

Novel trends of electrochemical oxidation of amino-substituted triphenylamine derivatives

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Abstract

A series of amino-substituted triphenylamine derivatives have been synthesized and the electrochemical and spectral characteristics has been investigated. Triphenylamine is also used as a reference. *p*-Amino-triphenylamine (**1**) showed two reversible redox couples at $E_{1/2} = 0.59$ and 1.09 V in CH_2Cl_2 . The stable cation radical $\mathbf{1}^{+\bullet}$ was generated electrochemically and exhibited strong bands in the visible region as determined in situ by UV/Vis/NIR spectroelectrochemical methods. The second oxidation product $\mathbf{1}^{2+}$ could be generated electrochemically, but was not very stable after long time electrolysis at applied potentials higher than 1.15 V. *p,p'*-Diamino-triphenylamine (**2**), *p*-methyl-*p',p''*-diamino-triphenylamine (**2a**), *p*-methoxy-*p',p''*-diamino-triphenylamine (**2b**) and *p,p',p''*-triamino-triphenylamine (**3**) are more stable in CH_3CN than in CH_2Cl_2 during cyclic scans at oxidation potentials. The oxidation potentials of the various amino-substituted TPA derivatives and the stability of the oxidized products are solvent-dependent and relate to the molecular structures.

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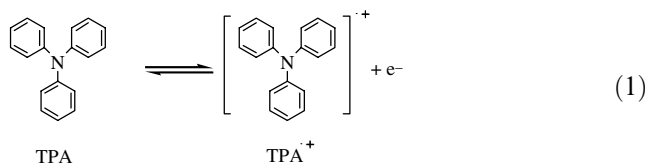
Keywords: Amino-substituted triphenylamine; Electrochemical oxidation; Spectroelectrochemistry; Cation radicals; Dication

1. Introduction

In 1968, Adams and co-workers [1] reported that anodic oxidation of triphenylamine (TPA) leads to TPA cation radical ($\text{TPA}^{+\bullet}$). The stability of the cation radical varies markedly with *para*-substitution. Because of the low ionization potentials, reversible redox behavior and good film-forming properties [2,3], TPA-containing monomers [1,4] and polymers [3] have been synthesized and their charge injection and electroluminescent efficiency have been studied [4–7]. Today, the highly electron-rich TPA derivatives have been chosen

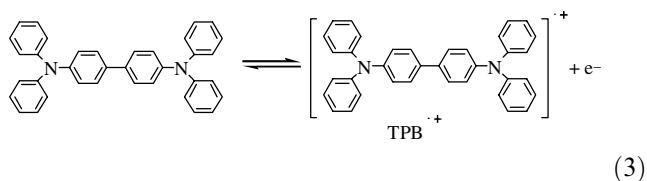
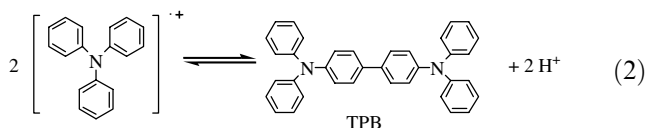
as important candidates for electrical and optical applications such as organic photoconductors, electroluminescence and electrochromic devices [8–10].

The characteristic structure feature of TPA is the nitrogen center, the electroactive site of TPA, which is linked to three electron-rich phenyl groups in a propeller-like geometry [11]. The anodic oxidation pathway of TPA was well reported [1] and is shown in Eqs. (1)–(3). The electrogenerated cation radical $\text{TPA}^{+\bullet}$ dimerized to form tetraphenylbenzidine (TPB), which is more easily oxidized than the TPA molecule.



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The electrochemical properties of TPA are affected when some of the hydrogen atoms are substituted with groups of different electronic strengths [1,4]. It was found that $\text{TPA}^{+\cdot}$ was stabilized when electro-donating groups (methyl, methoxy) were substituted at the *para*-phenyl positions. However, electron-withdrawing groups (nitro, halide) deactivate the cation radical [1]. Nelson and Adams [12] and Vallat and Laviron [13] also reported the effect of *para*-substitution on the rate of benzidine formation. The electro-oxidation of TPA was similar to the anodic oxidation of tertiary aromatic amines, such as *N,N'*-dimethylaniline, where tetramethylbenzidine formation was observed due to the dimerization of the *N,N'*-dimethylaniline cation radical [14]. Recently, kinetic analyses of these short-lived cation radicals have been carried out using ultramicroelectrode voltammetry [15], rapid-scan cyclic voltammetry [16] and electron transfer stopped-flow methods [17].

