure 9. CVs of 0.32 mmol PPDA ($1H^+$) during controlled potential coulometry at 0.21 V vs. Ag/AgCl in aqueous solution containing phosphate buffer (pH 6.5, c = 0.2 M), after the consumption of: (a) 0 C, (b) 15 C, (c) 30 C, (d) 45 C and (d) 65 C. Scan rate: 50 mV s⁻¹, t=25 °C.

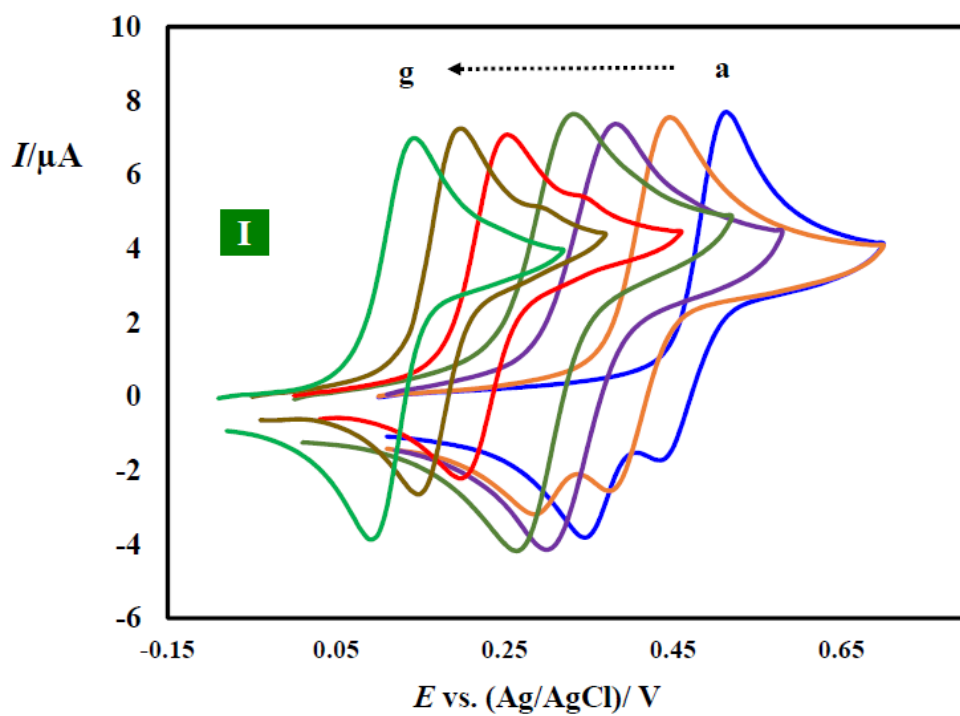
Figure 10. Cyclic voltammogram of 1.0 mM PPDA (**1**) at a glassy carbon electrode in phosphate buffer solution (c = 0.2 M, pH = 8.3). Scan rate: 10 mV/s, t=25 °C.

Figure 11. CVs of 0.5 mmol PPDA (**1**) during controlled potential coulometry at 0.12 V vs. Ag/AgCl in aqueous solution containing phosphate buffer (pH 8.5, c = 0.2 M), after the consumption of: (a) 0 C, (b) 25 C, (c) 50 C, (d) 71 C and (d) 98 C. Scan rate: 50 mV s⁻¹, t=25 °C.

