

# Electrochemical characterization of small organic hole-transport molecules based on the triphenylamine unit

Sung Jie Yeh, Che Yu Tsai, Chih-Yen Huang, Guey-Sheng Liou, Shu-Hua Cheng \*

Department of Applied Chemistry, National Chi Nan University, Puli, Nantou Hsien 545, Taiwan

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## Abstract

A series of substituted triphenylamine-containing organic compounds are synthesized and their hole-transport properties are examined by electrochemical and spectroelectrochemical methods. Several substituted triphenylamines exhibited irreversible electron-transfer reactions both in the oxidative and reductive scan. On the other hand, the cyclic voltammograms of the *p*-phenylenediamine series are well defined. *N,N'*-bis(4-nitrophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (NPD) exhibited two reversible oxidation redox couples at +1.00 and +1.28 V vs. Ag/AgCl in dichloromethane solution. There is one reversible reduction redox couple at -1.12 V and one irreversible wave with  $E_{p,c}$  at -1.87 V. Cyano-substituted *p*-phenylenediamine (CPD) exhibited similar oxidation redox couples. Amino-substituted *p*-phenylenediamine (APD) is easier to oxidize than NPD and CPD. APD exhibits two reversible oxidation redox couples at +0.40 and +0.70 V and two extra irreversible oxidation waves at +1.26 and +1.52 V. Optically transparent thin-layer electrode (OTTLE) coupled with UV/Vis/NIR spectroscopy was used to examine the oxidation products of the above reactions. The electrogenerated cation and dication of the substituted *p*-phenylenediamine are very stable in the spectroelectrochemical studies. Oxidation of the compound APD exhibited a distinguished absorption pattern, which is different from those of compound NPD and compound CPD.

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**Keywords:** Triphenylamine; Cyclic voltammetry; Spectroelectrochemistry

## 1. Introduction

Arylamine-containing aromatics have been used as hole-transporting molecules in the optoelectronic fields, both in photoreceptor devices [1] and organic light emitting diodes (OLEDs) [2,3]. The redox properties, ion transfer process, electrochromism and photoelectrochemical behavior of *N,N,N',N'*-tetra-substituted-1,4-phenylenediamines [4–7] are of importance for technological application. A new material with longer life, higher efficiency and appropriate HOMO energy level of the molecules is in increasing demands. Many kinds of polymers containing the arylamine or *p*-phenylenediamine monomer have been synthesized and investigated. Thus, the understanding of the hole-injection and -transport properties in these artificial low molecular

systems helps us to design the devices for electronic communication [8].

The anodic oxidation of triphenylamine in aprotic solvent is well studied in 1966 [9]. The one-electron oxidation product, triphenylamine cation, is not stable. The chemical follow-up reaction produces tetraphenylbenzidine by tail-to-tail coupling. This is accompanied by loss of two protons per dimer. When the phenyl groups are substituted at the *para* position, the couple reactions are greatly prevented. In fact, *p*-substituted triarylamines often give stable cation radicals [10].

Although triphenylamine-based organic thin layer [11–13] has attracted much attention in a wide variety of optoelectronics, their electrochemistry has not been explored in detail. The redox potentials determine how easily the material is oxidized at the anode/HTL interface (HTL = hole-transport layer) or how easily its cation radical is reduced at the HTL/EL interface (EL = electroluminescent layer) for a two-layer

\* Corresponding author. Tel: +886-49-2910960x4151; fax: +886-49-2917956.

E-mail address: [shcheng@ncnu.edu.tw](mailto:shcheng@ncnu.edu.tw) (S.-H. Cheng).

light-emitting diodes. It is very important to understand the electrochemical properties of the triphenylamine-based model molecules, which will help us to design suitable monomer and permit tuning of the redox potentials of the polymer.

Here, we report the electrochemical behavior of a series of triphenylamine-containing organic compounds with varied oxidation potentials. These monomers are designed as the starting materials of the aromatic polyamides, which are thermally stable polymers and applicable in organic electroluminescent elements. This paper is the background to a project based on triarylamine-containing aromatic polyamide film for evaluating the potential as active components for a wide range of OLEDs and display.