In 1974, Nelson and co-workers [18] studied the electrochemical oxidation of TPA derivatives, in which all the *para*-phenyl positions were substituted. It was observed that the cation radicals of these derivatives were stable in CH_3CN , and the second electron oxidation was followed by rapid chemical reactions. The carbazoles were obtained with a relatively high yield by the intramolecular cyclization of the dication accompanied by elimination of two protons [18].

In our previous study [4], it was observed that amino groups exhibited quite unique properties in the electrochemistry of TPA. Since amino groups are the most strongly electron-donating groups, their roles in the TPA system are interesting and worthy of investigation. However, little information about multi-amino-substituted TPA can be obtained from the literature. In this continuation study, we aimed to explore the electrochemical and spectral effects of peripheral amino groups on TPA. The intramolecular electron transfer and electronic coupling effects in the oxidized states are also important in the design of new TPA-based polymers for luminescent electronic devices. It is well known that the electrically conductive polymer family of aromatic diamines such as phenylenediamine, benzidine, diamino-anthraquinone and their derivatives have been applied for their multi-functionality [19]. The multi-amino-substituted TPA derivatives are expected to possess novel

characteristics to modify both chemical and physical properties of the aromatic polymers.

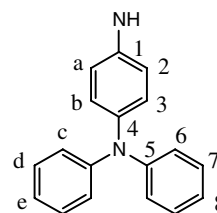
2. Experimental

The chemical structures of the compounds in this study are shown in Fig. 1. TPA was obtained from ACROS. The amino-substituted TPA derivatives were synthesized by reduction of the corresponding nitro-substituted derivatives [4].

2.1. *p*-amino-triphenylamine (I)

(I) was synthesized by Pd/C-catalyzed reduction of the *p*-nitrotriphenylamine obtained from the reaction of diphenylamine with 4-fluoronitrobenzene in the presence of sodium hydride [4]. In a 500-ml round-bottom flask, 20.84 g (0.072 mol) of the desired nitro compound and 0.4 g of Pd/C (10 wt% palladium on activated carbon) were dissolved/suspended in 300 mL of ethanol. The suspension solution was heated to reflux, and 15 mL of hydrazine monohydrate was added dropwise to the mixture, then the solution was stirred at the reflux temperature for 10 h. After cooling to room temperature, the solution was filtered to remove the catalyst, and the solid obtained from the filtrate was recrystallized from ethanol + water under nitrogen to give white needles (15.81 g, yield: 84.6%); m.p. = 148–150 °C measured by differential scanning calorimetry (DSC) at a scan rate of 10 °C/min.

IR (KBr): 3350, 3430 cm^{-1} (N–H stretch). ^1H NMR (DMSO- d_6 , δ , ppm): 6.59 (d, 2H, H_a), 6.90 (d, 4H, H_c), 7.16 (t, 4H, H_d), 6.79 ~ 6.88 (m, 4H, $\text{H}_b + \text{H}_e$), 5.065 (s, 2H, NH). ^{13}C NMR (DMSO- d_6 , δ , ppm): 146.2 (C^1), 115.0 (C^2), 121.0 (C^3), 135.3 (C^4), 147.9 (C^5), 121.4 (C^6), 129.0 (C^7), 128.1 (C^8). Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2$ (260.33): C, 83.04%; H, 6.19%; N, 10.76%. Found: C, 83.35%; H, 6.19%; N, 10.72%.



The other amino-substituted TPA derivatives were obtained and characterized in a similar way. All the chemicals were of analytical grade. Organic solvents were degassed by purging with pre-purified nitrogen gas and dried before use [20]. Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried in vacuo prior to use.

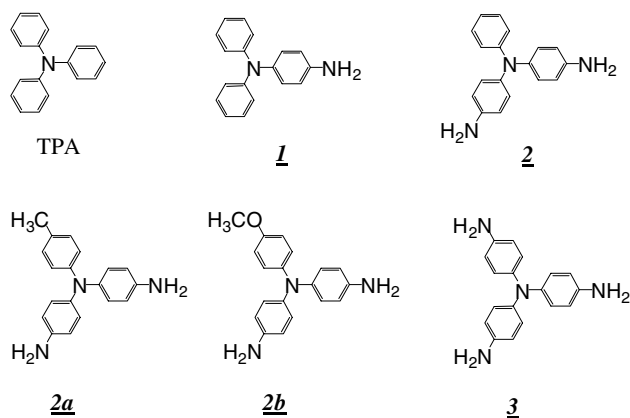


Fig. 1. Chemical structures of the triphenylamine derivatives in this study.

