

# Substituent effects on the electrochemical and spectral characteristics of $N,N,N',N'$ -tetraaryl- $p$ -phenylenediamine derivatives

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## Abstract

Mixed-valence compounds of  $N,N,N',N'$ -tetraaryl- $p$ -phenylenediamine derivatives (PDs) with various electron-donating and -withdrawing substituents have been synthesized and their electrochemical and spectral characteristics have been investigated. According to the molecular symmetry, PDs are grouped as two series. The two series of PDs follow Hammett relationships both in the first and the second half-wave oxidation potentials. The isomeric cation radical/dication redox couples occur at the same potentials and the cation radicals exhibit similar absorption maxima and band shapes in the NIR regions, implying the highly delocalized electronic structures in the singly oxidized states. The stability of the oxidation products was monitored with UV/vis/NIR spectroelectrochemical investigations. PDs with electron-withdrawing substituents are stable after one electron oxidation, while PDs with electron-donating substituents are stable after one and two electron oxidation.

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## 1. Introduction

Intramolecular electron transfer (ET) processes have been studied extensively in the mixed-valence (MV) systems [1–3]. The usually employed one-dimensional MV compounds contain two or more redox states connected via a  $\sigma$ - or  $\pi$ -bridge molecule. The well-known Creutz–Taube ion [1],  $[(\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5]^{5+}$ , is the most extensively studied for inorganic MV systems. The interest in pure organic MV systems is currently increasing [2,3], especially for the diamine derivatives. For example, Nelsen and coworkers [4] studied a number of  $p$ -phenylenediamine cation radicals using both the time-dependent theory and spectroscopic measurements. Triphenylamine (TPA) derivatives have been

known as hole-transporting materials and widely used in multilayer organic light-emitting diodes [5]. Therefore, TPA-based diamine systems are recently synthesized and investigated [6–8].

The properties of MV systems depend strongly on the extent of electronic interaction between the redox centers. In accordance with the Robin–Day classification [9], MV systems are divided into three categories: class I with negligible electronic coupling between the two different redox sites (complete valence trapping); class II with moderate electronic coupling; class III with strong electronic coupling (the electron is delocalized over the two redox centers).

Several structural parameters control the electronic coupling, thus the rate of ET processes, in MV systems. Lambert and Nöll [2,10] investigated the effects of bridge length on TPA-based diamine systems. Significant electronic coupling was observed for the  $N,N,N',N'$ -tetra-4-methoxyphenyl- $p$ -phenylenediamine cation radical [2].

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Recently, an experimental and theoretical study of the  $N,N,N',N'$ -tetraphenyl-*p*-phenylene diamine cation radical has been reported and a symmetrical delocalized class III structure was proposed [11].

Although many TPA-based diamine systems have been researched, the amine *N* atoms are always located in the same chemical structures. It is conceivable that the electronic coupling would be changed if the amine *N* atoms are located in a different situation. In this study, we design the structurally isomeric  $N,N,N',N'$ -tetraaryl-*p*-phenylenediamine derivatives (PDs) by introduction suitable substituents at the outer-phenyl positions. Then, we provide a convenient and effective method based on the electrochemical and spectroelectrochemical characterization to identify the electronic structures of PDs. The electrochemical method used here is cyclic voltammetry (CV), which is a simple way to measure the HOMO energy of the molecules. The stability and spectral features of the oxidized products can be monitored by the spectroelectrochemical experiments. The results would reflect the electronic states of the oxidized products. We investigated their electrochemical and spectroscopic properties in order to observe the substituent effects on the electronic structure and the molecular delocalization and thus clarify intramolecular ET processes. The understanding of the degree of delocalization and the intramolecular ET characteristics is important for the design of new TPA-containing materials as electronic switching or storage units for organic optoelectronic devices [5] and as high-spin compounds in organic magnets [12].

## 2. Experimental

The molecular structures of PDs are shown in Fig. 1. Series 1 were synthesized by the condensation of  $N,N'$ -diphenyl-*p*-phenylenediamine with appropriate substituted benzene as shown in the previous studies [13].