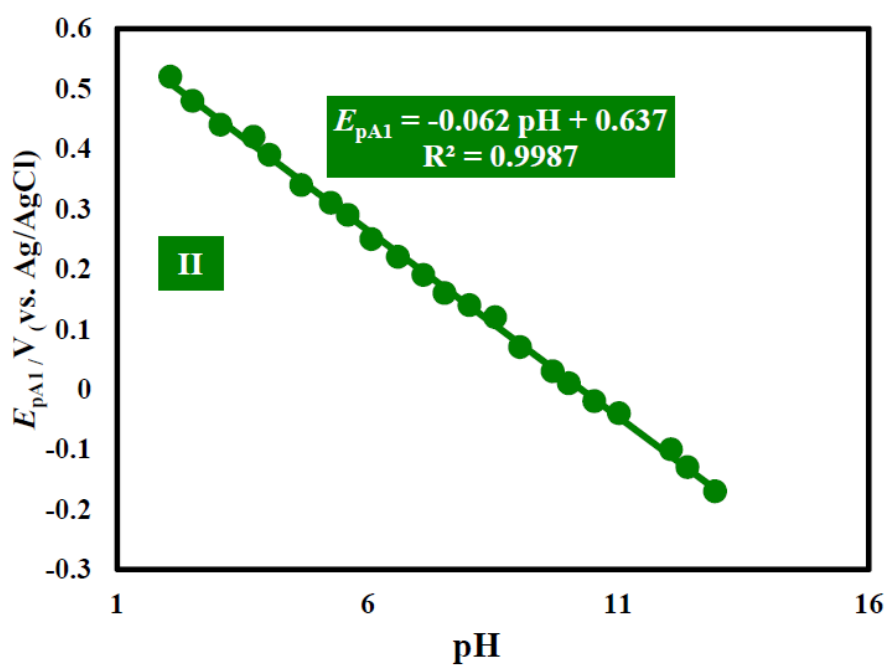


<Figure 1>

1
2
3
4
5
6
7



1



2

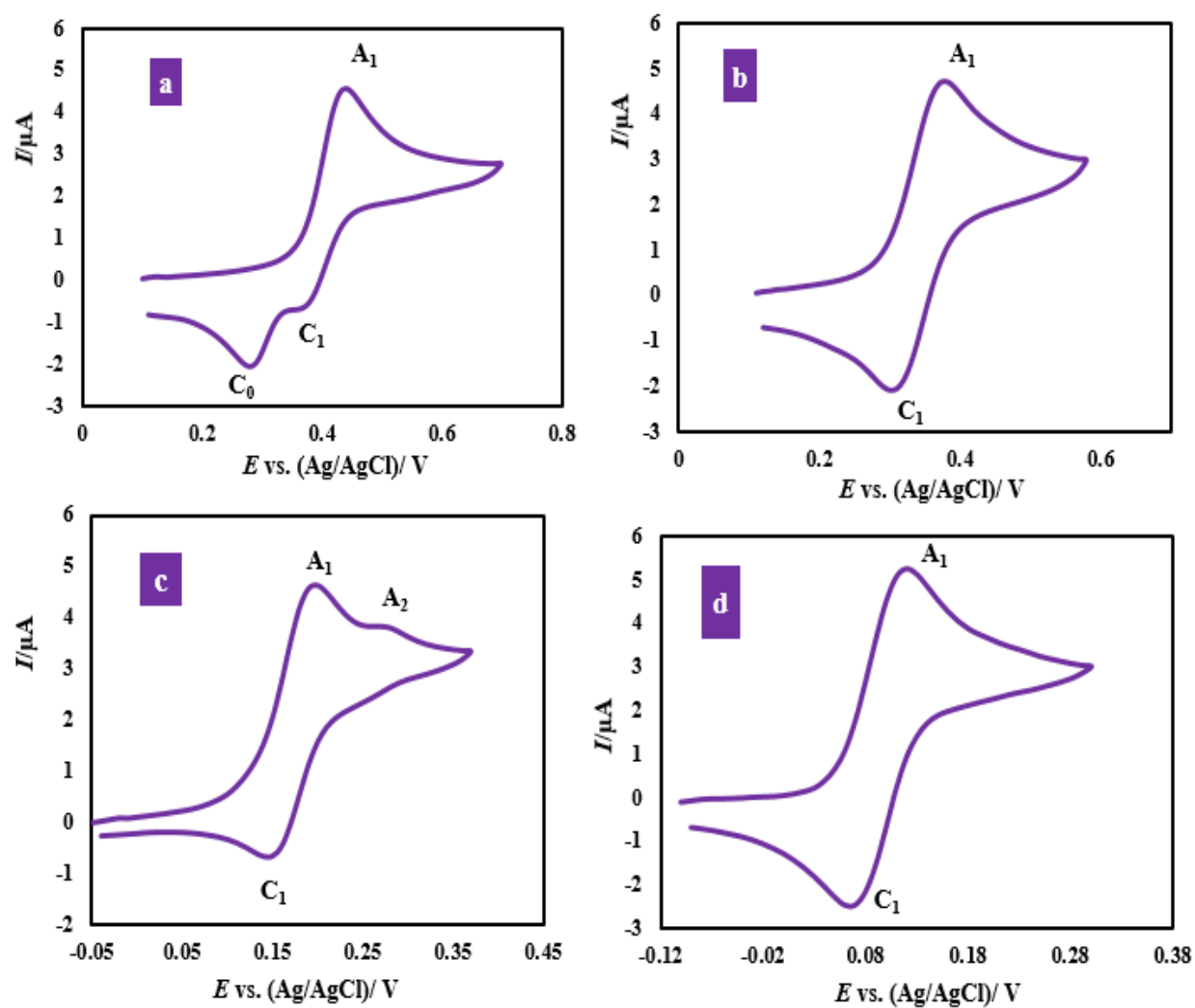
3

