First Redox Polymer Bearing One-Step Successive Two-Electron-Transfer Process Based on Redox Potential Inversion

Toyohiko Nishiumi, Yuya Chimoto, Yuki Hagiwara, Masayoshi Higuchi, and Kimihisa Yamamoto*

Department of Chemistry, Faculty of Science & Technology, Keio University, Yokohama 223-8522, Japan

Received September 12, 2003
Revised Manuscript Received February 7, 2004

Introduction

The multielectron-transfer reaction is fundamentally one of the most important processes in chemical[1] and energy conversions.[2] Benzoquinone,[3] phenylenediamine,[4] and their derivatives,[5] which undergo a two-step two-electron-transfer reaction, have received much attention as key materials in the field of biological systems and energy storage.[2b] Generally, these compounds having two redox sites, in which two redox couples are observed during cyclic voltammetry (CV), show a two-step, two-electron-transfer ($A + e \rightleftharpoons B$: E_1; $B + e \rightleftharpoons C$: E_2), since the second electron-transfer (E_2) is more difficult than the first one (E_1) ($E°_2 < E°_1$) due to Coulombic repulsion[6] ("electron-transfer" is abbreviated E). In contrast, for the two-electron-transfer systems of the E_1E_2 process having a large redox-potential inversion[7] between the first electron-transfer (E_1) and the second one (E_2) ($E°_2 \gg E°_1$), it was investigated as a single redox couple using cyclic voltammetry.[8] The process is classified as a one-step successive two-electron-transfer. The molecules capable of a reversible and fast one-step, two-electron-transfer[9] are expected to be widely applied as an efficient electron-transfer mediator catalyst and as an electrode material in a polymer battery which has a high energy density. However, these compounds are very rare. Therefore, until now, most applications are based on the one-electron process, e.g., the redox couple for only the first one-electron process of polyaniline,[2b,10] which is well-known as a conducting polymer, that takes part in a polymer battery despite showing a two-step, two-electron transfer per two aniline units. In this study, we found a series of phenylenediamine molecules having a fast one-step successive two-electron-transfer which has a large redox potential inversion. Novel polymers with polyaniline units having the one-step, two-electron-transfer were synthesized. They possess a greater energy density when compared to that of conventional polyaniline.[11]

Experimental Section

General. The NMR spectra were recorded using a JEOL JMN400 FT-NMR spectrometer (400 MHz) in $CDCl_3$ + TMS internal standard solution. The MALDI−TOF mass spectra were obtained using a Shimadzu/Kratos KOMPACT MALDI mass spectrometer (positive mode; matrix: dithranol). The infrared spectrum was obtained from a potassium bromide pellet using a JASCO FT-IR-460Plus. The molecular weight was determined in THF solution using a TDA302 TriSEC detector (Viscotek) with Shodex GPC columns.

* Corresponding author: e-mail yamamoto@chem.keio.ac.jp.

Materials. Aniline, 2,3,5,6-tetramethyl-1,4-benzoquinone, S-BINAP, $Pd_2(dba)_3$, and *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) were purchased from the Aldrich Chemical Co. 2,3,5,6-Tetramethyl-1,4-benzoquinone, 2,5-dibromo-1,4-benzoquinone, and 4,4′-methylenedianiline were from Tokyo Kasei Co., Ltd. All other chemicals were purchased from the Kantoh Kagaku Co. The following compounds were prepared according to literature procedures: *N*,*N*′-diphenylanthraquinonediimine (AQI),[12a,b] *N*,*N*′-diphenylduroquinone-1,4-diimine (TMI),[12c] and *N*,*N*′-diphenyl-1,4-benzoquinone-1,4-diimine (PDI).

