

A Novel Synthetic Metal Catalytic System

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π -Conjugate polymers, polyanilines and polypyrroles, served as catalysts in dehydrogenative oxidation reactions of benzylamines, 2-phenylglycine, and 2,6-di-*tert*-butylphenol under oxygen. The catalytic activity was controlled by protonic acid doping. The reversible redox of the polyaniline catalyst under oxygen was supported by UV-visible spectroscopy. Polyaniline and transition metal such as copper(II) chloride or iron(III) chloride formed a complex, which was effective in the dehydrogenative oxidation of cinnamyl alcohol or mandelic acid. In the complex system, transition metals are considered to electronically interact through a π -conjugate polymer chain. Protonic acid doping and transition metal doping play an important role in reversible redox processes of polyanilines.

Introduction

π -Conjugate polymers have received wide interest due to their high potential in a variety of applications as conducting polymers. Among π -conjugate polymers, polyanilines are particularly attractive based on their excellent electrical properties and stability.¹ An extensive investigation has been undertaken to hopefully provide more useful materials such as batteries,² light-emitting diodes,³ antistatic packagings and coatings,⁴ microelectronic devices,⁵ electrochemical chromatography,⁶ and corrosion inhibitors to protect semiconductors or metals.⁷

Polyanilines in various oxidation states interconvert each other, which permits us to construct a reversible redox cycle for catalytic reactions. In previous papers,⁸ we demonstrated that polyanilines serve as synthetic metal catalysts in dehydrogenative oxidation under oxygen. The catalytic activity has been revealed to be controlled by protonic acid doping. Coordination of transition metals to the nitrogen atoms affords the complexes, in which transition metals are considered to interact through a π -conjugate chain. The characteristics of π -conjugate polymers are reflected on the complexes, which are expected to provide a novel catalytic system. Complexation with copper(II) chloride or iron(III) chloride affords a more efficient synthetic metal catalyst in the dehydrogenation reaction.^{8a,9} The complex catalyst con-

sisting of palladium(II) acetate and polyaniline or polypyrrole is capable of inducing the Wacker oxidation.¹⁰ Efficient redox systems for the catalytic reactions are achieved in both cases. We describe herein the full scope of the novel synthetic metal catalytic systems based on the redox properties of polyanilines and polypyrroles.

Results and Discussion

Polyaniline-Catalyzed Dehydrogenative Oxidation of Benzylamines. A catalytic oxidative dehydrogenation of the benzylamine **1** proceeded on treatment with a catalytic amount of polyaniline under oxygen to give the *N*-benzylidenebenzylamine **2** (eq 1 and Table 1). The imine **2a** is considered to be derived by dehydrogenation to benzylideneamine and transamination with benzylamine. α -Disubstituted benzylamine **1b** was also oxidized to the corresponding imine **2b**, which was detected as the hydrolyzed product, benzophenone (run 18). *N,N*-Dimethylformamide (DMF) or 1-methyl-2-pyrrolidinone (NMP) was used as a solvent although polyaniline employed here was only partially soluble (runs 2 and 3). *N*-Benzylformamide was obtained as a byproduct in the former case via the amine exchange of DMF with benzylamine. The almost insolubility in acetonitrile or ethanol required a longer reaction time (runs 6 and 10). The blue supernatant of the heterogeneous acetonitrile mixture indicates the involvement of an oxidized form of polyaniline in the dehydrogenation reaction. Oxygen is essential for the catalytic reaction since only a small amount of **2a** was produced under nitrogen (run 5). A distinct difference in the yields of **2a** was not observed when the reaction was carried out in the dark (run 4).¹¹

The relationship between protonic acid doping and catalytic activity was studied because protonation of emeraldine base increases the conductivity of polyanilines.¹² Higher activity was attained with an increase of doping (run 9), but **2a** was produced only in 12% yield with the deprotonated polyaniline (run 11).

Electrochemical properties of polyanilines are known to depend on the polymerization method. A large differ-

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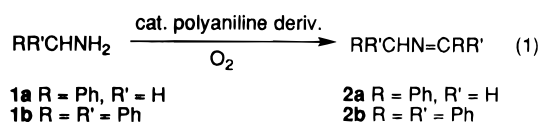
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Table 1. Oxidation of 1^a