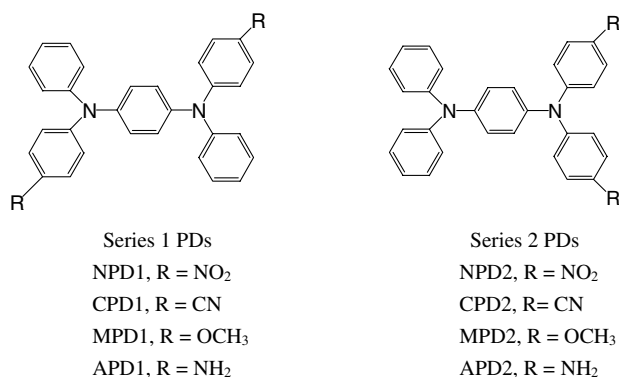


Fig. 1. Chemical structure of PDs in this study.

Series 2 were synthesized by a modification method. NPD2 and CPD2 were synthesized by the condensation of  $N,N$ -diphenyl-*p*-phenylenediamine (also called *p*-amino-triphenylamine) with 4-fluoronitrobenzene and 4-fluorobenzonitrile, respectively, in the presence of sodium hydride as a base. APD2 was prepared by Pd/C-catalyzed reduction of the dinitro compound NPD2. MPD2 was obtained by the condensation of  $N,N$ -diphenyl-*p*-phenylenediamine with 4-iodoanisole using Cu powder as a catalyst [14]. The obtained PDs were characterized by <sup>1</sup>H and <sup>13</sup>C NMR on a Varian 300 spectrometer with DMSO-*d*<sub>6</sub> as the solvent and with tetramethylsilane as the internal reference. Elemental analysis was measured by Elementar Vario EL III, Germany. The melting points of the compounds were measured with a Perkin–Elmer differential scanning calorimeter 6 (DSC 6).

All the chemicals were of analytical grade. Organic solvents were degassed by purging with pre-purified nitrogen gas and dried before use [15]. The water residue in dry CH<sub>2</sub>Cl<sub>2</sub> was estimated about 0.004% (v/v). Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried in vacuo prior to use.

Cyclic voltammetry was performed with a Bioanalytical System Model CV-27 potentiostat and a BAS X-Y recorder. It 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. A platinum wire was used as the auxiliary electrode. All cell potentials were taken with the use of a home-made Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.54 V vs. Ag/AgCl). Spectroelectrochemistry was conducted with an electrolytic cell which 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 characterization of PDs

The PD derivatives in this study are grouped as two series according to the molecular geometries. Series 1 PDs are the derivatives with molecular symmetry perpendicular to the *N*-phenylene-*N* axis (the free rotation of the diarylamino groups in solution at room temperature is assumed), and thus the molecules have equivalent nitrogen sites in terms of the chemical structure. Series 2

PDs are the derivatives in which the two *N*-phenylene-*N* nitrogen atoms are chemically different.

*N,N,N',N'*-Tetraaryl-*p*-phenylenediamine derivatives possess two electroactive amine *N* centers, which are easy to oxidize. For example, the cyclic voltammogram of NPD2 shows two redox couples at  $E_{1/2} = 0.94$  and 1.28 V vs. Ag/AgCl in  $\text{CH}_2\text{Cl}_2/0.1$  M TBAP solution (Fig. 2) referring to two reversible oxidations. The other PDs also show two sequential, reversible oxidation waves and their oxidation potentials are listed in Table 1. The substituent effect on the redox potentials for triphenylamine systems has been studied in 1991 [16]. It is also noted that the redox potentials of both Series 1 and Series 2 PDs agree with the order predicted from the electron-donating-withdrawing properties of the substituents at the phenyl group, the Hammett relationship [17]. The two redox potentials in  $\text{CH}_2\text{Cl}_2$  solution versus the substituent constant ( $2\sigma$ ) are thus plotted as Fig. 3.

The amine *N* atoms in Series 1 PDs are chemically equivalent, meaning that the electrons are populated equally on the two atoms. Removal of the first electron is assumed from the nonbonding orbital of either one of the *N* atoms. The oxidation potentials are controlled

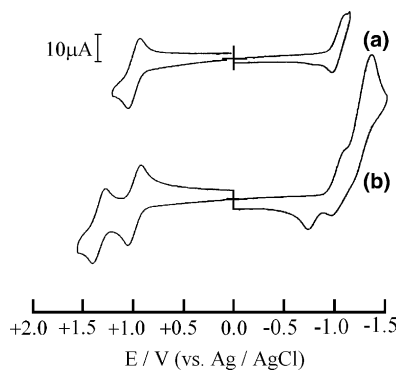


Fig. 2. Cyclic voltammogram of NPD2 in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP. Scan rate = 0.1 V/s.