Synthesis of *N*,*N*′-Diphenyl-2,3,5,6-tetramethyl-1,4-phenylenediamine (TMA). Bromobenzene (3.96 g, 25.2 mmol), 2,3,5,6-tetramethyl-1,4-phenylenediamine (2.07 g, 12.6 mmol), sodium *tert*-butoxide (3.63 g, 37.8 mmol), $Pd_2(dba)_3$ (23 mg, 0.025 mmol), and S-BINAP (47 mg, 0.21 mmol) were dissolved in tetrahydrofuran (120 mL) in a Schlenk flask under argon. The reaction mixture was then heated to a gentle reflux. Analysis by TLC after 17 h showed complete consumption of the starting bromide. The mixture was cooled to room temperature, taken up in ethyl acetate (80 mL), and washed with a 2.0 M aqueous sodium hydroxide solution, followed by brine. The organic phase was dried over sodium sulfate, filtered, and concentrated. The TMA compound (1.31 g, 33%, white powder) was isolated by silica gel chromatography (hexane:dichloromethane = 1:1). TMA: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS standard, ppm) δ 7.16 (dd, J = 7.3, 7.3 Hz, 4H), 6.73 (t, J = 7.3 Hz, 2 H), 6.49 (d, J = 7.3, 4H), 5.22 (s, 2H), 2.17 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS) δ 146.8, 135.8, 133.1, 129.2, 117.7, 113.1, 15.4. IR (KBr, cm^{-1}) 3407, 1601, 1498, 1415, 1305, 1271, 747, 697. TOF-MS 315 $[M]^+$. Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.21; H, 7.50; N, 8.80.

Spectral DATA of TMI. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS standard, ppm) as mixture of two syn/anti isomers, δ 7.31 (dd, J = 7.8, 7.8 Hz, 4H), 7.06 (t, J = 7.8 Hz, 2 H), 6.82 (d, J = 7.8, 4H), 2.2 (br, 6H), 1.4 (br, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS) as mixture of two syn/anti isomers, δ 151.6, 128.8, 123.6, 119.9, 14.7. IR (KBr, cm^{-1}) 3050, 2921, 1578, 1481, 1229, 776, 752, 694. TOF-MS 315 $[M + H]^+$. Anal. Calcd for $C_{22}H_{24}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.99; H, 7.03; N, 8.98.

Synthesis of PTMI. Duroquinone (0.82 g, 5.0 mmol), 4,4′-methylenedianiline (0.99 g, 5.0 mmol), and DABCO (3.36 g, 30.0 mmol) were dissolved in chlorobenzene (60 mL). Titanium(IV) tetrachloride (1.42 g, 7.5 mmol) was dropwise added. The addition funnel was rinsed with chlorobenzene (10 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was then concentrated. The reaction mixture was reprecipitated in methanol. The cyclic oligomers were removed by GPC. PTMI (15%, orange powder) was then obtained. PTMI: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS standard, ppm) δ 7.02 (4H), 6.65 (4H), 3.86 (2H), 2.06 (6H), 1.27 (6H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS standard, ppm) δ 61.4, 149.4, 138.0, 136.8, 129.2, 120.1, 40.8, 15.3. IR (KBr, cm^{-1}) 3018, 2919, 1579, 1510, 1496, 1230, 818. Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 83.55; H, 6.81; N, 8.43. M_w = 25 100; M_w/M_n = 1.87.

The reductive PTMI was easily obtained using the following procedure. PTMI (100 mg, 0.31 mmol), $SnCl_2$ (0.58 g, 3.1 mmol,) and Sn (0.36 g, 3.1 mmol) were dissolved in MeCN (50 mL). Trifluoroacetic acid (0.35 g, 3.1 mmol) was added, and the reaction mixture was vigorously stirred at room temperature for 1 h and then triethylamine added for quenching. The precipitate was removed by filtration and concentrated. The reaction mixture was reprecipitated in methanol. The reduced PTMA (44 mg, 44%, white powder) was purified by silica gel chromatography (chloroform, ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS standard, ppm) δ 6.96 (4H), 6.38 (4H), 5.10 (2H), 3.76 (2H), 2.13 (12H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS standard, ppm) δ 144.8, 136.0, 132.7, 129.3,