run	substrate	cat.	oxidant for polymzn	anal.	atm	solvent	time, h	yield, %
1	1a	—	—	—	O ₂	MeCN	50	trace
2	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	O ₂	NMP	10	77
3	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	O ₂	DMF	10	74
4	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	O ₂	DMF	10	69 ^b
5	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	N ₂	DMF	10	15
6	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	O ₂	EtOH	40	53
7	1a	polyaniline	(NH ₄) ₂ S ₂ O ₈	C _{6.00} H _{6.71} N _{1.00} Cl _{0.55}	O ₂	MeCN	50	79
8	1a	polyaniline	VO(OEt)Cl ₂	C _{6.00} H _{4.04} N _{0.99} Cl _{1.28}	O ₂	MeCN	50	87
9	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{3.93} N _{1.00} Cl _{0.44}	O ₂	MeCN	50	75
10	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	O ₂	MeCN	50	61
11	1a	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.28} N _{0.97}	O ₂	MeCN	50	12
12	1a	polyaniline ^c	(NH ₄) ₂ S ₂ O ₈	C _{6.00} H _{5.18} N _{0.98} Cl _{0.52}	O ₂	NMP	10	77
13	1a	polyaniline ^c	(NH ₄) ₂ S ₂ O ₈	C _{6.00} H _{4.20} N _{0.96} Cl _{0.02}	O ₂	NMP	10	4
14	1a	poly(<i>o</i> -anisidine)	(NH ₄) ₂ S ₂ O ₈	C _{7.00} H _{6.98} N _{0.97} Cl _{0.38}	O ₂	MeCN	50	65
15	1a	poly(<i>o</i> -toluidine)	(NH ₄) ₂ S ₂ O ₈	C _{7.00} H _{7.89} N _{0.98} Cl _{0.28}	O ₂	MeCN	50	86
16	1a	poly(<i>N</i> -methylaniline)	(NH ₄) ₂ S ₂ O ₈	C _{7.00} H _{6.70} N _{1.02} Cl _{0.26}	O ₂	MeCN	50	91
17	1a	poly(3-(hexyloxy)aniline)	(NH ₄) ₂ S ₂ O ₈	C _{12.00} H _{15.50} N _{0.87} Cl _{0.74}	O ₂	MeCN	50	67
18	1b	polyaniline	Cu(BF ₄) ₂	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	O ₂	DMF	10	66
19	1a	polypyrrole	(NH ₄) ₂ S ₂ O ₈	C _{4.00} H _{3.60} N _{0.99} Cl _{0.28}	O ₂	MeCN	50	73
20	1a	polypyrrole	(NH ₄) ₂ S ₂ O ₈	C _{4.00} H _{3.60} N _{0.99} Cl _{0.28}	N ₂	MeCN	50	38
21	1a	poly(<i>N</i> -methylpyrrole)	(NH ₄) ₂ S ₂ O ₈	C _{5.00} H _{5.04} N _{0.97} Cl _{0.16}	O ₂	MeCN	50	74
22	1a	poly(<i>N</i> -methylpyrrole)	(NH ₄) ₂ S ₂ O ₈	C _{5.00} H _{5.04} N _{0.97} Cl _{0.16}	N ₂	MeCN	50	36

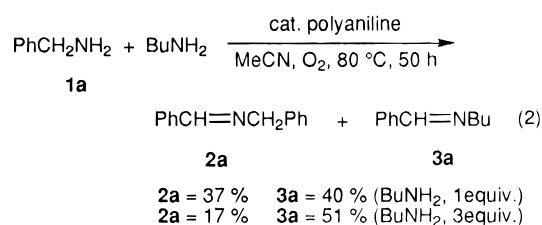
^a **1**, 1.0 mmol; cat., 10 mg; solvent, 1.0 mL. Reaction temperature, 80 °C. ^b In the dark. ^c Highly soluble polymer.

ence was not observed when polyanilines polymerized with (NH₄)₂S₂O₈ or Cu(BF₄)₂ were used in the dehydrogenative oxidation (runs 7 and 9). Use of the polyaniline polymerized with VO(OEt)Cl₂ gave a better result, because it is confirmed by elemental analysis to be highly protonated and oxidized (run 8).

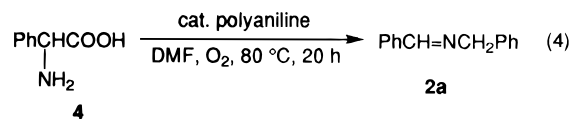
While various dopants such as dodecylbenzenesulfonic acid (DBSA) vary the solubility of polyaniline,¹³ highly soluble polyaniline with HCl as a dopant has been reported to be prepared by chemical oxidation with an equimolar of (NH₄)₂S₂O₈.¹⁴ Use of thus-obtained polyaniline in NMP, however, resulted in the similar yield of **2a** as observed above (run 12). Dedoping of the polyaniline again decreased the catalytic activity (run 13).

Substituent effects of polyaniline derivatives were studied. Poly(*o*-toluidine) and poly(*N*-methylaniline) showed a little higher activity (runs 15 and 16). High solubility of poly(3-(hexyloxy)aniline) did not affect the oxidation reaction much under the conditions employed here (run 17).