4

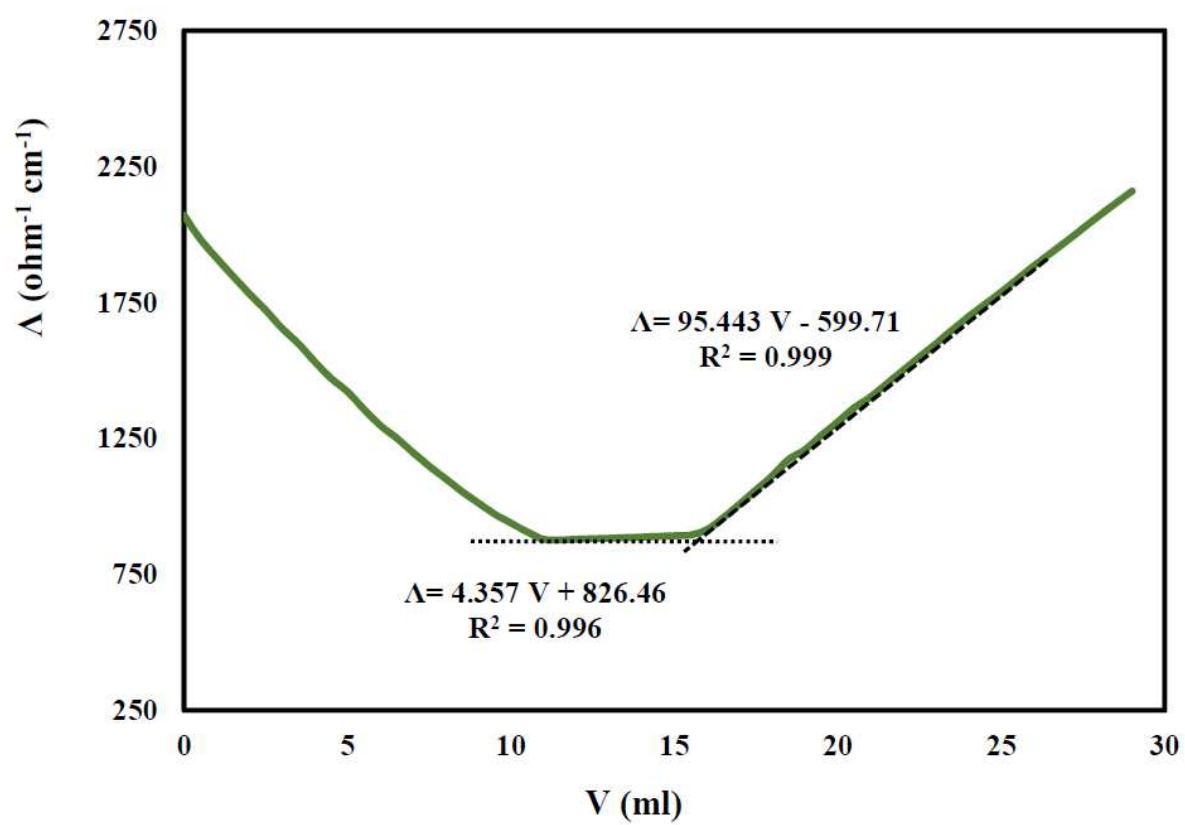
5

6

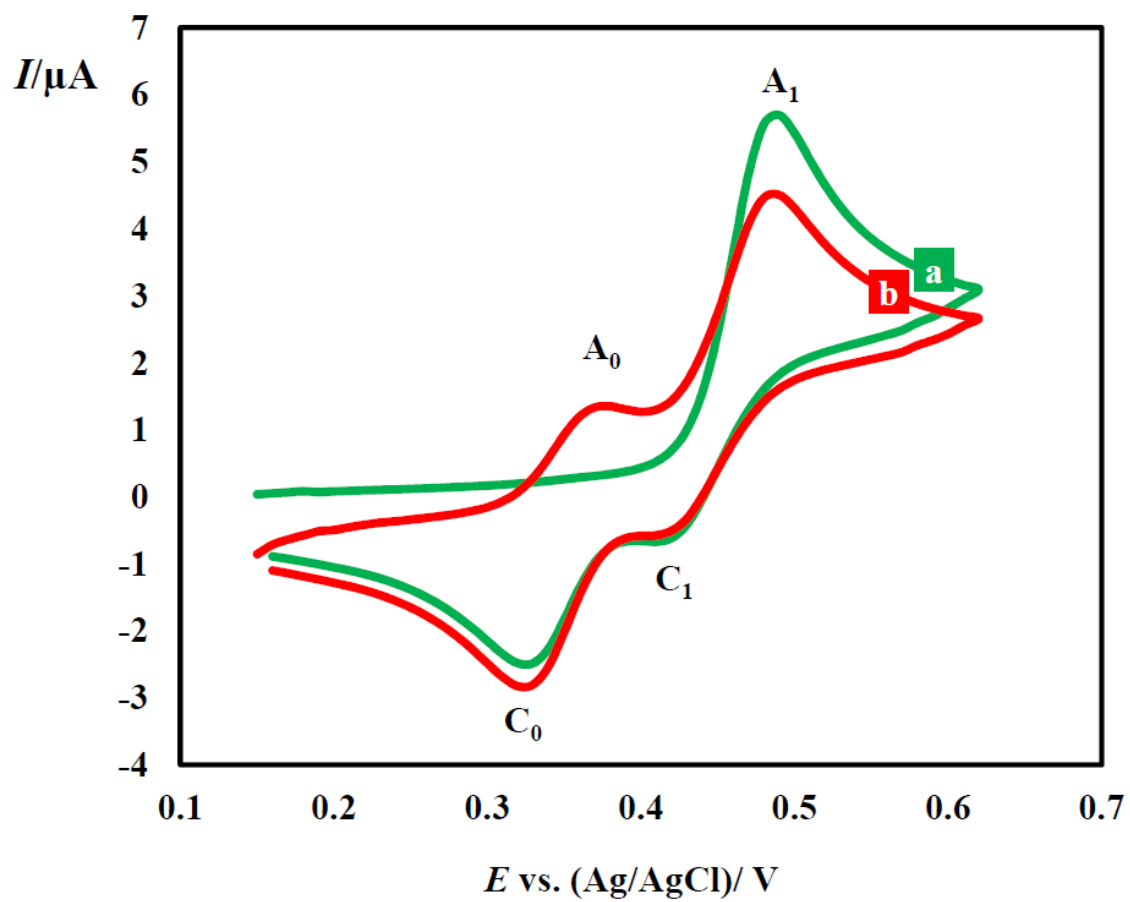
<Figure 2>