10.1021/ma035370x CCC: $27.50
Published on Web 03/12/2004

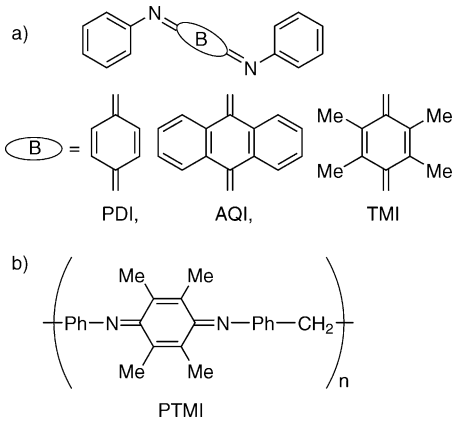

Figure 1. (a) PDI derivatives possessing two-electron-transfer process. (b) Novel polyaniline derivatives bearing one-step, two-electron-transfer unit.

125.4, 113.2, 30.3, 15.3. IR (KBr, cm^{-1}) 3388, 3011, 2913, 1655, 1612, 1510, 1467, 807.

Electrochemical Measurements. The electrochemical analyses were performed using an electrochemical workstation (BAS Co., Ltd., model ALS-660) under the following conditions. Cyclic voltammetry (CV) was carried out in an N_2 atmosphere. A glassy carbon (GC) disk electrode (0.071 cm^2) was used as the working electrode and polished with 30 μm alumina before the experiments. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/Ag^+ one, which was placed in the main cell compartment. The formal potential of the ferrocene/ferrocenium couple was 0.076 V vs this reference electrode in MeCN. All potentials are quoted with respect to this Ag/Ag^+ reference electrode. The potential was normalized to the ferrocene/ferrocenium couple in MeCN. The scanning rate was 100 mV/s. In all cases, a 0.2 M solution of tetrabutylammonium tetrafluoroborate ($TBABF_4$) in MeCN was used.

UV−Vis Spectroelectrochemical Analysis. The controlled-potential absorption spectra were obtained using an optically transparent thin-layer electrode quartz cell (light path length = 1 mm). The working and the counter electrodes were platinum mesh and a platinum coil, respectively. The potential was applied using a Hokuto-Denko potentio/galvanostat, model HA-501G, and referred to an Ag/Ag^+ reference electrode. The potential was normalized to the ferrocene/ferrocenium couple in MeCN. The spectra were measured using a Shimadzu UV-3150PC spectrophotometer. All spectroelectrochemical measurements were carried out at ca. 25 °C under a nitrogen atmosphere.

Results and Discussion

N,*N*′-Diphenyl-1,4-benzoquinonediimine (PDI) showing a stable two-electron redox function in the presence of a Lewis acid[4a] is the redox unit structure of polyaniline. We found that the potential gap (ΔE) between first electron ($E°_1$) and second one ($E°_2$) decreases by the introduction of a more bulky unit in the phenyl ring at the center of the PDI (SI Table 1, Supporting Information), and the *N*,*N*′-diphenylanthraquinonediimine (AQI)[12a,b] and *N*,*N*′-diphenyl-2,3,5,6-tetramethyl-1,4-benzoquinonediimine (TMI)[12c] (Figure 1), which have a moderate steric hindrance, show a one-step successive two-electron-transfer. In the presence of a Lewis acid, AQI and TMI show a sharp and single two-electron reversible redox couple at the potentials of 0.03 and 0.30 V (vs Fc/Fc^+), respectively (Figure 2a). For the one-electron-transfer process during cyclic voltammetry, the potential peak separation (ΔE_p) between the anodic (E_{pa}) and cathodic (E_{pc}) peaks is determined to be 57 mV at 25 °C;[8] however, for AQI and TMI, the

