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Electrochemically Controlled Multiple Hydrogen Bonding between Triarylamines and Imidazoles

Hsu-Chun Cheng,[†] Kuo Yuan Chiu,[†] Yi-Jung Tu,[†,‡] Te-Fang Yang,*,[†] and Yuhlong Oliver Su*,[†,‡]

Department of Applied Chemistry, National Chi Nan University, 1 University Road, Puli 545, Nantou, Taiwan, and Department of Chemistry, National Chung Hsing University, 250, Kuo Kuang Road, Taichung 402, Taiwan

yosu@ncnu.edu.tw; tfyang@ncnu.edu.tw

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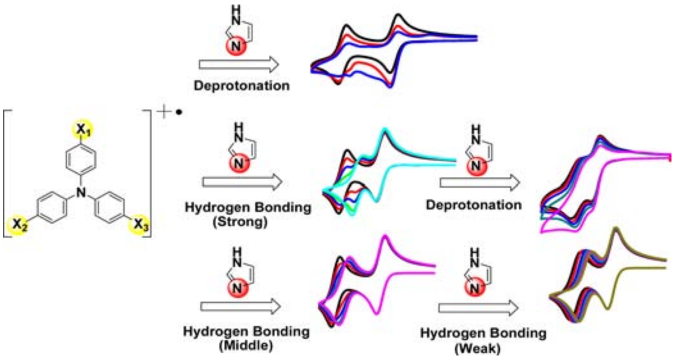
ABSTRACT



By increasing the number of amino substituents on triarylamine, the extent of hydrogen bonding between the oxidized form of triarylamine and imidazole could be electrochemically controlled. Three behaviors, depending on the interaction between oxidized amine and imidazole, were obtained in CV patterns. DFT calculation was used to confirm that the electron density of protons of the amino group decreased as the amino moiety increased.

Electrochemically controlled intermolecular hydrogen bonding has attracted much recent attention because of its unique electrochemical behavior and contribution to molecular designs in supermolecular chemistry.[1−9] The interaction between H-acceptor and H-donor could be monitored in real-time by cyclic voltammograms (CVs) and digital simulation. Similar model systems of electrochemically induced hydrogen bonding could be traced to the report of the interaction between reduced lariat ethers and metal ions.[10] Two potential shift modes, called binary and incremental, were classified according to the binding strength. The potential shift modes of binary and incremental would exhibit two resolved waves or a shifted wave, respectively. The primary interaction found by those studies between the H-acceptor and H-donor is 1:1, and it occurs in the reductive aspect of CVs.[2−8] The case of phenylenediamines and pyridine is an example of hydrogen bonding that was induced in the oxidation part of CVs.[11]

[†] National Chi Nan University.

[‡] National Chung Hsing University.

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The unusual electrochemical behavior, potential inversion, occurs because the potential of the dication is more negative than that of the cation radical, due to the strong hydrogen bonding. The hydrogen bond strength has been effected by the different *para*-position substituents on a phenyl group.

Although numerous formations and properties of hydrogen bonding have been investigated over the past several years,[12] there is a lack of information about the binding extent of hydrogen bonding that is induced electrochemically, especially in the oxidation aspect of CVs and at multiple hydrogen bonding active sites.

Herein, we have systematically studied the effect of *para* amino substituents in triarylamines (Figure 1) on the induced hydrogen bonding in the presence of imidazole (HIm) and 1-methylimidazole (MeIm) when triarylamines are oxidized. The amino group acts not only as the binding site of a hydrogen bond but also as the electron-donating group. With the increase in the redox nitrogen center, the charge has been shared over the whole molecule when the triarylamine was oxidized. The distribution of the charge would affect the extent of hydrogen bonding interaction between the oxidized triarylamines and imidazole.

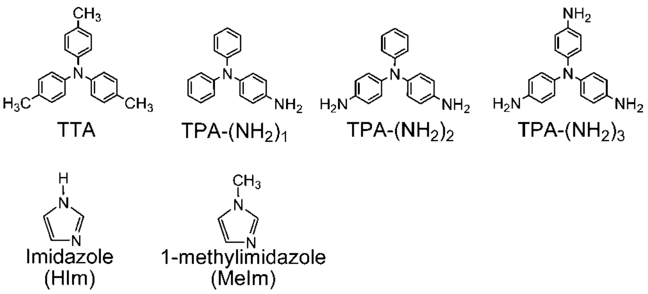

Figure 1. Chemical structures of the triarylamines and imidazoles in this study.

Figure S1 of the Supporting Information shows the CV of tritolylamine (TTA) in the absence and presence of imidazoles in CH_3CN. The CVs remained unchanged, indicating no significant interaction between $TTA^{+\bullet}$ and imidazoles. This indicated that the hydrogen bonding active site was located on the amino groups.