## 2. Experiment

The chemical structures of the compounds in this study are shown in Tables 1 and 2. Amino-substituted triphenylamine (I) was synthesized by hydrogen or hydrazine Pd/C-catalyzed reduction of the nitro-substituted triphenylamine (II) resulting from the reaction of diphenylamine with 2,4-dinitrobenzene in the presence of sodium hydride. The cyano-substituted triphenylamine (III) and DCPD were prepared by condensation of 4-nitrophthalonitrile with diphenylamine and *N,N'*-diphenyl-1,4-phenylenediamine, respectively. Triphenylamine containing dicarboxylic acid substituents (IV) was readily obtained by the alkaline hydrolysis reaction of the dinitrile compound (III). The synthesis and characterization of the substituted *p*-phenylenediamine derivatives, NPD, APD, CPD and CAPD were published elsewhere [14,15].

All the chemicals were of analytical grade. Organic solvents were degassed by purging with pre-purified ni-

trogen gas and dried before use [16]. Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried in vacuo prior to use.

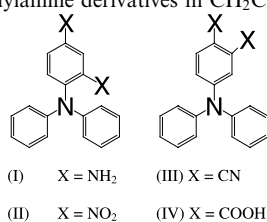
Electrochemistry was performed with a Bioanalytical System Model CV-27 potentiostat and a BAS X–Y recorder. Voltammograms are presented with the positive potential pointing to the right and with increasing anodic currents pointing upwards. Cyclic voltammetry was conducted with the use of a three-electrode cell in which a BAS glassy carbon electrode (area = 0.07 cm<sup>2</sup>) was used as a working electrode. The glassy carbon electrode was polished with 0.05 μm alumina on Buehler felt pads and was ultrasonicated for 1 min to remove the alumina residue. The auxiliary compartment contained a platinum wire separated by a medium-porosity glass frit. All cell potentials were taken with the use of a Ag/AgCl, KCl(sat.) reference electrode. 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 working electrode, a platinum wire as auxiliary electrode, and a Ag/AgCl reference electrode. Absorption spectra were measured with a Jasco V-570 UV/Vis/NIR spectrophotometer.

## 3. Results and discussion

### 3.1. Electrochemical studies

We have examined four triphenylamine derivatives and their cyclic voltammograms were very complicated both in the oxidation and reduction scan. The electrochemical data for the triphenylamines were shown as Table 1. All the electron-transfer reaction were irreversible, except that one reversible redox in the reduction scan was observed for the cyano-substituted triphenylamine and one reversible redox in the reduction

Table 1  
Electrochemical characteristics (V vs. Ag/AgCl) of triphenylamine derivatives in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP



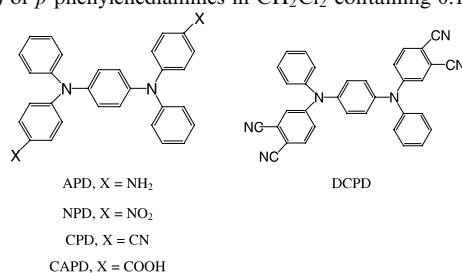
Compound	Oxidation	Reduction	
	$E_{p,a}$	$E_{p,c}$ (first)	$E_{p,c}$ (second)
(I)	+0.63 (+0.51) <sup>b</sup>		
(II)	+1.58 (+1.48)	-0.87 <sup>a</sup> (-0.88 <sup>a</sup> )	-1.36 (-1.30)
(III)	+1.55 (+1.43)	-1.86 (-1.63 <sup>a</sup> )	(-2.20)
(IV)	+1.50 (+1.40)	-1.34 (-1.25)	

Scan rate = 0.1 V/s.

<sup>a</sup> Half-wave potential for a reversible redox.

<sup>b</sup> The data in the parenthesis were obtained in CH<sub>3</sub>CN.