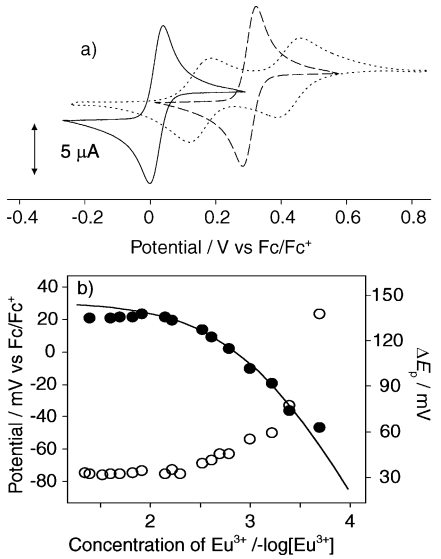

Figure 2. (a) Cyclic voltammograms of PDI (0.2 mM, dotted line), AQI (0.2 mM, solid line), and TMI (0.2 mM, dashed line) in MeCN solution containing 1.0 M trifluoroacetic acid and 0.2 M $TBABF_4$. (b) Nernst plot of 0.2 mM AQI with Eu^{3+}: experimental (●), theoretical curve obtained from condensation profile (solid line), and relative ΔE_p (○) in MeCN solution containing 0.2 M $TBABF_4$.

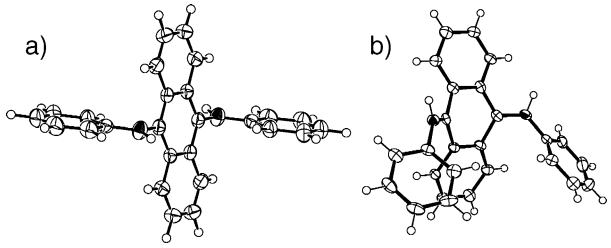

Figure 3. ORTEP diagrams of (a) the AQA and (b) its dication (as the perchlorate salt).

ΔE_p values are 30 and 34 mV, respectively. The redox wave of AQI is in good agreement with the shape of the two-electron-transfer wave (28.5 mV at 25 °C) in the CV. Their peak currents (I_{pa} and I_{pc}) are more than 2 times higher than that of the one-electron-transfer compounds. Digital simulations of the CV[14] and differential pulse voltammetry (DPV)[15] reveal that the ΔE_p of AQI is at least −180 mV (SI Figure 1). These results indicate a one-step successive two-electron-transfer process.

In the Nernst plots of AQI in the presence of europium(III) trifluoromethanesulfonate (Eu^{3+}),[16,17] a flat area was observed below $-\log[Eu^{3+}] < 2.5$ (Figure 2b). The ΔE_p in this region showed 30 ± 1 mV (SI Figure 4c) with a 180 mV potential inversion (SI Figure 1). The lack of a slope in the Nernst plots means that the Eu^{3+} ion transfer does not participate in the electron-transfer. The AQI coordinated with Eu^{3+} ion on the two imine sites gives rise to only the one-step successive two-electron-transfer. The titration results of AQI with Eu^{3+} ion based on the UV−vis spectra also support the following mechanism.