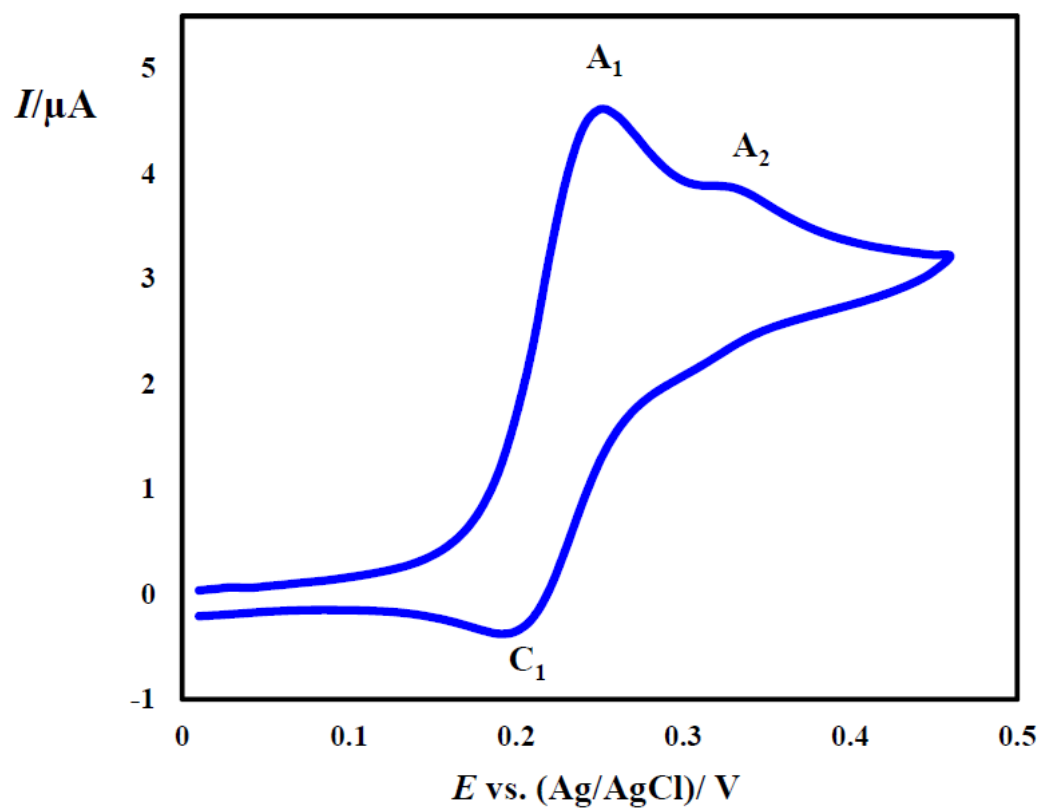
<Figure 3>



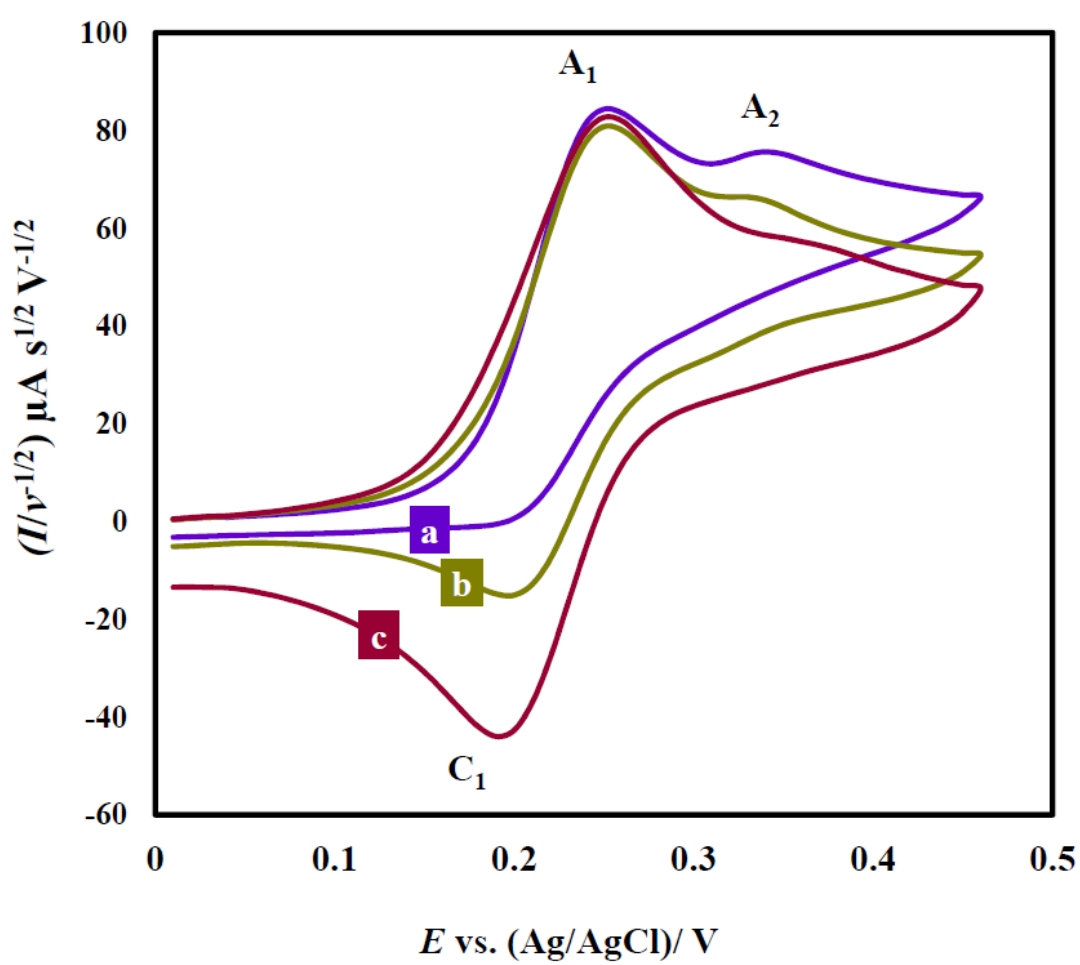
<Figure 4>



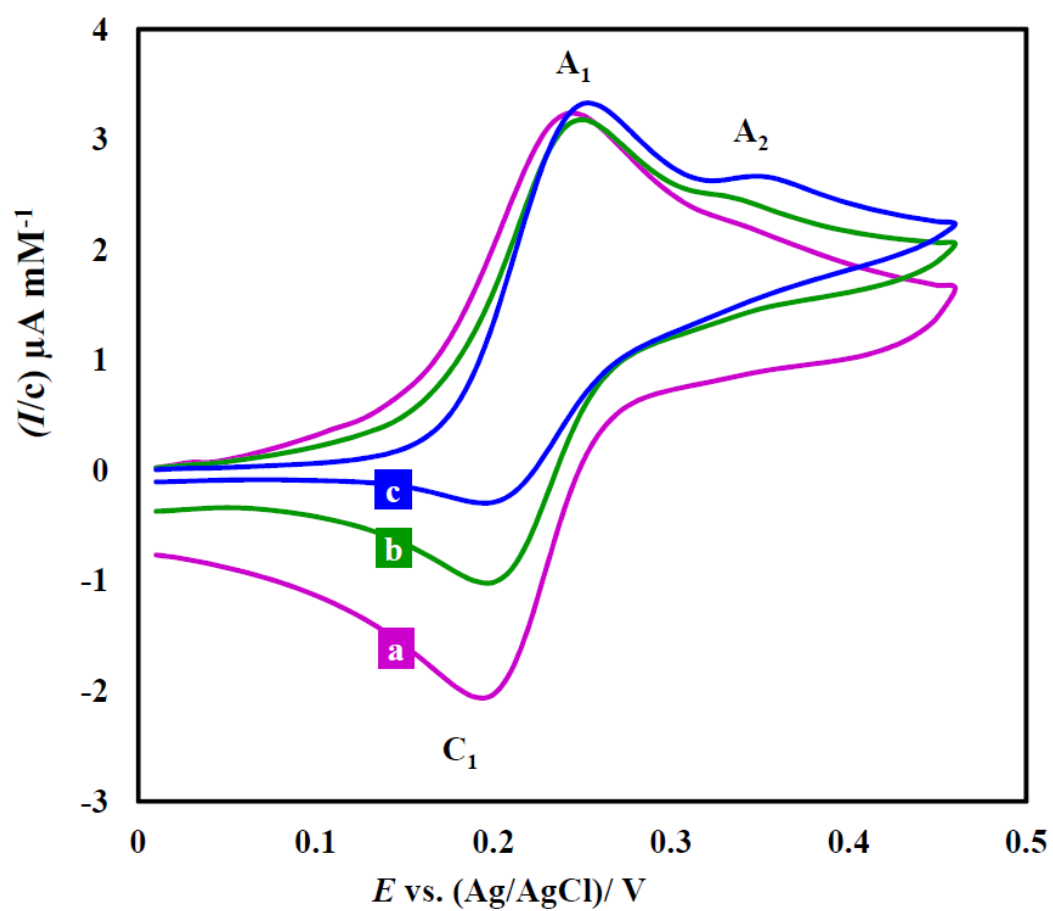