Table 1

Half-wave potentials (V vs. Ag/AgCl) of PDs in  $\text{CH}_2\text{Cl}_2/\text{TBAP}$  and the  $2\sigma$  values of the substituents

Compound	2nd $E_{1/2}$	1st $E_{1/2}$	$\Delta E^a$	$2\sigma^b$
NPD1	1.28	1.00	0.28	2.540
NPD2	1.28	0.94	0.34	2.540
CPD1	1.26	0.93	0.33	2.000
CPD2	1.27	0.91	0.36	2.000
MPD1	0.97	0.52	0.45	-0.536
MPD2	0.97	0.48	0.49	-0.556
APD1	0.70	0.40	0.30	-1.320
APD2	0.71	0.34	0.37	-1.320

Scan rate = 0.1 V/s.

<sup>a</sup>  $\Delta E = 2\text{nd } E_{1/2} - 1\text{st } E_{1/2}$ .

<sup>b</sup> The Hammett substitution constants are obtained from Chem. Rev. 91 (1991) 165.

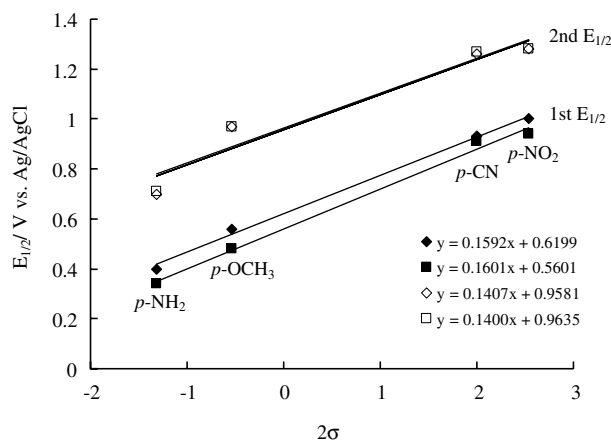


Fig. 3. Plot of half-wave potentials vs.  $2\sigma$  for PDs.

by the  $\pi$ -electron structures, therefore, it is likely to observe the Hammett relation for Series 1 PDs. From the molecular viewpoints, the amine *N* atoms in Series 2 PDs are not chemically equivalent and, therefore, the electron populations are affected by the substituents. For example, the *N* atom close to the methoxy groups is electron richer than the *N* atom on the other side. On the other hand, the *N* atom close to the nitro groups

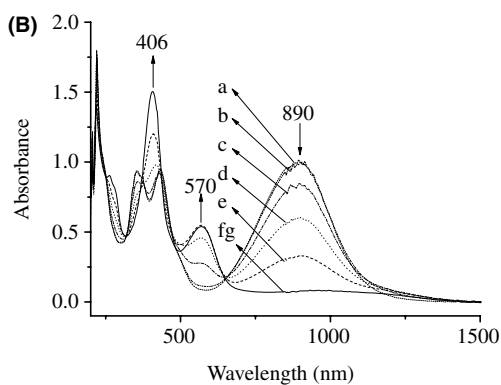
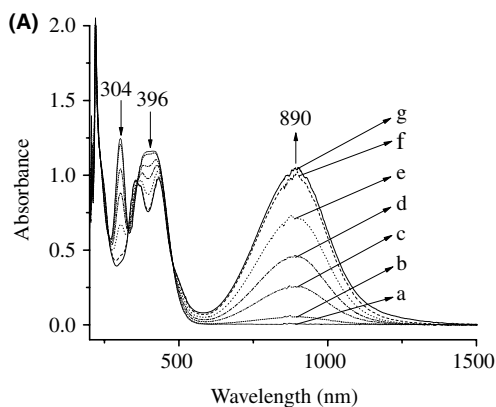


Fig. 4. Absorption spectral change of  $1 \times 10^{-3}$  M NPD2 in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP. (A)  $E_{\text{appl.}}$  = (a) 0.76; (b) 0.85; (c) 0.91; (d) 0.94; (e) 0.97; (f) 1.03; (g) 1.10 V. (B)  $E_{\text{appl.}}$  = (a) 1.13; (b) 1.19; (c) 1.25; (d) 1.28; (e) 1.31; (f) 1.37; (g) 1.46 V.

is electron deficient compared to the *N* atom on the other side. The first electron removal may involve the electron richer *N* atom if the electrons are populated in a localized way. The fact is that the first oxidation potentials of Series 2 PDs also follow the Hammett behavior, meaning that the electron is removed from the orbital in which both amine *N* atoms are contributed.