Electrochemistry was performed with a Bioanalytical System Model CV-27 potentiostat and a BAS X-Y recorder. Cyclic voltammetry was conducted with the use of a three-electrode cell in which a BAS glassy carbon electrode (area = 0.07 cm²) was used as a working electrode. The glassy carbon working electrode was polished with 0.05 μm alumina on Buehler felt pads and was ultrasonicated for 1 min to remove the alumina residue. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a home-made Ag|AgCl|KCl(sat.) reference electrode, which was separated from the test solution by a medium-porosity glass frit. The spectroelectrochemical cell was composed of a 1 mm cuvette, a platinum gauze (Aldrich, 100 mesh, 0.9 cm × 1.8 cm) thin layer as the working electrode, a platinum wire as the auxiliary electrode, and the Ag|AgCl reference electrode. Absorption spectra were measured with a Jasco V-570 UV/Vis/NIR spectrophotometer. ¹H and ¹³C NMR spectra were measured on a Varian 300 spectrometer with DMSO-d₆ as the solvent and with tetramethylsilane as the internal reference.

3. Results and discussion

3.1. Electrochemical and spectroelectrochemical characterization of triphenylamine

TPB formation during oxidation of the TPA molecule was proved by spectroelectrochemistry using an optically transparent thin-layer electrode (OTTLE) cell coupled with UV/Vis/NIR spectroscopy and the results are shown in Fig. 2. The inset cyclic voltammogram indicated that TPA was irreversibly oxidized at $E_{p,a} = 1.25$ V in the first scan. A new pair of redox peaks corresponding to TPB was observed at $E_{1/2} = 0.84$ V ($E_{p,a} = 0.90$ V, $E_{p,c} = 0.78$ V) in the uninterrupted second scan.

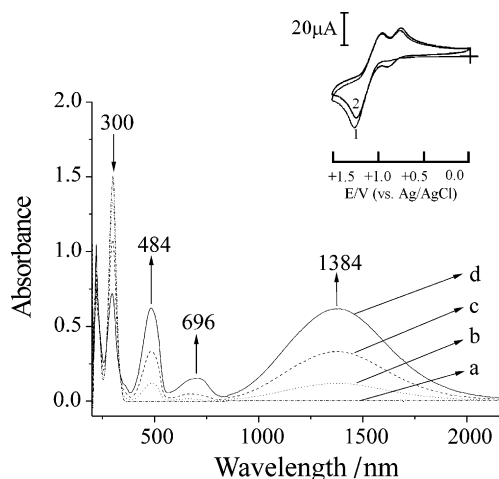
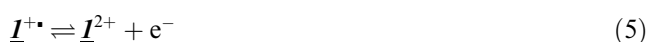


Fig. 2. Absorption spectral change of 5×10^{-4} M TPA in CH₂Cl₂ containing 0.1 M TBAP. E_{app} : (a) 0.92, (b) 0.95, (c) 0.98 and (d) 1.01 V. Inset: cyclic voltammogram of 1×10^{-3} M TPA in CH₂Cl₂ containing 0.1 M TBAP. Scan rate = 0.1 V/s. It should be noted that cyclic voltammograms are plotted with the cathodic current positive upwards.

The characteristic peak of TPA at 300 nm [21] decreased and three new bands at 484, 696 and 1384 nm grew up steadily upon electrochemical oxidation. The oxidation of the TPB molecule was also conducted in a separate OTTLE experiment. The one-electron oxidation product, TPB^{•+}, exhibited absorption at wavelengths of 484 and 1384 nm. At oxidation potentials higher than 1.00 V, the peak at around 700 nm corresponding to TPB²⁺ grew up. Therefore, this confirms the dimerization reaction mechanisms of TPA^{•+} leading to TPB. A small amount of TPB²⁺ was also found during the oxidation of TPA as shown by the absorbance at 696 nm.