The reaction path of dehydrogenation has not been elucidated. Butylamine did not undergo the present dehydrogenation reaction. Catalytic oxidation of benzylamine in the presence of an equimolar amount of butylamine led to the imines **2a** and **3a** in 37% and 40% yields, respectively (eq 2). The unsymmetrical imine **3a** is considered to be derived by transamination with butylamine. Use of 3 mol equiv of butylamine raised the ratio of **3a**.



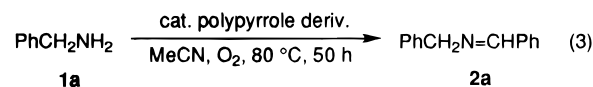
Polypyrrole-Catalyzed Dehydrogenative Oxidation of Benzylamine. Polypyrroles constitute a redox

Table 2. Oxidation of 4^a

run	polyaniline, anal.	yield, %
1	C _{6.00} H _{6.34} N _{0.98} Cl _{0.57}	40
2	C _{6.00} H _{4.50} N _{1.00} (BF ₄) _{0.11}	62
3	C _{6.00} H _{4.39} N _{0.98}	55

^a **4**, 1.0 mmol; polyaniline, 10 mg; DMF, 1.0 mL.

system like polyanilines, so they are expected to serve as synthetic metal catalysts. Indeed, polypyrrole and poly(*N*-methylpyrrole) catalyzed the dehydrogenation of **1a** to **2a** under oxygen (runs 19 and 21, and eq 3). The reaction, however, proceeded to some extent under nitrogen (runs 20 and 22), which is presumably accounted for by the over reduction of the pyrrole ring.¹⁵

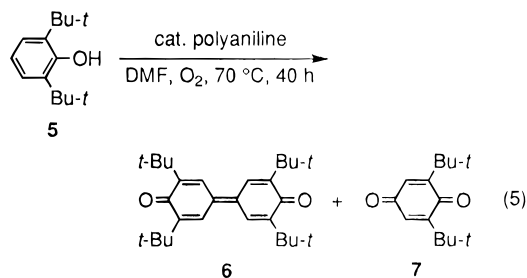


Polyaniline-Catalyzed Dehydrogenative Oxidation of 2-Phenylglycine. Polyaniline catalyst was effective in the oxidation of 2-phenylglycine (**4**) to give **2a** (eq 4 and Table 2). It should be noted that the dehydrogenation reaction of the amino moiety accompanies decarboxylation. The catalytic activity is controlled by protonic acid doping. Use of the less doped polyaniline led to the higher yield of **2a**, being in contrast to the finding that the doped polyaniline gave the better result in the oxidation of **1a**. Protonic acid doping is essential for smooth redox of polyaniline as described later, but

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Table 3. Oxidation of 5^a

run	polyaniline, anal.	yield, %		recovery of 5, %
		6	7	
1	—	trace	0	99
2	C _{6.00} H _{6.34} N _{0.98} Cl _{0.57}	33	0	66
3	C _{6.00} H _{4.49} N _{0.99} Cl _{0.01}	61	12	27
4	C _{6.00} H _{4.39} N _{0.98}	81	14	3

^a 5, 1.0 mmol; polyaniline, 10 mg; DMF, 1.0 mL.

the decarboxylation step in oxidation of **2a** is assumed to require the appropriate basicity of the catalyst.

Polyaniline-Catalyzed Dehydrogenative Oxidation of 2,6-Di-*tert*-butylphenol. The synthetic metal catalytic system is applied to the oxidative coupling of 2,6-di-*tert*-butylphenol (**5**) (eq 5 and Table 3). The phenol **5** was dimerized to the diphenoquinone **6**. One-electron oxidation of the phenolate seems to be involved as a reaction path. Higher conversion and yield were attained with the undoped polyaniline, although the *p*-quinone was formed via oxygenation. The results shown in Table 3 indicate that the similar reactivity of the catalyst is necessary as observed in the case of 2-phenylglycine.

Redox Behavior of Polyaniline. Catalysis appears to depend on the reversible redox cycle of polyanilines under oxygen. The redox process was monitored by UV-visible spectra of the partially soluble polyaniline as shown in Figure 1. The blue NMP solution showed a broad absorption around 640 nm assignable to charge transfer from benzenoid of polyaniline to quinoid.¹² The absorption disappeared on treatment with benzylamine under nitrogen at 80 °C (Figure 1b). The spectral change indicates that the charge transfer absorption decreases with reduction of a quinoid moiety to a benzenoid one. The absorption reappeared with coloring to blue only by bubbling oxygen into the mixture for 20 min. The oxidative interconversion of the leucoemeraldine base has been reported to be accomplished by oxygen leading to the emeraldine form.¹⁶