As the substituents vary from electron-withdrawing to electron-donating groups, generally, the first half-wave potentials of Series 2 PDs usually occurred at less positive potentials by 0.02–0.08 V than Series 1 PDs. Series 1 and Series 2 PDs possess a similar Hammett slope (the  $\rho$  value), which reflects the sensitivity of the reaction to the electronic effect of the substituents. Noticeably, the second half-wave oxidation potentials are exactly the same for corresponding Series 1 and Series 2 PDs. The cation radicals are oxidized at the same potentials, indicating the similarity in the electronic structure for the singly oxidized state and thus implying the high electronic coupling for the PDs.

The electronic coupling constant of two diabatic (noninteracting) states describes the communication between the redox centers [2,5,11]. The relationship between  $\Delta E$  (the difference of the first and the second oxidation redox potentials) and the coupling constant has been discussed [18]. It was reported that the statistical  $\Delta E$  value for non-interacting centers is 35.6 mV [2],

while larger redox potential splitting corresponds to more communication between the redox centers. In our study, the  $\Delta E$  for all PDs lies between 280 and 490 mV in  $\text{CH}_2\text{Cl}_2$ , comparable to the potential separation for *N,N,N',N'*-tetra-4-methoxyphenyl-*p*-phenylenediamine (485 mV) and other TPA-based PDs [2]. The electronic interactions between the two amine *N* atoms in PDs can be further proved by UV/vis/NIR spectroelectrochemistry.

### 3.2. Spectroelectrochemical characterization of PDs

Typically, neutral PDs exhibited absorption maxima at around 300 nm in  $\text{CH}_2\text{Cl}_2$ , which is characteristic of TPA chromophores [2,13]. The absorption maxima for amino-, cyano- and methoxy-substituted PDs deviate from 300 nm by 5–44 nm and nitro-substituted PDs exhibited absorption maxima at about 300 and 400 nm, suggesting that these substituents involved in the electronic interaction. Significant interaction was found in cyanovinyl-substituted triarylaminines, where an intense band at around 500 nm was observed [19].

Fig. 4 shows the spectral changes for NPD2 at various electrode potentials. The absorption peaks at 304 and 396 nm are characteristic for NPD2. After one-electron oxidation, the peaks decreased gradually while two new split peaks at 356 and 432 nm and a very broad and