$$AQI + H^+ \rightleftharpoons AQIH^+ \ (K_1),$$

$$AQIH^+ + H^+ \rightleftharpoons AQIH_2^{2+} \ (K_2)$$

$$AQIH_2^{2+} + e \rightleftharpoons AQA^{\bullet+} \ (E_1),$$

$$AQA^{\bullet+} + e \rightleftharpoons AQA^{12b} \ (E_2)$$

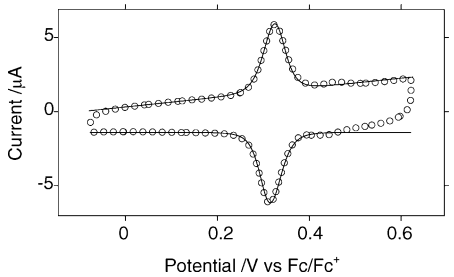

Figure 4. Cyclic voltammograms of (○) adsorbed PTMI on GC electrodes (0.071 cm^2) obtained in MeCN containing 1.0 M TFA and 0.2 M $TBABF_4$ at 100 mV/s. The amount of adsorbed PTMI was estimated to be 0.71 $\mu g/cm^2$. $E_{i/2}$ (the width at half current) of E_{pc} and E_{pa} and ΔE ($E_{pc} - E_{pa}$) were 57, 54, and 11 (mV), respectively. (dashed curve) Simulation. Parameter values: $T = 298$ K, $E°_2 = 0.302$ V, $k_{s,2} = 50\ s^{-1}$, $\alpha = 0.5$, $E°_1 = 0.342$ V, $k_{s,1} = 50\ s^{-1}$, $\alpha = 0.5$. The baseline of the anodic curve was corrected to fit.

Below $-\log[Eu^{3+}] = 2$, the spectrum change is saturated during the titration. The concentration profile of this equilibrium prepared using the theoretical UV−vis spectra shapes and theoretical titration curves (SI Figure 2) reveals that the first and second coordination constants (K_1 and K_2) are 5.0×10^3 and 3.0×10^2, respectively (SI Figure 3). The theoretical Nernst plot based on the concentration profile is in good agreement with the experimentally obtained one (Figure 2b). On the basis of the spectroelectrochemical analysis, the absorption of the radical cation was not detected in the redox reaction (SI Figure 5). These results supported the idea that the redox mechanism obeys the above scheme; i.e., AQI coordinated with two acids exhibits a one-step reversible two-electron-transfer.

The molecular structures of the dications as the proton coordinated oxidized form and the neutral *N*,*N*′-diphenylanthracene-9,10-diamine (AQA)[12b] form as the reduced state were confirmed by single-crystal X-ray analysis (Figure 3).[18] The redox reaction of AQI is accompanied by a significant conformation change between the reduction and oxidation forms; i.e., the *N*-phenyl ring rotates from syn to anti and the anthracene ring from bent to planar during the oxidation. We postulated that the redox potential inversion is based on this significant structural change. The speculation is also supported by MO calculations.

To explain the redox potential inversion arising from the large structural changes, the geometries of the neutral, radical cation, and dications were determined by a full optimization[19] of the conformation using the B3LYP density functional with 6-31G* as the basis set. The results from the X-ray crystal structures of the dications and neutral one determined the same structures. Since the crystal of the one-electron oxidized species could not be obtained due to the very small disproportionation constant, the calculated structure of the monocation radical state was used, which is reasonable because of the good agreement with the crystal and the calculated results and small difference (ca. 0.012 eV) in the structural energies of the ox and red forms. According to the Franck−Condon principle, a structural relaxation of the molecule occurs after the electron-transfer, which results in a change in the SOMO level. ΔU_{SOMO} is defined as the difference in each SOMO level between the radical cation with its optimized structure and with its conformation of the neutral state before the oxidation.[9a] The ΔU_{SOMO} values of PDI, AQI, and TMI were calculated to be 0.16, 0.61, and 0.63 eV, respectively. The large ΔU_{SOMO} means a greater structural relaxation energy. It is suggested that the increasing SOMO level due to the structural change results in the promotion of the second electron removal. The combination of the X-ray structural analysis and MO calculation reveals that PDI hardly changes the conformation during electron-transfer, but AQI and TMI drastically change after the one-electron oxidation (benzenoid, quinoid exchange),[9a] which is caused by the steric hindrance between the bulky anthracene or tetramethylbenzene unit and the outer *N*-phenyl rings when reduced to the benzenoid, and the bond to the *N*-phenyl rings was bent in the vertical direction. As a conclusion, the large potential inversion increasing the SOMO level after electron-transfer due to the steric hindrance at the center of the PDI promotes the second electron-transfer.