Table 2  
Electrochemical characteristics (V vs. Ag/AgCl) of *p*-phenylenediamines in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP



Compound	Oxidation				Reduction	
	Fourth	Third	Second	First	First	Second
APD	+1.52 <sup>b</sup> (+1.50 <sup>b</sup> ) <sup>a</sup>	+1.26 <sup>b</sup> (+1.13 <sup>b</sup> )	+0.70 (+0.58)	+0.40 (+0.35)		
NPD			+1.28 (+1.25)	+1.00 (+0.97)	-1.12 (-1.08)	-1.87 <sup>b</sup> (-1.60 <sup>b</sup> )
CPD			+1.26 (+1.24)	+0.93 (+0.92)		
CAPD			+1.16 <sup>b</sup> (+1.43 <sup>b</sup> )	+0.87 <sup>b</sup> (+1.08 <sup>b</sup> )		
DCPD					-1.48 (-1.45)	-1.96 <sup>b</sup> (-1.73 <sup>b</sup> )

Scan rate = 0.1 V/s.

<sup>a</sup>The data in the parenthesis were obtained in CH<sub>3</sub>CN.

<sup>b</sup>Irreversible peak potential.

scan was observed for the nitro-substituted triphenylamine. The results indicate that the electrogenerated cation radical and anion radicals are very reactive. This is consistent with the fact that stable triphenylamine cation radical is formed only if all *para* positions are substituted [10].

The oxidation of the unsubstituted triphenylamine was conducted in our lab. It was oxidized at  $E_{p,a} = +1.18$  V in CH<sub>2</sub>Cl<sub>2</sub>. The potential difference between the triphenylamine derivatives and the unsubstituted one can be interpreted in terms of the electrophilicity induced by the electron-donating amine substituents and the electron-withdrawing nitro/cyano/carboxylic acid substituents to the lone pair of nitrogen atom on the triphenylamine.

The structures of substituted *p*-phenylenediamine in this study are shown as Table 2. Electrochemical analyses of the *p*-phenylenediamine by cyclic voltammetry in dichloromethane and acetonitrile have been performed. The voltammetric waves in the two solvents are similar, while a little difference in potentials was found. Multiple electrochemically reversible reactions are observed for all the substrates. The electrochemical data for this series also present the effects of electron withdrawing/donating ability of the substituents.

Fig. 1 shows the cyclic voltammogram for NPD. The two reversible oxidation couples at +1.00 and +1.28 V correspond to successive one electron removal from the *p*-phenylenediamine functionality to yield a stable delocalized radical cation (NPD<sup>•+</sup>) and a quinonoid-type dication (NPD<sup>2+</sup>), respectively [17]. Both triarylamine centers are strongly coupled by the fact that the redox couple separation is 280 mV, which is larger than the statistical value for noninteracting center, where the

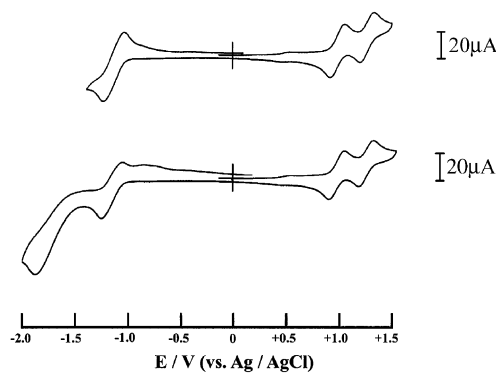


Fig. 1. Cyclic voltammogram of 1 mM NPD in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. Scan rate = 0.1 V/s.

separation of the first and the second oxidation redox couple is 35.6 mV [18]. In the reductive scan, there is one reversible redox couple at  $E_{1/2} = -1.12$  V and one irreversible wave at  $E_{p,c} = -1.87$  V. The nitrogen atoms of the substituted nitro group are formally positive, thus, the reduction reactions involve the addition of electrons to the nitro groups. Besides, the irreversible reduction wave indicates that the reduction reaction is a complicated process of electron transfer coupled with chemical reactions.

Fig. 2 shows the cyclic voltammogram for APD. There are two reversible redox couples at +0.40 and +0.70 V, respectively. Additionally, two irreversible oxidation waves were observed at +1.26 and +1.52 V. However, no reduction waves were observed within the solvent window. The electron-donating properties of the amino substituents on the phenyl groups may contribute to the shift of the oxidation potential to the negative direction.