Protonic acid doping plays an important role in the redox behavior of polyaniline as mentioned above. To obtain further information of the redox behavior, *in situ* UV-visible spectra at a given redox potential were measured.¹⁷ The broad absorption around 640 nm based on charge transfer from benzenoid to quinoid and 340 nm peak based on $\pi-\pi^*$ transition of the phenyl ring were observed in NMP solution of the undoped polyaniline.¹² The broad 640 nm absorption successively increased and blue-shifted at a potential from 0.2 V to 0.5 V vs SCE (Figure 2a). The absorption around 340 nm inversely decreased at a positive potential. These spectral changes are explained by the partial electro-

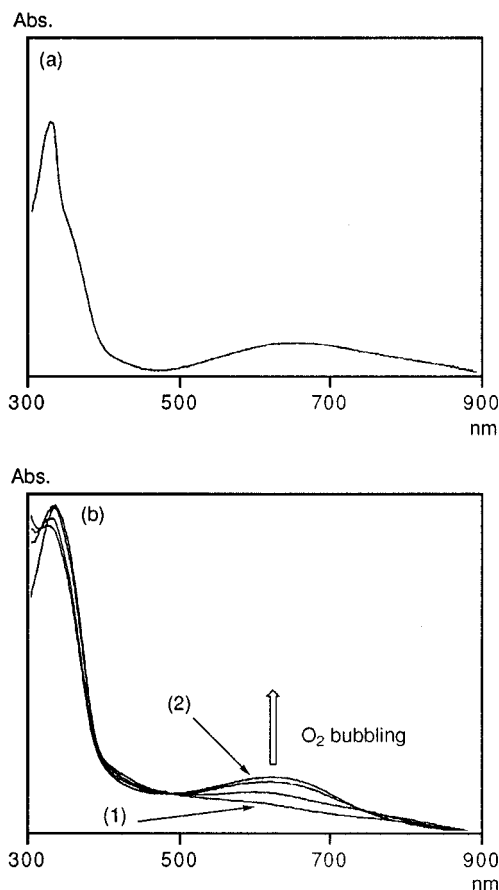


Figure 1. (a) UV-visible spectra of polyaniline (anal. C_{6.00}-H_{4.50}N_{1.00}(BF₄)_{0.11}) in NMP. (b) (1) Treatment with benzylamine under nitrogen at 80 °C for 2 h. (2) O₂ was bubbled into the solution at room temperature for 20 min.

chemical oxidation of the emeraldine form to the pernigraniline one bearing a quinoid structure. On the other hand, at a negative potential between 0.0 and -0.6 V, no hypochromic change was observed except for the slight red shift (Figure 2b). These results indicate that the undoped polyaniline is reduced with difficulty at a negative potential.

In contrast to the above-mentioned behavior, a hypochromic change occurred from 0.0 V to -0.6 V in the case of the protonic acid-doped polyaniline (Figure 3). The broad 620 nm absorption based on charge transfer increased at a positive potential, being accompanied by a blue-shift above 0.3 V. The 340 nm absorption based on $\pi-\pi^*$ transition accordingly decreased. These spectral changes imply that the protonic acid-doped emeraldine salt of polyaniline is oxidized to the pernigraniline form as observed in the undoped polyaniline. On the other hand, the broad 620 nm absorption decreased and the 340 nm one increased at a negative potential between 0.0 V and -0.6 V, indicating that the protonic acid-doped polyaniline is reduced to the leucoemeraldine form. This spectral redox behavior of the protonic acid-doped polyaniline was reversible between 0.5 and -0.6 V.

The above-mentioned results indicate that protonic acid doping is involved in the redox of polyaniline. The presence of a proton source permits the reduction of the quinoid moiety of polyaniline into the benzenoid one. In the undoped polyaniline solution, however, there is not enough a proton source to perform the reduction.

Dehydrogenative Oxidation with the Polyaniline-Transition Metal Complex. Doping of polyaniline with

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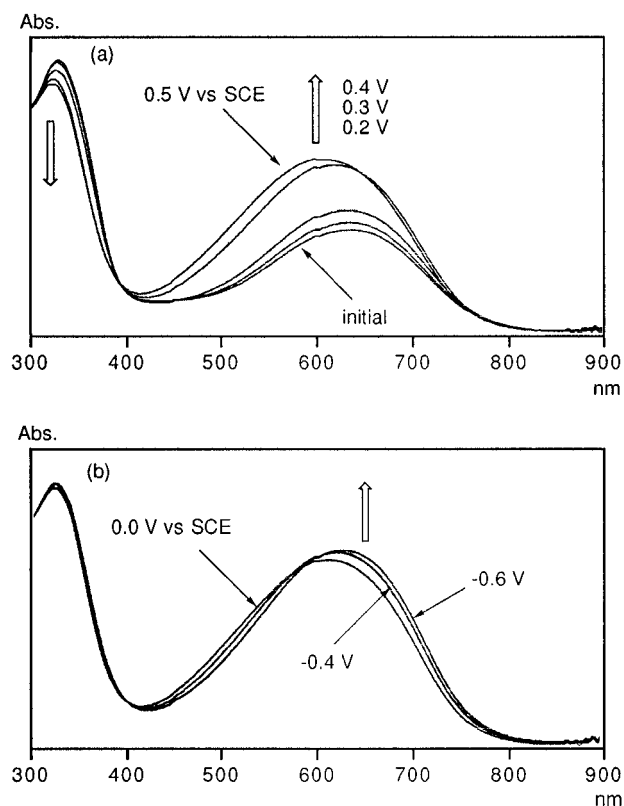