3.2. Electrochemical and spectroelectrochemical characterization of monoamino-triphenylamine

Fig. 3 shows the cyclic voltammogram of *p*-amino-triphenylamine (**1**) in CH₂Cl₂ solutions. There are two reversible redox couples at $E_{1/2} = 0.59$ and 1.09 V, identical to reported data [22]. The two redox couples correspond to the formation of cation radical **1**^{•+} and dication **1**²⁺, respectively. However, some instability of the dication (**1**²⁺) was observed. If the potential was held at the positive end for 5 min then returned to 0.0 V, the second reduction wave shifted from 1.03 to 0.99 V with an enhanced reduction current and a sharper peak shape (Fig. 3(c) and (d)), implying slow kinetics in the reaction of the dication (**1**²⁺) to the products. The oxidation reactions can be described in EEC mechanism shown below.



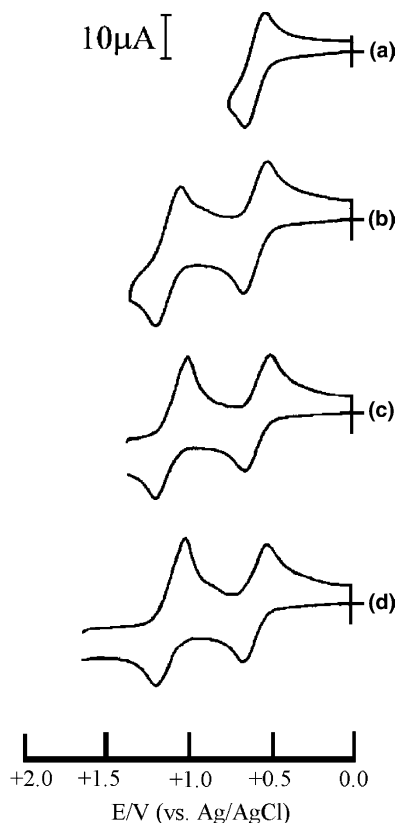


Fig. 3. Cyclic voltammograms of 1×10^{-3} M \underline{I} in CH_2Cl_2 containing 0.1 M TBAP. Scan rate = 0.1 V/s. The potential is held at the positive end for (a) 0, (b) 0, (c) 5 and (d) 5 min.



The products generated in Eq. (6) are responsible for the change of voltammograms in Fig. 3(c) and (d). According to the literature [18], *N*-(*p*-aminophenyl)carbazole is the most likely product.

The oxidation products of \underline{I} were further examined by spectroelectrochemical methods and the results are shown in Fig. 4. When the applied potentials increased stepwise from 0.41 to 0.77 V, the absorbance at 300 nm, characteristic for \underline{I} [21], decreased gradually and two new bands grew up at 374 and 660 nm. The new spectrum was assigned as that of the cation radical $\underline{I}^{+\cdot}$, similarly to the absorption wavelength for $\text{TPA}^{+\cdot}$ (655 nm) obtained by photooxidation [1]. When the potential was stepped back to 0.41 V, 96% absorbance at 300 nm was obtained. The reversibility test indicates the great stability of the cation radical in the solution. When the potential was moved further positively, corresponding to the second electron removal (Fig. 4(B)), the peaks at 374 and 660 nm gradually disappeared and three new bands at 266, 466 and 890 nm grew up steadily. When the potential was returned to 0.91 V, about 80% of the spectrum could be obtained. At applied potentials higher than 1.15 V, the resulting spectrum deviated from the isosbestic points. These phenomena indicated that