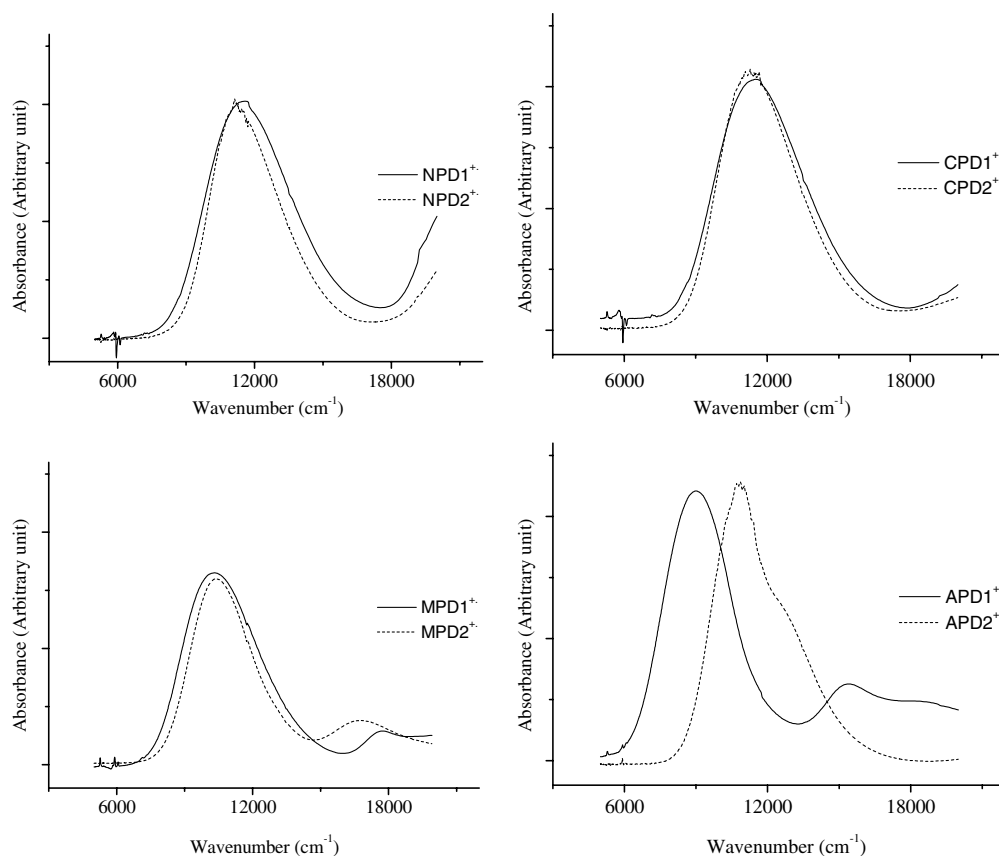


Fig. 5. NIR bands of cation radicals for all PDs from spectroelectrochemistry in  $\text{CH}_2\text{Cl}_2/0.1$  M TBAP.

intense band at 890 nm appeared (Fig. 4(A)). The spectral pattern was similar to that of  $\text{NPD1}^{+\cdot}$  and was assigned as the cation radical  $\text{NPD2}^{+\cdot}$  [13]. The spectrum of NPD2 was recovered when the applied potential was stepped back to +0.76 V. The reversibility was 95% based on the absorbance at 304 nm. In fact, upon the first electron oxidation to the monocation radicals, all PDs showed good stability and reversibility.

When the potential was adjusted to more positive values, corresponding to the second electron oxidation, the spectral change was shown as in Fig. 4(B). The characteristic peaks for  $\text{NPD2}^{+\cdot}$  disappeared and new bands at 406 and 570 nm appeared. When the applied potential was stepped back to 1.13 V, only 20% absorbance remained, implying that the oxidation product (dication) was not stable. The second oxidation product for CPD2 is also unstable. The dication may undergo follow-up chemical reactions in the media as shown in the previous study on the anodic oxidation of 1,4-diaminobenzene in methanol/water mixture [20]. However, the second oxidation products for MPD2 and APD2 reflected good stability. The electron-donating properties of methoxy and amino substituents contribute to the stability of dications.

The cation radicals of PDs are characterized by the NIR absorption bands, which are not attributed to the system subunits (localized TPA) or to the bridging spacer (phenylene). The spectra are very similar to the cation radicals of symmetric PDs in the previous studies [2,5], implying that the unsymmetric PDs (both Series 1 and Series 2) in this report are also delocalized states after one-electron transfer. Fig. 5 shows the NIR bands for the cation radicals in wavenumbers. The absorption maxima and band shape for the cation radicals in Series 1 PDs are very similar to those of Series 2 PDs, indicating the almost identical HOMO–LUMO energy gaps. The exceptional deviation for  $\text{APD1}^{+\cdot}$  and  $\text{APD2}^{+\cdot}$  spectra suggests that the peripheral amino group is also involved in the oxidized state. The absorption peaks at higher wavenumber for methoxy- and amino-substituted PDs are expected from the electronic transition of localized triphenylamine cation radicals [2].

#### 4. Conclusions

Structurally isomeric PDs with various electron-donating and -withdrawing substituents were synthesized. The two redox-active nitrogen centers linked by phenylene group are responsible for the two reversible redox couples in the oxidative scans. A direct evidence of electronic delocalization for PDs in the singly oxidized states can be obtained by electrochemical and spectral methods. The estimation of the electronic coupling and the reorganization energy from the NIR

absorption bands using semiclassical Marcus model will be further studied.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jelechem.2005.01.010.

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