The triarylamines (TPA$-$(NH$_2$)$_x$) exhibit two reversible oxidation waves in CH_3CN in the range of $E = -0.50$ to $+1.20$ V, corresponding to the formation of the cation radical ([TPA-(NH$_2$)$_x$]$^{+\bullet}$) and dication ([TPA-(NH$_2$)$_x$]$^{+2}$) (Table. 1).[13] With the increase in the amino-substituent group, both of the redox couples shift negatively in potential due to the electron-donating effect.

In Figure 2, the CV of TPA-(NH$_2$)$_1$ shows two reversible redox couples at $E_1^{ox} = +0.55$ and $E_2^{ox} = +1.02$ V. As 0.50 equiv of HIm was added to the solution of TPA-(NH$_2$)$_1$, the first oxidative current increased but the second one decreased. Two new waves were observed at $E_{pa} = +0.95$ V and $E_{pc} = +0.21$ V. Addition of 1.00 equiv of HIm caused dramatic changes in the voltammetry as shown in Figure 2. The current at $E_{pa} = +0.58$ V greatly increased. In addition, the return peaks for TPA-(NH$_2$)$_1$ reduction further decreased, and new, broad oxidation peaks appeared at negative potentials. This indicated that a strong interaction was observed between the oxidized TPA-(NH$_2$)$_1$ and HIm. The irreversible redox couple has been attributed to deprotonation.[7]

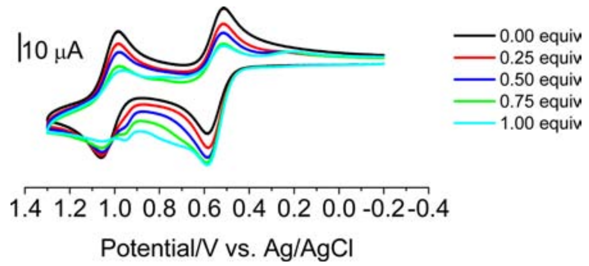

Figure 2. Cyclic voltammetry of 1.0×10^{-3} M TPA-(NH$_2$)$_1$ in 0.1 M TBAP/CH_3CN and various concentrations of imidazole. Scan rate = 0.1 V/s. Working electrode: glassy carbon (area: 0.07 cm^2).

TPA-(NH$_2$)$_2$ has two redox couples at $E_1^{ox} = +0.38$ and $E_2^{ox} = +0.73$ V (Figure 3, black line). In the presence of 0.50 equiv of HIm, the current of the second oxidation (at $E_2^{ox} = +0.73$ V) gradually decreased and the first oxidation slightly increased. The original second oxidation disappeared completely when 1.00 equiv is used. When HIm was added, the appearance of the new wave on the negative side of the second oxidation wave was assigned as the new second oxidation that is associated ($E_{2'}^{ox} = +0.58$ V) with HIm. The cathodic shift of the second redox couple is caused by the hydrogen bonding interaction between the oxidized TPA-(NH$_2$)$_2$ and HIm (Scheme 1),[8] and the shift in potential is -0.15 V. Upon adding over 1.00 equiv of imidazole, the second redox couple became irreversible, due to deprotonation (Supporting Information).[7] In order to understand the redox-dependent hydrogen bonding interaction between the oxidized TPA-(NH$_2$)$_2$ and HIm, we carried out digital simulation to fit the experimental CV.[15] Since previous models were well established by means of simulation, their values could be used here as a first approximation.[7,8] A good fit was obtained (Figure 3B), and the detailed parameters are displayed in the Supporting Information (Table S1).

For TPA-(NH$_2$)$_3$, there are two redox potentials at $E_1^{ox} = +0.20$ and $E_2^{ox} = +0.59$ V (Figure 4A). To our surprise, there was a two-step change in the second oxidation potential. Before 1.00 equiv of HIm was added to the solution, the value of the potential shift was only -0.07 V by two resolved wave mode. Addition of excess HIm can move the gradual potential shift wave in the cathodical

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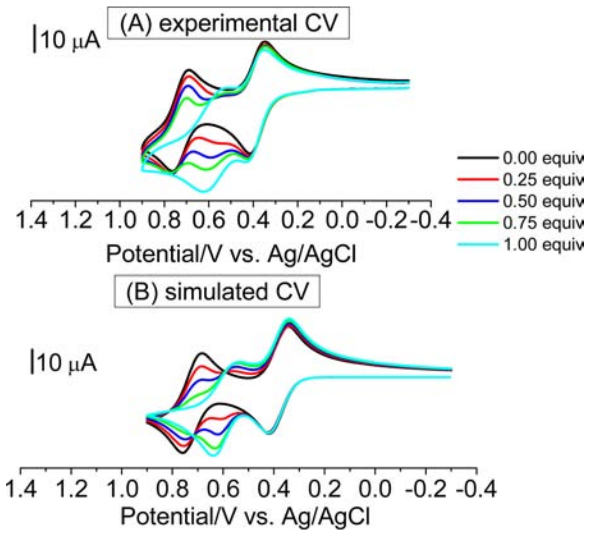
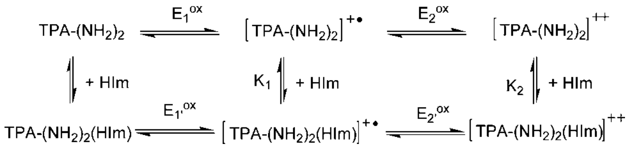