Figure 2. UV-visible spectra of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) in NMP. (a) Electrochemical oxidation. (b) Electrochemical reduction.

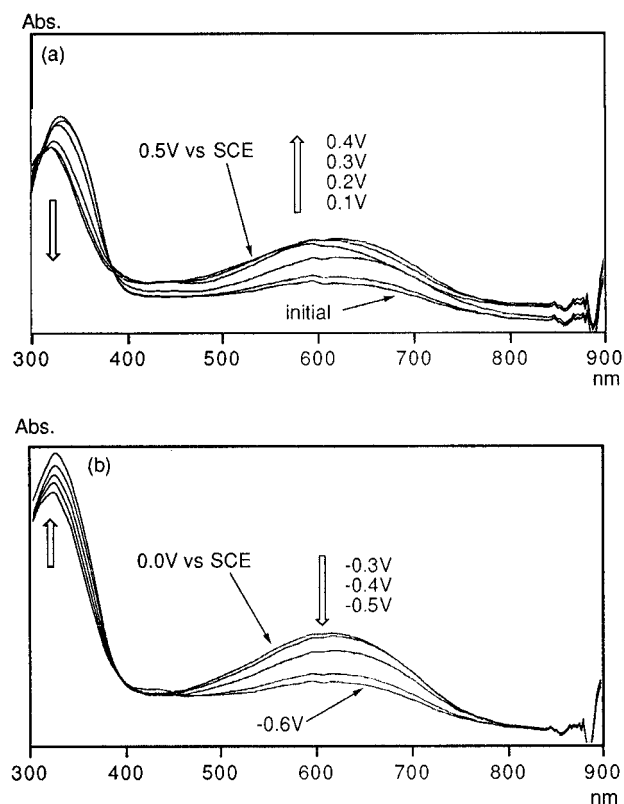
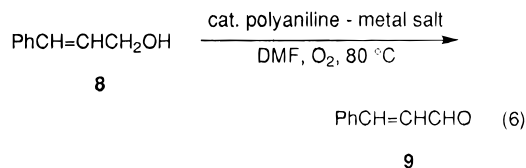


Figure 3. UV-visible spectra of the doped polyaniline (anal. $C_{6.00}H_{6.34}N_{0.98}Cl_{0.57}$) in NMP. (a) Electrochemical oxidation. (b) Electrochemical reduction.

copper(II) chloride constitutes an efficient catalyst for the dehydrogenation of cinnamyl alcohol (**8**) to cinnamaldehyde (**9**) in DMF (eq 6 and Table 4). The oxidation did

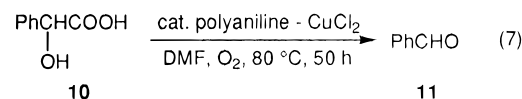
Table 4. Oxidation of 8^a



run	substrate	polyaniline, mg ^b	metal salt, equiv	atm	time, h	yield, %
1	PhCH=CHCH ₂ OH	10	—	O ₂	10	trace
2		—	CuCl ₂ 0.1	O ₂	10	5
3		10	CuCl ₂ 0.1	O ₂	10	44
4		20	CuCl ₂ 0.2	O ₂	10	68
5		10	CuCl ₂ 0.2	N ₂	10	9
6		10	FeCl ₃ 0.1	O ₂	20	39
7	PhCH ₂ OH	10	CuCl ₂ 0.1	O ₂	20	trace

^a **8**, 1.0 mmol; DMF, 1.0 mL. ^b Anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$.

Table 5. Oxidation of 10^a



run	polyaniline, anal.	CuCl ₂ , equiv	yield, %
1	—	0.1	6
2	$C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$	—	13
3	$C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$	0.1	32
4	$C_{6.00}H_{4.49}N_{0.99}Cl_{0.01}$	0.1	55

^a **10**, 1.0 mmol; polyaniline, 10 mg; DMF, 1.0 mL.

not proceed catalytically under nitrogen (run 5). A poor result was obtained with each individual component (runs 1 and 2), indicating that a combination of synthetic metal catalyst with copper(II) chloride is required for the oxidation. Increase in the catalytic amount of both components raised the yield of **9** (run 4). Iron(III) chloride was similarly used instead (run 6). Failure in the dehydrogenation of benzyl alcohol might be explained by the difference in their redox potentials (run 7).