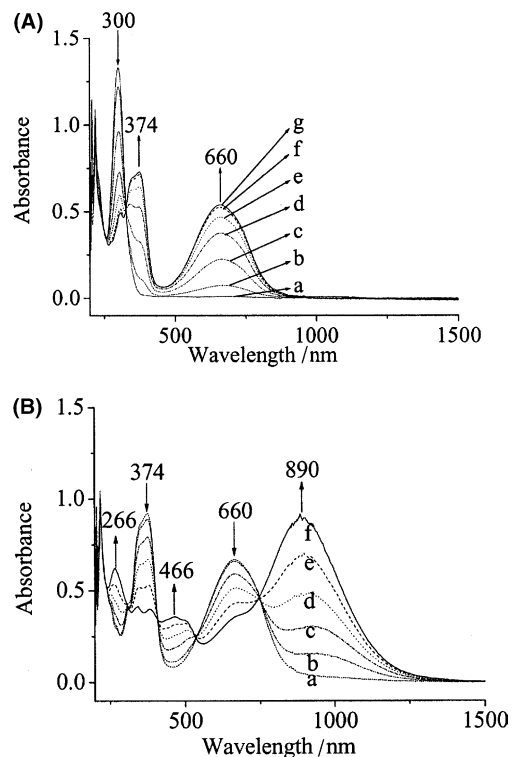


Fig. 4. Absorption spectral change of 5×10^{-4} M \underline{I} in CH_2Cl_2 containing 0.1 M TBAP. (A) $E_{\text{appl.}}$: (a) 0.41, (b) 0.50, (c) 0.56, (d) 0.59, (e) 0.62, (f) 0.68 and (g) 0.77 V. (B) $E_{\text{appl.}}$: (a) 0.91, (b) 1.00, (c) 1.06, (d) 1.09, (e) 1.12 V and (f) 1.18 V.

the dication \underline{I}^{2+} could be generated by careful control of the applied potential. However, it was not very stable after long time electrolysis at higher oxidation potentials, consistent with the results obtained in CV (Fig. 3(c) and (d)).

The electrochemistry of \underline{I} was compared with the structural isomer, *o*-amino-triphenylamine (also called *N,N*-diphenyl-*o*-phenylenediamine) [23]. Surprisingly, *o*-amino-triphenylamine is irreversibly oxidized in CH_2Cl_2 ($E_{\text{p,a}} = 1.00$ and 1.38 V) and in CH_3CN ($E_{\text{p,a}} = 0.95$ and 1.28 V). A new redox couple at $E_{1/2} = 0.25$ V was observed by continuous multi-cyclic scans between 0.0 and 1.40 V. Dihydrophenazine formation was assumed for the new redox couple because a similar oxidation potential was reported for 5,10-diaryl-5,10-dihydrophenazine ($E_{1/2} = 0.27$ V in DMF) [24]. Spectroelectrochemical monitoring of the oxidation of *o*-amino-triphenylamine is shown in Fig. 5. The absorption spectra obtained were identical to the reported data, in which cyclic dihydrophenazine was proposed as the oxidation product [23].

The electrochemical and spectral properties of \underline{I} are also compared with another structure isomer, *N,N'*-diphenyl-*p*-phenylenediamine, which exhibited oxidation potentials at $E_{1/2} = 0.50$ and 1.00 V in CH_2Cl_2 (not shown). The absorption peak of the *N,N'*-diphe-

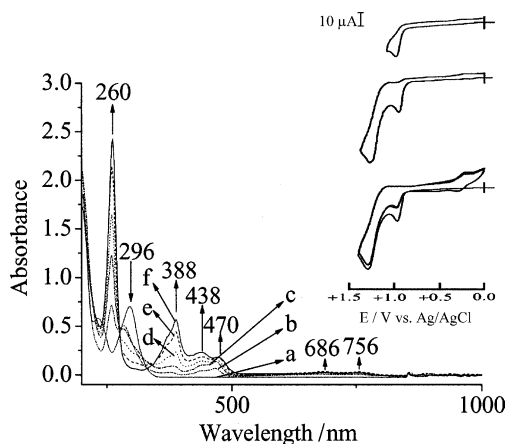


Fig. 5. Absorption spectral change of 5×10^{-4} M *o*-amino-triphenylamine in CH_3CN containing 0.1 M TBAP. E_{appl} : (a) 0.00, (b) 0.88, (c) 0.92, (d) 0.95, (e) 0.98 and (f) 1.02 V. Inset: Cyclic voltammogram of 1×10^{-3} M *o*-amino-triphenylamine in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s. The third CV is obtained by continuous cyclic scanning.

nyl-*p*-phenylenediamine cation radical appeared at 709 nm and disappeared upon further oxidation to the dication (a blue-shift peak at around 530 nm appeared) [25]. In spite of the similar oxidation potentials for **1** and *N,N'*-diphenyl-*p*-phenylenediamine, their absorption spectra are quite different, implying different electronic structures in each oxidation state.