On the basis of these results, polyaniline derivatives (Figure 1b) bearing a one-step successive two-electron-transfer unit were synthesized by dehydration. The polymer adsorbed on the glassy-carbon electrode shows a reversible single redox wave at 0.32 V (vs Fc/Fc^+ in CH_3CN containing of 1.0 M TFA, Figure 4), which is much higher than that of the first redox couple of the polyaniline. The redox couple with a 54−57 mV half-wave width is ascribed to the one-step successive two-electron-transfer by the CV simulaton based on $\Delta E_{i/2} = 90.6/n$ mV, where n is the stoichiometric number of electrons and $n > 1.5$.[20,21] The absorption of the radical cation of PTMI was not detected in the redox reaction based on a spectroelectrochemical analysis. The fully oxidized form of the obtaind polymer is stable because the methyl substitution prevents the side reaction such as Michael addition or cross-linking,[11] The materials possessing one-step successive two-electron-transfer units based on the redox potential inversion are expected to be suitable for high-density energy storage due to suppression of the Coulombic repulsion and fast reversible multielectron-transfer. We first demonstrated that the novel polyaniline with a one-step, two-electron-transfer unit shows a stable redox at high potential with a higher energy density (163 A h/kg) (SI Figure 6) when compared to that of polyaniline.

Acknowledgment. We thank Dr. M. Shiro of Rigaku for his competent assistance in the crystallography. This work is partially supported by the CREST project from JST, a Grant-in-Aid for priority area, for scientific research, and 21st century COE program (Keio-LCC) from the MEXT, and a research grant from the Kanagawa Academy Science and Technology (Project No. 23).

Supporting Information Available: Calculation of absorbance simulation, condensation profile, electrochemical digital simulation, spectroelectrochemical analysis, CIF files, heterogeneous electron-transfer kinetics, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198. (b) Yamamoto, K.; Oyaizu, K.; Tsuchida, E. *J. Am. Chem. Soc.* **1996**, *118*, 12665.

(2) (a) Bulovic, V.; Gu, G.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *Nature (London)* **1996**, *380*, 29. (b) Oyama, N.; Tatsumi, T.; Sato, T.; Sotomura, T. *Nature (London)* **1995**, *373*, 598.

(3) (a) Gupta, N.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6384. (b) Lehmann, M. W.; Evans, D. H. *J. Electroanal.*

Chem. **2001**, *500*, 12. (c) Ganesan, V.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 2559. (d) Kamimura, T.; Nishiumi, T.; Higuchi, M.; Yamamoto, K. *Electrochem. Solid State Lett.* **2004**, *7*, H9.

(4) (a) Wolf, J. F.; Forbes, C. E.; Gould, S.; Shacklette, L. W. *J. Electrochem. Soc.* **1989**, *136*, 2887. (b) Boyer, M. I.; Quillard, S.; Louarn, G.; Froyer, G.; Lefrant, S. *J. Phys. Chem. B* **2000**, *104*, 8952.

(5) (a) Wegner, G.; Nakabayashi, N.; Cassidy, H. G. *J. Polym. Sci., Part A: Polym. Lett.* **1968**, *6*, 97. (b) Wegner, G.; Nakabayashi, N.; Duncan, S.; Cassidy, H. G. *J. Polym. Sci., Part A: Polym. Chem.* **1968**, *6*, 3395. (c) Nakabayashi, N.; Wegner, G.; Cassidy, H. G. *J. Org. Chem.* **1969**, *34*, 749. (d) Nakabayashi, N.; Wegner, G.; Cassidy, H. G. *J. Polym. Sci., Part A: Polym. Chem.* **1969**, *7*, 1269. (e) Yamamoto, K.; Asada, T.; Nishide, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1211. (f) Yamamoto, T.; Kimura, T.; Schiraishi, K. *Macromolecules* **1999**, *32*, 8886.

(6) (a) Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434. (b) Lindeman, S. V.; Rosokha, S. V.; Sun, D.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 843.