<Figure 5>



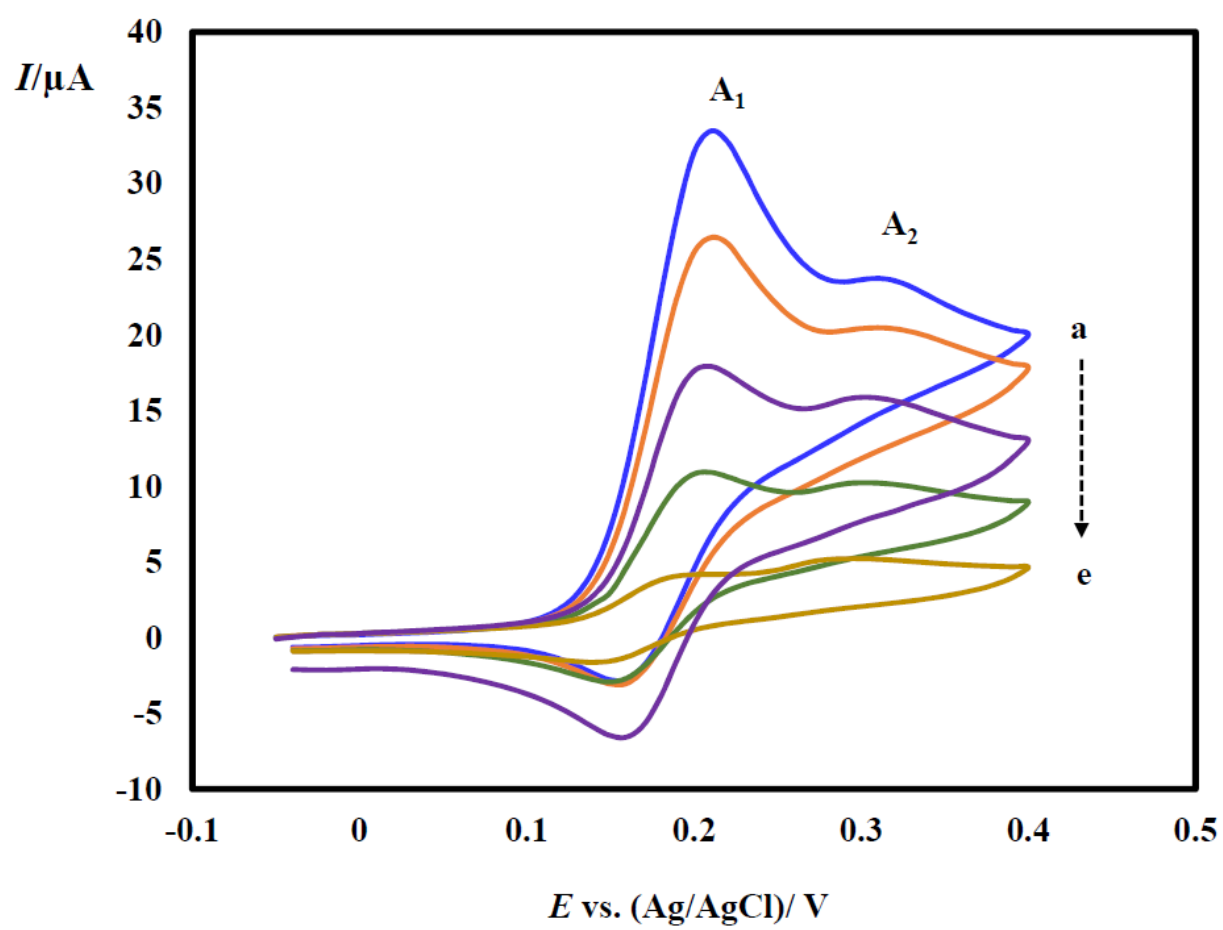
<Figure 6>



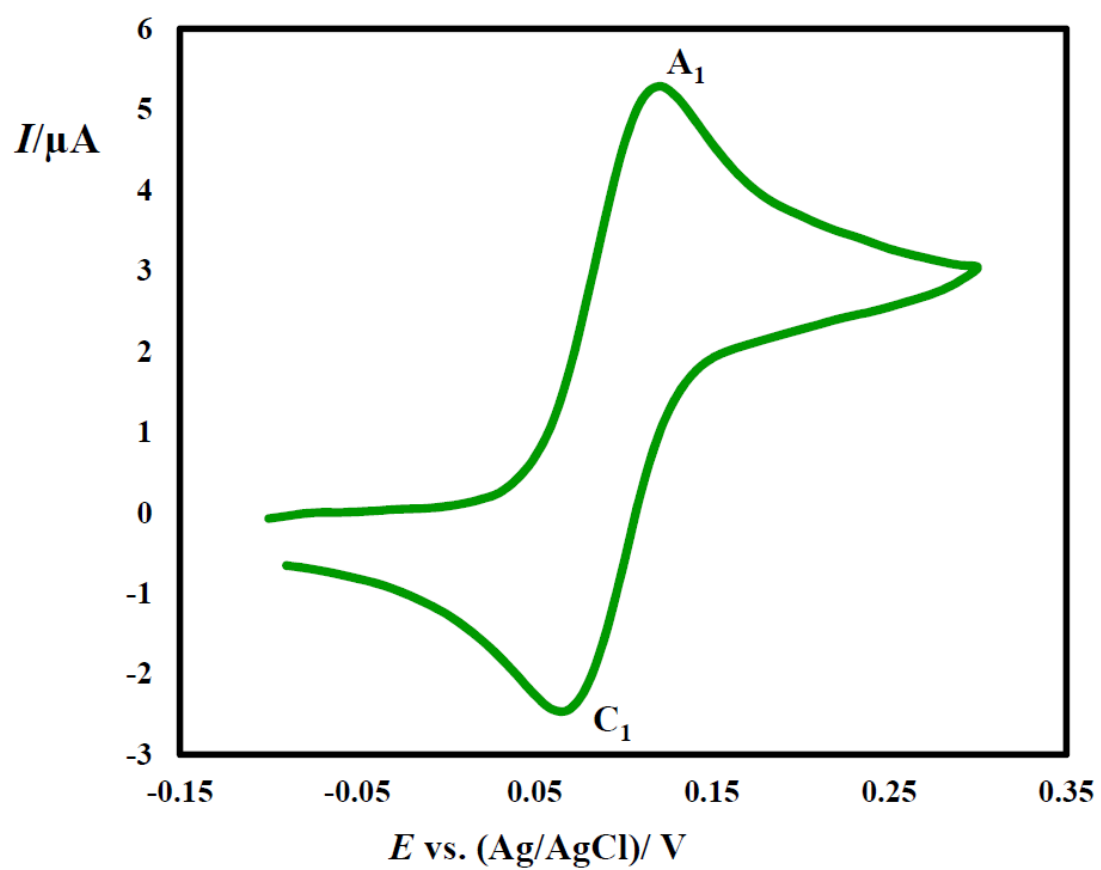