The catalytic system was applicable to the decarboxylative dehydrogenation of mandelic acid (**10**) to give benzaldehyde (**11**, eq 7). The results shown in Table 5 indicate that the cooperative catalysis of polyaniline and copper(II) chloride is essential. The effect of protonic acid doping of polyaniline was observed as mentioned above. Use of the less doped polyaniline led to the better yield (runs 3 and 4).

Complexation of Polyaniline with Copper(II) Chloride. The insoluble species recovered in the oxidation reaction of **8** in the presence of copper(II) chloride in DMF involved one copper species to two aniline units of polyaniline ($C_{6.00}H_{5.82}N_{1.01}(BF_4)_{0.11}(CuCl_2)_{0.53}$). It suggests that the complexation of copper(II) chloride with polyaniline affords the real catalyst that induces the dehydrogenative oxidation reaction.

Complexation is supported by UV-visible spectra of the undoped polyaniline with copper(II) chloride. Addition of copper(II) chloride to the NMP solution of the polyaniline resulted in a blue shift of the absorption around 640 nm as shown in Figure 4a. This shift ($\Delta\lambda$) depended on the amount of copper(II) chloride giving the saturation curve for complexation (Figure 4b).

The cyclic voltammetry is also indicative of complexation. The half-wave potential of the undoped polyaniline-CuCl₂ complex in NMP was 0.46 V vs SCE, being in contrast to 0.29 V for that of the undoped polyaniline (Figure 5). The wave shape of the complex was broader.

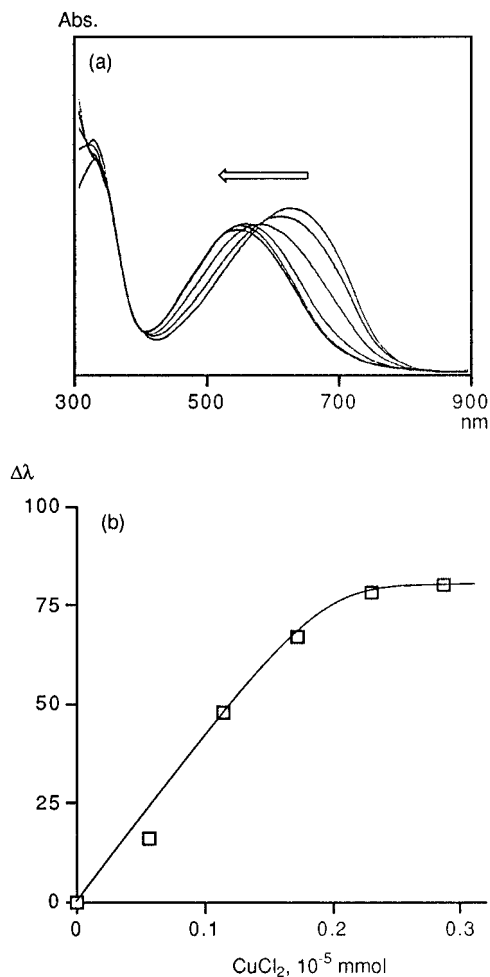


Figure 4. (a) UV-visible spectra of the undoped polyaniline (anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) in NMP on successive addition of $CuCl_2$ as shown in (b): plots of $\Delta\lambda$ vs the amount of $CuCl_2$.

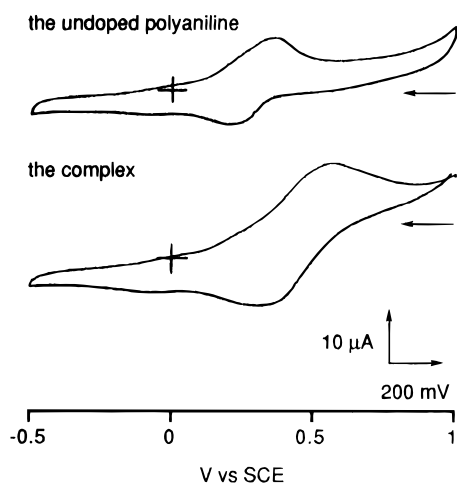


Figure 5. Cyclic voltammetry of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) and its complex with $CuCl_2$ in NMP. Scan rate is 50 mV s^{-1} .

These results appear to be accounted for by the complexation, which is considered to raise the catalytic activity.