(7) (a) Evans, D. H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3983. (b) Hu, K.; Evans, D. H. *J. Electroanal. Chem.* **1997**, *423*, 29. (c) Speiser, B.; Würde, M.; Maichle-Mössmer, C. *Chem. Eur. J.* **1998**, *4*, 222. (d) Dümmling, S.; Speiser, B.; Kuhn, N.; Weyers, G. *Acta Chem. Scand.* **1999**, *53*, 876.

(8) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.

(9) (a) Bellec, N.; Boubekeur, K.; Carlier, R.; Hapiot, P.; Lorcy, D.; Tallec, A. *J. Phys. Chem. A* **2000**, *104*, 9750. (b) Guerro, M.; Carlier, R.; Boubekeur, K.; Lorcy, D.; Hapiot, P. *J. Am. Chem. Soc.* **2003**, *125*, 3159. (c) Hapiot, P.; Kispert, L. D.; Konovalov, V. V.; Savéant, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 6669.

(10) Pohl, H. A.; Engelhardt, E. H. *J. Phys. Chem.* **1962**, *66*, 2085.

(11) The two-electron oxidized form per two aniline units known as the pernigraniline form is not stable because the nucleophilic reactions easily take place; therefore, the second redox reaction is not available for the battery electrode. See following references for details. (a) Han, C.-C.; Jeng, R.-C. *Chem. Commun.* **1997**, 553. (b) Barbero, C.; Morales, G. M.; Grumelli, D.; Planes, G.; Salavagione, H.; Marengo, C. R.; Miras, M. C. *Synth. Met.* **1999**, *101*, 694. (c) Mikhael, M. G.; Padias, A. B.; Hall, Jr., H. K. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1673.

(12) (a) Hall, H. K., Jr.; Padias, A. B.; Williams, P. A.; Gosau, J.-M.; Boone, H. W.; Park, D.-K. *Macromolecules* **1995**, *28*, 1. (b) Ding, Y.; Boone, H. W.; Anderson, J. D.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **2001**, *34*, 5457. (c) Boone, H. W.; Bryce, J.; Lindgren, T.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1997**, *30*, 2797.

(13) (a) Yamamoto, K.; Higuchi, M.; Takai, H.; Nishiumi, T. *Org. Lett.* **2001**, *3*, 131. (b) Yamamoto, K.; Higuchi, M.; Nishiumi, T.; Takai, H. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1827.

(14) Rudolph, M.; Reddy, D. P.; Felberg, S. W. *Anal. Chem.* **1994**, *66*, 589A.

(15) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(16) The redox activation effect of Eu^{3+} is 100 times greater than that of the proton. See the Supporting Information (SI Figure 2, 4) and ref 3d for more details.

(17) In the case of proton addition, the third and fourth proton coordinations with the two-electron reduced PDI $2H^+$, which is not a related reaction for the one-step, two-electron-transfer mechanism, take places in concentrated acidic solution. However, the rare-earth metals such as Eu^{3+} act as a Lewis acid under mild conditions and prevent the extra coordination due to the size effect. See the following references for details. Nakajima, T.; Harada, M.; Osawa, R.; Kawagoe, T.; Furukawa, Y.; Harada, I. *Macromolecules* **1989**, *22*, 2644.

(18) teXsan. Single-Crystal Structure Analysis Software. Version 1.11. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, 1999.

(19) Gaussian 98 (Revision A.11): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 2001.

(20) (a) Laviron, E. *J. Electroanal. Chem.* **1979**, *100*, 263. (b) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *114*, 89. (c) Zhang, J. Anson, F. C. *J. Electroanal. Chem.* **1992**, *331*, 945.

(21) The analysis of the EE process on the surface was done by the included software. CHI750a Electrochemical Analyzer/ Workstation. Version 2.06J. CH Instruments, Inc., 3700 Tennison Hill Drive, Austin, TX 78738, 2001.

MA035370X