<Figure 7>



<Figure 8>

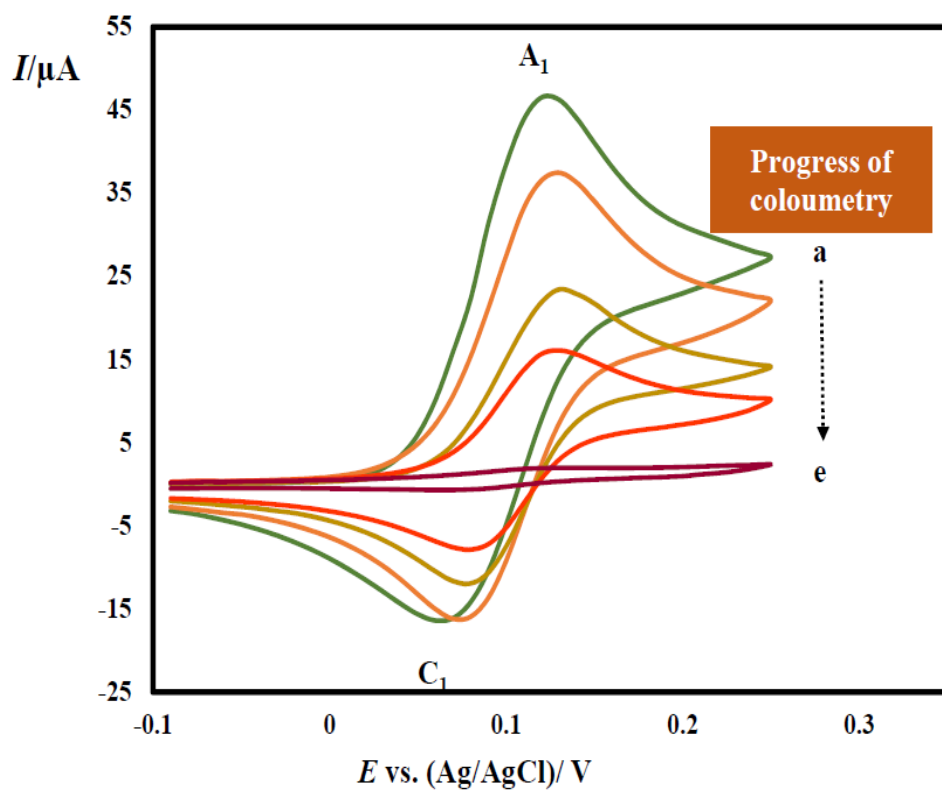


<Figure 9>



<Figure 10>

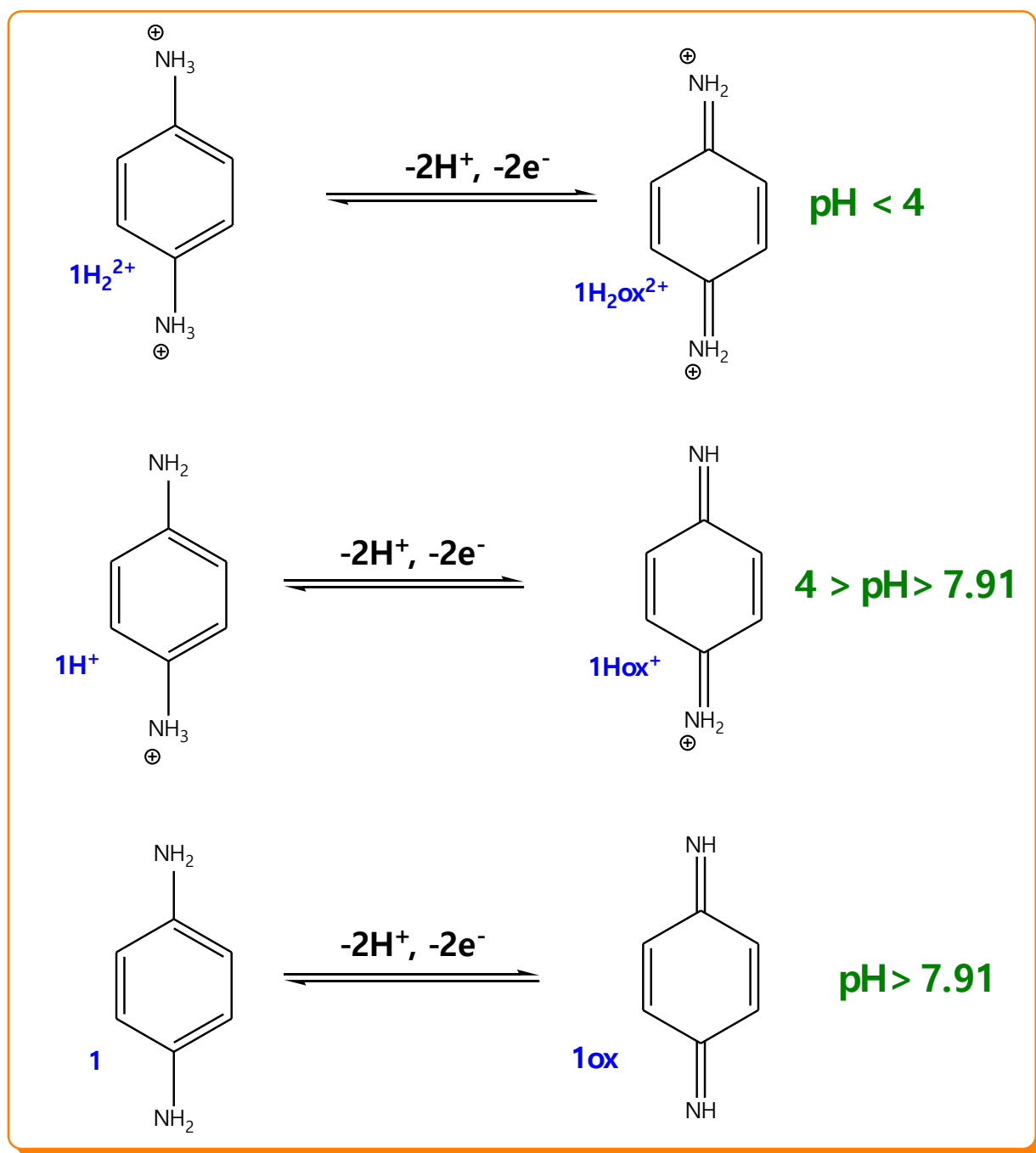