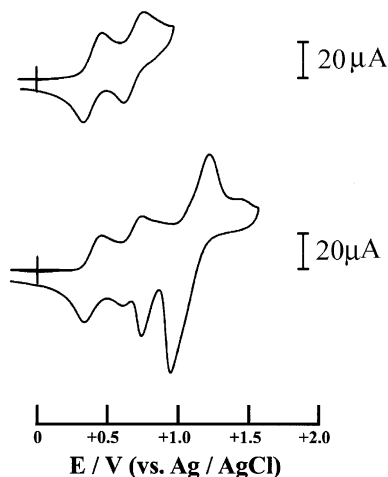


Fig. 2. Cyclic voltammogram of 1 mM APD in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP. Scan rate = 0.1 V/s.

The cyano-substituted *p*-phenylenediamine, shortened as CPD, exhibited two reversible redox couples at +0.93 and +1.26 V. The oxidation potentials were very close to those of NPD. CAPD was the carboxylic acid-substituted compound, which exhibited the broad oxidation waves at +0.87 and +1.16 V. DCPD was the tetra-cyano-substituted compound. Only one reversible redox couple was observed at -1.48 V for DCPD. Meanwhile, no oxidation waves were obtained by cyclic voltammetric measurements.

### 3.2. Spectroelectrochemical studies

Optically transparent thin-layer electrode (OTTLE) coupled with UV/Vis/NIR spectroscopy was used to examine the oxidation products of the above reaction. Fig. 3 showed the spectral changes for NPD at various electrode potentials. The absorption peaks at 305 and 416 nm are characteristic for NPD. After one-electron

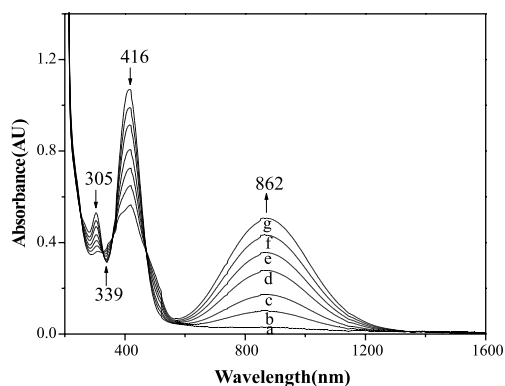


Fig. 3. Absorption spectral change of  $1.91 \times 10^{-4}$  M NPD in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.  $E_{\text{appl.}}$  = (a) 0.90 (b) 0.96 (c) 0.98 (d) 1.00 (e) 1.02 (f) 1.04 and (g) 1.10 V.

oxidation, the absorbance at 305 and 416 nm decreased gradually, while a new broad band at 862 nm appeared. The spectral pattern was assigned as the spectrum of radical cation  $\text{NPD}^+$ , the product obtained by one-electron removal from the lone pair of nitrogen atom on *p*-phenylenediamine. The spectrum was very similar to the chemical oxidation of methoxy-substituted phenylenediamine, where a broad and intense absorption band rises near 1000 nm [17].

When the oxidation potential was adjusted to 1.36 V, corresponding to the second electron oxidation of NPD, the absorbance at 862 nm decreased and a new band at 556 nm appeared (Fig. 4). The spectrum was assigned as the dication  $\text{NPD}^{2+}$ , the product obtained by another one-electron removal from the other nitrogen atom on *p*-phenylenediamine. The one- and two-electron oxidations of CPD produced absorption spectra similar to those of  $\text{NPD}^+$  and  $\text{NPD}^{2+}$ . The results suggested that the nitro- and cyano-substituted *p*-phenylenediamine were oxidized in a similar way.