Further studies on the redox behavior of the undoped polyaniline- $CuCl_2$ complex in NMP were done by *in situ* UV-visible spectra at a given redox potential.¹⁷ At 0.3 V vs SCE, the broad absorption around 600 nm based on charge transfer increased together with the blue shift. On the contrary, the absorption around 320 nm based

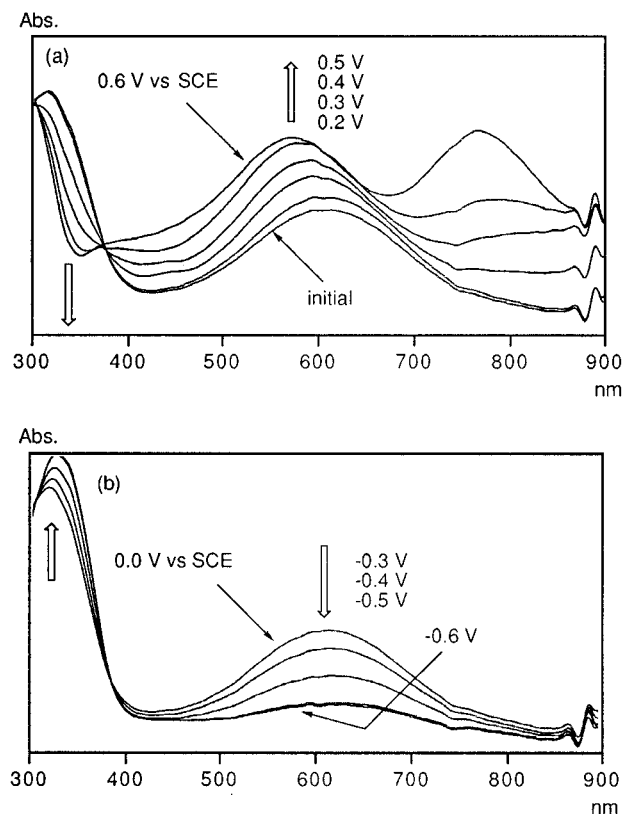
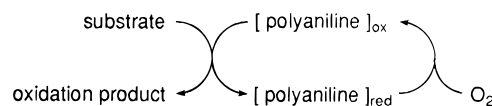


Figure 6. UV-visible spectra of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$)- $CuCl_2$ complex in NMP. (a) Electrochemical oxidation. (b) Electrochemical reduction.

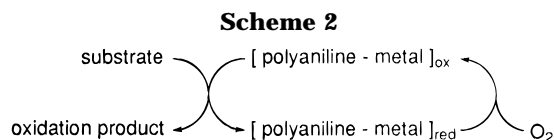
Scheme 1



on $\pi-\pi^*$ transition was reduced at the same potential. Similar spectral changes are obtained in the case of undoped and doped polyanilines. Such electrochemical behavior was observed between 0.2 and 0.5 V as illustrated in Figure 6a. A new absorption appeared around 780 nm at 0.6 V. At a negative potential below 0.0 V, the decrease of the broad absorption around 600 nm was accompanied by an increase in the one around 320 nm with isosbestic points (Figure 6b). These observations indicate that the polyaniline of the complex is partially reduced electrochemically to the leucoemeraldine form. The redox transformation was almost reversible between 0.6 and -0.6 V. Such a spectral change is similar to the one in protonic acid-doped polyaniline. In the complex catalytic system, a copper dopant is considered to contribute to the formation of a reversible redox cycle.

Conclusion

Polyanilines or polypyrroles serve as catalysts for the dehydrogenative oxidation of benzylamines, phenylglycine, and 2,6-di-*tert*-butylphenol under oxygen. The catalysis is considered to be based on the reversible redox of π -conjugate polymers (Scheme 1). The activity of the synthetic metal catalytic system is controlled by protonic acid doping. Complexes of polyaniline with transition metals such as copper(II) chloride or iron(III) chloride serve as synthetic metal complex catalysts in the



oxidation reaction (Scheme 2). In this system, transition metals are considered to be coordinated to polyaniline and electronically interact with each other through a π -conjugate chain. Since π -conjugate polymers are known to form a sequential potential field, the similar kind of field is considered to be attained in the complex system. The present systems are furthermore envisaged to provide combinational catalysis.

Experimental Section

Polyaniline Polymerized with Ammonium Peroxodisulfate. Polyaniline was prepared by chemical oxidation of aniline with ammonium peroxodisulfate in an acidic medium.⁵ A solution of aniline (20.4 g, 219 mmol) in 1 M HCl (300 mL) was placed in an ice/water bath and cooled. A solution of ammonium peroxodisulfate (11.5 g, 50.4 mmol) in 1 M HCl (200 mL) cooled in an ice/water bath was added dropwise to the solution of aniline over about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned dark green and the salt of polyaniline began to precipitate. After the addition of ammonium peroxodisulfate was completed, the mixture was stirred for additional 2 h. Polyaniline (4.49 g) was then filtered using a Büchner funnel, washed with 1 M HCl (300 mL), acetonitrile (300 mL), and then ether (300 mL), and dried in vacuum at room temperature for 24 h. The elemental analyses are shown in Table 1.