3.3. Electrochemical and spectroelectrochemical characterization of diamino-triphenylamine

Cyclic voltammograms of *p,p'*-diamino-triphenylamine (**2**) are shown in Fig. 6. In CH_2Cl_2 , one reversible redox couple was observed at $E_{1/2} = 0.41$ V. The second wave was observed at $E_{\text{p,a}} = 0.85$ V. The sharp reduction wave at 0.65 V on the reverse scan (Fig. 6(b)) implies that the two-electron oxidation product **2**²⁺ underwent follow-up chemical reactions and the products were irreversibly adsorbed onto the electrode surface. When the potential was scanned more positively (Fig. 6(c)), a large oxidation current at 1.78 V was observed and the reduction waves on the reverse scan were significantly affected. When CH_3CN was used as the solvent, two reversible oxidation redox reactions were observed at $E_{1/2} = 0.38$ and 0.74 V and an irreversible wave appeared at $E_{\text{p,a}} = 1.78$ V. The CVs in CH_3CN are simpler than those in CH_2Cl_2 . The inherent basicity of **2** may be responsible for the complicated shapes of the voltammetric curves in protic CH_2Cl_2 solvent.

The third *para*-phenyl position is further substituted by methyl and methoxy groups to explore their effects on diamino-triphenylamine. The two derivatives (**2a**) and (**2b**) exhibited similar voltammograms to (**2**) and the oxidation potentials are listed in Table 1. Apparently, the oxidation potentials shift negatively because

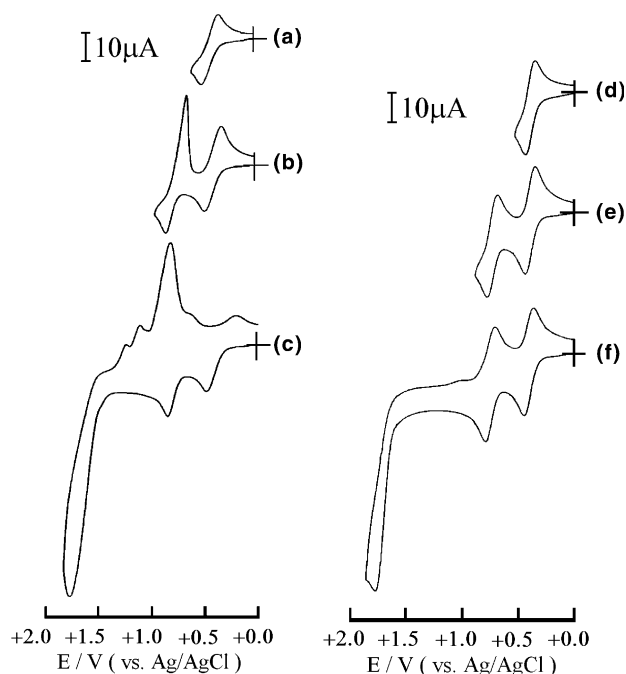


Fig. 6. Cyclic voltammogram of 1×10^{-3} M **2** containing 0.1 M TBAP. Scan rate = 0.1 V/s. (a)–(c): in CH_2Cl_2 . (d)–(f): in CH_3CN .

Table 1
Half-wave potentials of triphenylamine derivatives

Index	4th	3rd	2nd	1st
<i>E</i> _{1/2} /V vs. Ag AgCl in CH_2Cl_2				
TPA				1.25 ^a
1			1.09	0.59
2		1.78 ^a	0.85 ^b	0.41
2a		1.70 ^a	0.85 ^b	0.38
2b		1.65 ^a	0.83 ^b	0.34
3	1.75 ^a	1.50 ^a	0.63 ^b	0.23
<i>E</i> _{1/2} /V vs. Ag AgCl in CH_3CN				
1			1.03	0.54
2		1.78 ^a	0.74	0.38
2a		1.78 ^a	0.74	0.35
2b		1.70 ^a	0.66	0.28
3	1.70 ^a	1.53 ^a	0.58	0.17

^a Irreversible peak potential.

^b Oxidative peak potential.

of the electron-donating ability of methyl and methoxy groups.

Owing to the stability consideration, the oxidations of diamino-triphenylamine derivatives were examined by spectroelectrochemistry in CH_3CN . It was observed that the first oxidation product, the cation radicals (**2**⁺, **2a**⁺ and **2b**⁺) are stable and can be returned to their original neutral states by suitable control of the applied potentials (recovery ratios are 80%, 85% and 95%, respectively). When the electrolysis potentials were set at the second-electron oxidation potentials, only **2b**²⁺ could be recovered to **2b**⁺ by 80%. The other two

derivatives (**2**) and (**2a**) became dark black and some small black particles floating in the solution were observed. Apparently, the dication is not stable and may undergo decomposition or complicated oxidation reactions. With methoxy groups protected at the *para*-phenyl positions, the stability of the dication **2b**²⁺ is enhanced [1].