Figure 3. Cyclic voltammetry of 1.0 × 10^{-3} M TPA-$(NH_2)_2$ in 0.1 M TBAP/CH_3CN and various concentrations of imidazole. Scan rate = 0.1 V/s. working electrode: glassy carbon (area: 0.07 cm^2).

Scheme 1. Formation of Hydrogen Bonding between the Oxidized TPA-$(NH_2)_2$ and HIm



direction while the first oxidation wave has little change.[8] By using digital simulation (Figure 4B), the reaction mechanism (Scheme 2) and detailed parameters (Table S2 of the Supporting Information) of the interaction between oxidized TPA-$(NH_2)_3$ and HIm could be obtained.

To probe the effects of N–H on imidazole, 1-methylimidazole (MeIm) was used as the H-bond acceptor (see Supporting Information). The effects of N–H on MeIm were the same as those of N–H on the parent imidazole,

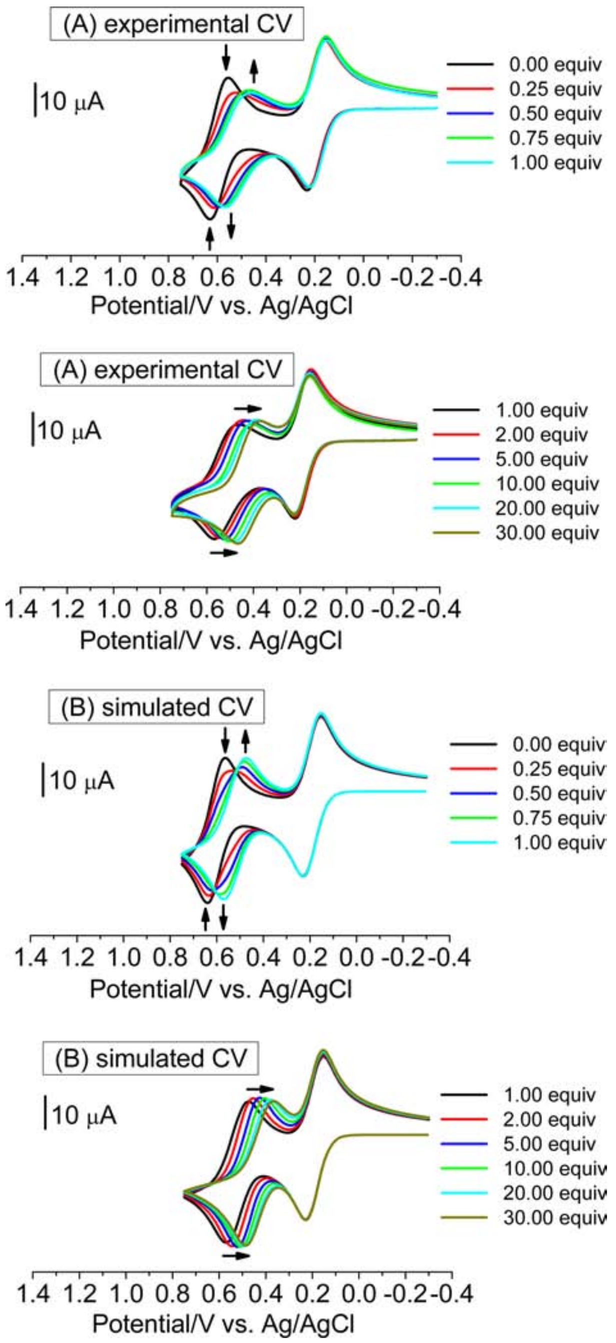


Figure 4. Cyclic voltammetry of 1.0 × 10^{-3} M TPA-$(NH_2)_3$ in 0.1 M TBAP/CH_3CN and various concentrations of imidazole. Scan rate = 0.1 V/s. working electrode: glassy carbon (area: 0.07 cm^2).

indicating that the sp^2 nitrogen atoms of imidazole were the primary active sites for hydrogen bonding.