1
2
3
4
5



<Figure 11>

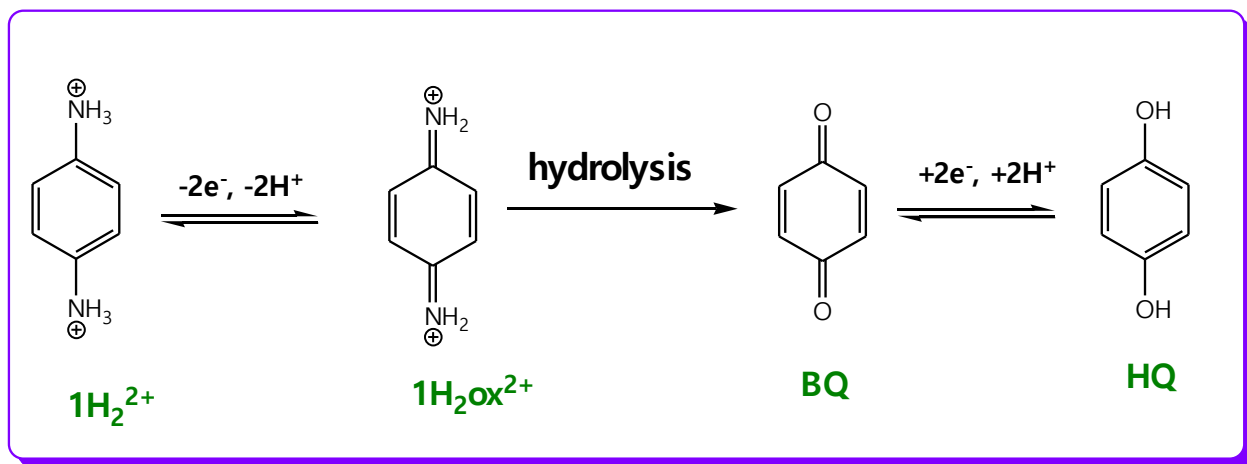
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