3.4. Electrochemical and spectroelectrochemical characterization of triamino-triphenylamine

The cyclic voltammograms of *p,p',p''*-triamino-triphenylamine (**3**) in CH₂Cl₂ and CH₃CN are similar to those of **2** except that one additional irreversible oxidation wave at 1.75 V was observed. Comparing the data listed in Table 1, the first redox couple of **3** occurred at $E_{1/2} = 0.23$ V, less positive than that for **2** by 0.18 V. Compound **2** is oxidized less positively than that for **1** by the same amount (in CH₂Cl₂). Therefore, the substitution of amino groups onto the TPA molecule not only increases the molecular basicity but also shifts the oxidation to a more negative potential. The low oxidation potential of **3** is comparable with that reported for *p,p',p''*-tris(*N,N*-diphenylamino)triphenylamine, in which the redox potential was reported as 0.11 V vs. Ag|Ag⁺ (0.01 M) in CH₂Cl₂ solution [26]. It is noted that the oxidation redox potentials of amino-substituted TPA derivatives agree with the Hammett relationship in the electron-donating/withdrawing properties of the substituents at the *para*-phenyl positions [27]. The two redox potentials in CH₃CN vs. the substituent constant (3σ) are thus plotted as Fig. 7. The second oxidation potentials possess a higher Hammett slope (the ρ value), which reflects the sensitivity of the reaction to the electronic effect of the substituents.

Spectroelectrochemistry results indicate that the cation radical **3**⁺ can return to the neutral form with a lower recovery ratio (79%) than the diamino-triphenylamine derivatives. The dication **3**²⁺ is also unstable, similarly to **2**²⁺ and **2a**²⁺. Compared with the absorption spectra of the cation radicals, a broad distorted NIR band was observed for **2**⁺, **2a**⁺, **2b**⁺ and **3**⁺ with

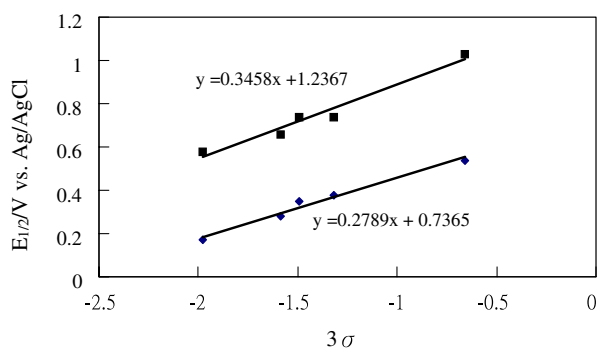


Fig. 7. Plot of half-wave potentials vs. 3σ for amino-substituted triphenylamine derivatives in this study.

absorption maxima at 900, 887, 862 and 838 nm, respectively. The spectral patterns are similar to the intervalence charge transfer (IV-CT) bands for mixed valence compounds [21], implying electron delocalization in these cation radicals. However, there is no IV-CT band observed for **1**⁺. The spectral similarity for **1**⁺ and TPA⁺ [1] suggest that the electron is localized at the central *N* atom.

4. Conclusions

In this study, amino-substituted TPA derivatives were synthesized and characterized electrochemically. The peripheral *p*-amino substituents exert a strong effect on the electronic structure of TPA and thus, affect their electrochemical oxidation potentials significantly. It is observed that triamino-substituted TPA is much easier to oxidize than diamino-substituted TPA, which in turn is much easier to oxidize than monoamino-substituted TPA. The first and the second half-wave potentials follow the Hammett relationship.

The stability of the oxidized products is monitored by spectroelectrochemistry. Monoamino-substituted TPA is more stable than di- and triamino-substituted TPA upon one- and two-electron oxidation. The oxidized products are more stable in CH₃CN than in CH₂Cl₂, especially for di- and triamino-substituted TPA. The cation radicals of di- and triamino-substituted TPA exhibited IV-CT absorption bands in the NIR region, implying electronic coupling between the active *N* centers.

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