These oxidation behaviors for TPA-$(NH_2)_x$ in the presence of HIm or MeIm can be qualitatively understood from a simple analysis of the structural features. When TPA-$(NH_2)_x$ was oxidized, the positive charge could be shared over the whole molecule, due to π-conjugation (phenyl bridge). This resulted in a weaker hydrogen bonding between TPA-$(NH_2)_x$ and HIm and no potential shift

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Scheme 2. Formation of Hydrogen Bonding between the Oxidized TPA-$(NH_2)_3$ and HIm

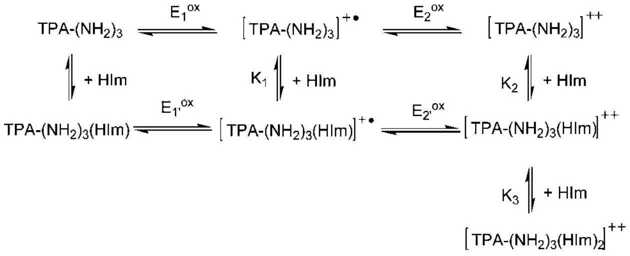

Table 1. Oxidation Potentials (V vs Ag/AgCl) of TPA-$(NH_2)_x$ in CH_3CN

molecule	cation radical	dication
TPA-$(NH_2)_1$	+0.55	+1.02
TPA-$(NH_2)_2$	+0.38	+0.73
TPA-$(NH_2)_3$	+0.20	+0.59

in the first oxidation. However, removal of a second electron produced a more positive charge on NH_2, resulting in a strong hydrogen bonding to HIm and thus the observed negative shift in the second oxidation wave. Thus, more NH_2 groups exhibited less positive charge on each NH_2, resulting in weaker hydrogen bonding between TPA-$(NH_2)_3$ and HIm. Consequently, a single shifted redox wave could be observed. In order to understand the Mülliken charge on each nitrogen and hydrogen atom of TPA-$(NH_2)_x$, the density functional theory (DFT) method in the Gaussian program has been adopted.[14] The geometries were optimized using the B3LYP function with the 3-21G basis set for C, H, and N atoms. As shown in Figure 5, the negative charge of a nitrogen atom of a TPA unit increased with the number of amino groups. It was also found that the negative charge value of a nitrogen atom on an amino-substituent unit increased. In contrast, the positive charge value of proton atoms on an amino-substituent unit decreased. Thus, with the increase in the negative charge on the amino groups, the order of the acidity of the protons on the amino substituents was found to be TPA-$(NH_2)_3$ < TPA-$(NH_2)_2$ < TPA-$(NH_2)_1$. Proton transfer (a strong interaction) could be observed between the oxidized TPA-$(NH_2)_1$ and HIm because of the strong acidity of the NH_2 protons. Thus, the electrochemically induced hydrogen bonding between the oxidized TPA-$(NH_2)_2$ and HIm could be also observed due to the decreased acidity of the NH_2 protons. When the NH_2 positive charge on NH_2 was smaller, such as in the dication of TPA-$(NH_2)_3$, the formation of hydrogen bonding was even weaker, resulting in a small potential shift.

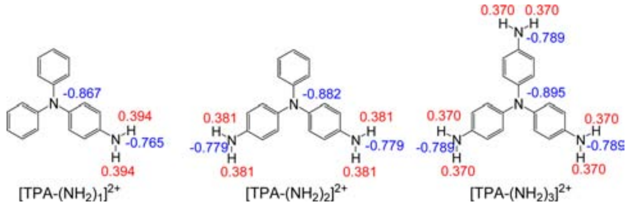

Figure 5. Charge distributions of $[\text{TPA-}(NH_2)_x]^{2+}$ molecules calculated by a DFT method at B3LYP/3-21G.

In conclusion, we reported an interaction between the induced oxidized TPA-$(NH_2)_x$ and imidazoles, using the electrochemical method. Using imidazole as a H-bond acceptor, hydrogen bonding between $[\text{TPA-}(NH_2)_x]^{+\bullet}$ and HIm occurred to a different extent with an increase in the number of amino groups. Accordingly, the electrochemical behaviors between $[\text{TPA-}(NH_2)_x]^{+\bullet}$ and imidazole are deprotonation, with strong and weaker hydrogen bonding when $x = 1, 2,$ and 3, respectively. In TPA-$(NH_2)_3$, a 1:2 ratio of an H-acceptor to the H-donor system was monitored in the oxidative aspect. To the best of our knowledge, this has been rare. The results might be useful for predicting the extent of hydrogen bonding in the electrochemically controlled system and further supermolecules.

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Supporting Information Available. Material on the experimental and simulated procedures for TPA-$(NH_2)_x$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The Digisim 3.03 Program from the BASi company was used in this study.

The authors declare no competing financial interest.