1

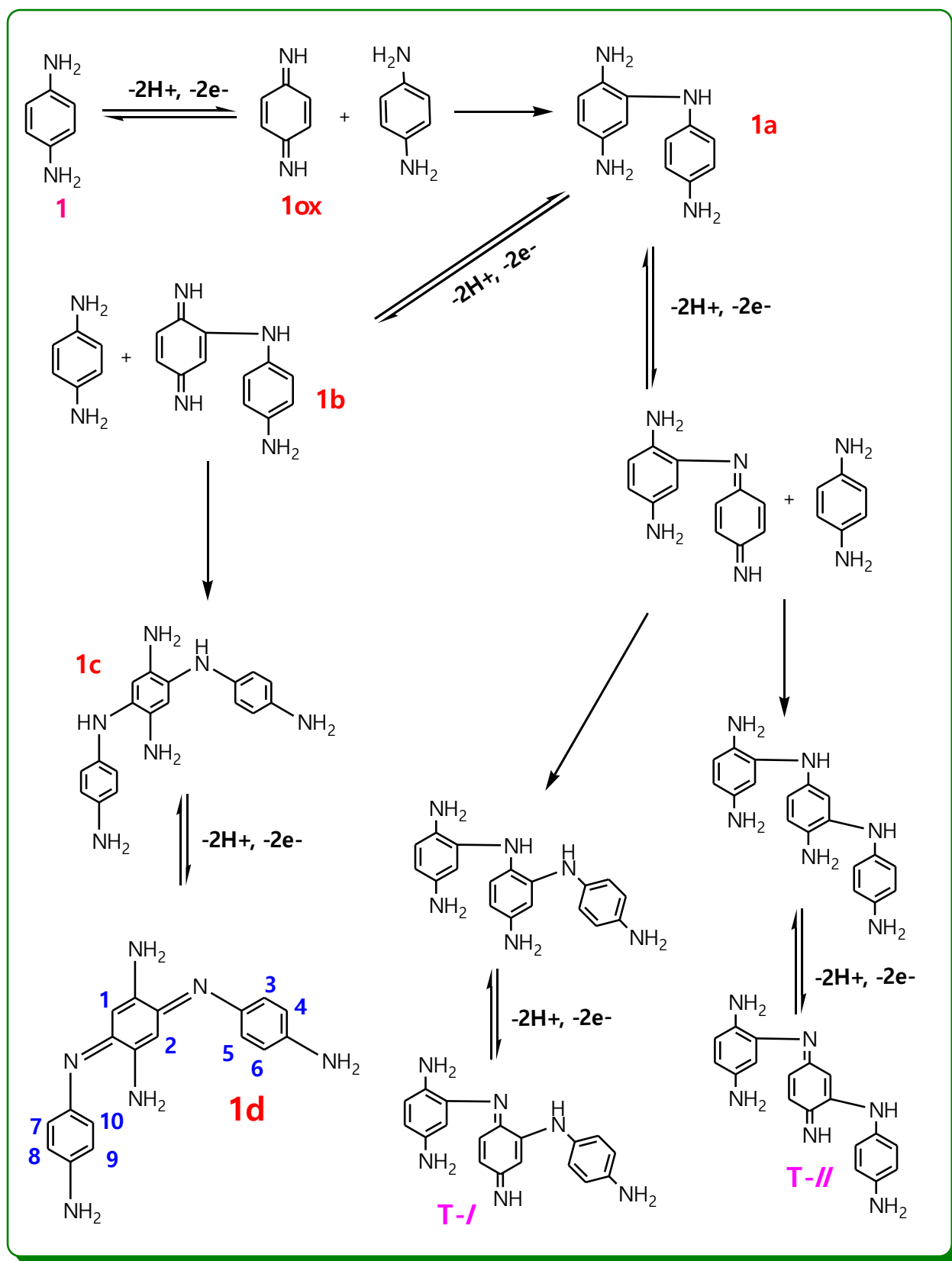


< Scheme 1 >

2
3
4
5
6
7
8
9
10



< Scheme 2 >



< Scheme 3 >