The oxidation products of APD were also examined by OTTLE methods and the results were shown as Figs. 5 and 6. The first electron oxidation product exhibited a spectrum with three new peaks at 420, 650 and 1112 nm. The second electron oxidation product exhibited a spectral pattern with an enhanced peak at 982 nm. Apparently, the spectral patterns of the oxidized APD were completely different from those of the oxidized NPD and CPD. The positive charge on the nitrogen atoms of the *p*-phenylenediamine after electron transfer may transfer onto the substituted amino group through electron resonance because of the electron-donating property of the amino group. The transferring acidic protons of the amino group after oxidation to form the quinoidal ring products [19] may result in the spectral differences between oxidized APD and oxidized NPD. The oxidation reactions can be summarized as

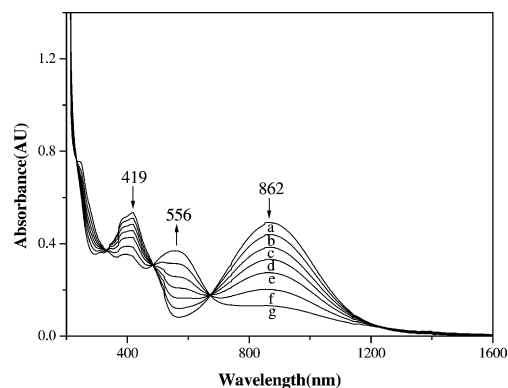


Fig. 4. Absorption spectral change of  $1.91 \times 10^{-4}$  M NPD in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.  $E_{\text{appl.}}$  = (a) 1.20 (b) 1.24 (c) 1.26 (d) 1.28 (e) 1.30 (f) 1.32 and (g) 1.36 V.

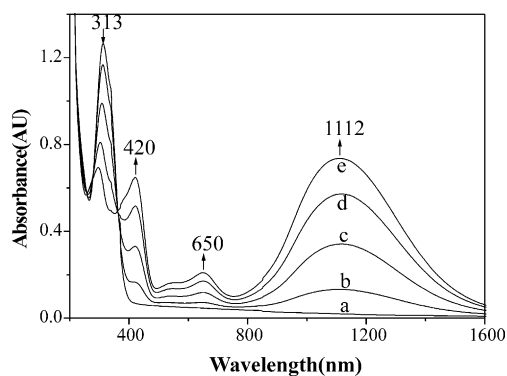


Fig. 5. Absorption spectral change of  $3.01 \times 10^{-4}$  M APD in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.  $E_{\text{appl.}}$  = (a) 0.20 (b) 0.36 (c) 0.40 (d) 0.44 and (e) 0.52 V.

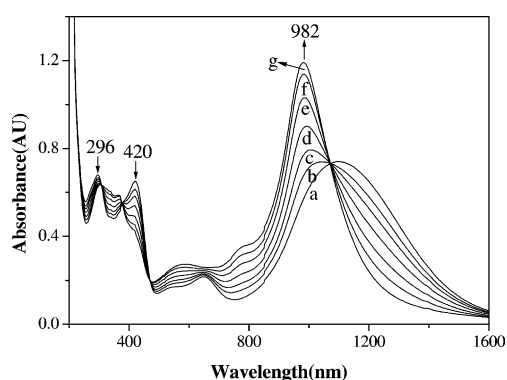
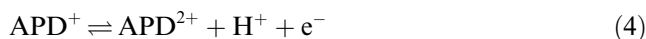


Fig. 6. Absorption spectral change of  $3.01 \times 10^{-4}$  M APD in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.  $E_{\text{appl.}}$  = (a) 0.58 (b) 0.64 (c) 0.66 (d) 0.68 (e) 0.70 (f) 0.72 and (g) 0.76 V.



#### 4. Conclusions

In this study, we synthesized and examined the electrochemical properties of the triphenylamine-containing organic compounds. Without proper protection, the substituted triphenylamines undergo irreversible oxidation and reduction electrochemically. On the other hand, the substituted *p*-phenylenediamine derivatives exhibited the well-defined cyclic voltammograms. The electrochemical oxidation and reduction potentials show

the effects of electron-donating groups (amino) and electron-withdrawing groups (nitro, cyano and carboxylic acid) on the electron moiety of *p*-phenylenediamine. The amino-substituted derivatives exhibited four oxidative waves and the spectroelectrochemical studies indicated that the one- and two-electron oxidation products are quite different from those of the nitro- and cyano-substituted *p*-phenylenediamine. The substituted *p*-phenylenediamine series are potential hole-transport molecules owing to their great stability after oxidation.

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