Polyaniline Polymerized with Cu(BF₄)₂. To aniline (0.93 g, 10.0 mmol) placed in an ice/water bath was added 42% HBF₄ aq (1.83 mL, 10.0 mmol) over 10 min. After the addition of 42% HBF₄ aq was completed, the mixture was stirred for additional 30 min. Cu(BF₄)₂ (4.74 g, 20.0 mmol) in acetonitrile (15 mL) was added to the solution, which was stirred in an ice/water bath for 2 h and at room temperature for 10 h. Workup and isolation of the polymer were carried out similarly as mentioned above. Polyaniline (0.86 g) was obtained as a black powder. Thus obtained polyaniline contains less than 2 ppm of copper species. The elemental analysis is shown in Table 1.

Polyaniline Polymerized with VO(OEt)Cl₂. To aniline (0.93 g, 10.0 mmol) placed in an ice/water bath was added 42% HBF₄ aq (1.83 mL, 10.0 mmol) over 10 min. After the addition of 42% HBF₄ aq was completed, the mixture was stirred for additional 30 min. VO(OEt)Cl₂ (2.47 mL, 20.0 mmol) in acetonitrile (15 mL) was added to the solution, which was stirred in an ice/water bath for 2 h and at room temperature for 10 h. Workup and isolation of the polymer were carried out similarly as mentioned above. Polyaniline (0.87 g) was obtained as a black powder. The elemental analysis is shown in Table 1.

Synthesis of Poly(3-(hexyloxy)aniline). To a mixture of K₂CO₃ (4.15 g, 30.0 mmol) and *m*-nitrophenol (2.78 g, 20.0 mmol) in acetonitrile (100 mL) was slowly added *n*-hexyl bromide (4.20 mL, 30.0 mmol) over 10 min. The mixture was refluxed for 30 h. The reaction mixture was filtered off and concentrated. 3-(Hexyloxy)nitrobenzene (3.00 g, yield 67%) was isolated by column chromatography eluting with chloroform. 3-(Hexyloxy)nitrobenzene (3.00 g, 13.4 mmol) in ethanol (30 mL) was treated with 3 atm of hydrogen in the presence of PtO₂ (50 mg, 0.22 mmol) at 60 °C for 3 days. After filtration of the reaction mixture, 3-(hexyloxy)aniline (2.20 g, yield 85%) was obtained by Kugelrohr distillation of the filtrate (oven temp 135 °C/0.5 mmHg); IR 3373, 2930, 1600 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.05 (t, 1H, *J* = 7.8 Hz), 6.33 (d, 1H, *J* = 7.8 Hz), 6.28 (d, 1H, *J* = 7.8 Hz), 6.25 (s, 1H), 3.92 (t, 2H, *J* = 6.6 Hz), 3.64 (br, 2H), 1.76 (quint, 2H, *J* = 6.6 Hz), 1.45 (m, 2H), 1.34 (m, 4H), 0.91 (t, 3H, *J* = 6.0 Hz). The solution of 3-(hexyloxy)aniline (2.20 g, 11.4 mmol) in 1 M HCl (50 mL)

was placed in an ice/water bath and cooled. A solution of ammonium peroxodisulfate (2.60 g, 11.4 mmol) in 1 M HCl (50 mL) cooled in an ice/water bath was dropwise added to the solution of 3-(hexyloxy)aniline over about 10 min with vigorous stirring. After the addition of ammonium peroxodisulfate was completed, the mixture was stirred in an ice/water bath for 90 min and at room temperature for 2 days. As the polymerization proceeded, the solution turned brown and the salt of poly(3-(hexyloxy)aniline) began to precipitate. The obtained polymer was then filtered using a Büchner funnel and washed with about 1 L of deionized water. The polymer was dissolved in DMF, reprecipitated in acetone, washed with ether (400 mL), and dried in vacuum at room temperature for 24 h. Poly(3-(hexyloxy)aniline) (1.00 g) was obtained as a black powder. The elemental analysis is shown in Table 1.

Highly Soluble Polyaniline Polymerized with Ammonium Peroxodisulfate.¹⁴ A solution of aniline (5.00 g, 50.4 mmol) in 1 M HCl (150 mL) was placed in an ice/acetone bath and cooled. A solution of ammonium peroxodisulfate (11.5 g, 50.4 mmol) in 1 M HCl (100 mL) cooled in an ice/acetone bath was added dropwise to the solution of aniline over about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned dark green and the salt of polyaniline began to precipitate. After the addition of ammonium peroxodisulfate was completed, the mixture was stirred for additional 2 h. Polyaniline was then filtered using a Büchner funnel, washed with 1 M HCl (300 mL), acetone (300 mL), and then ether (300 mL), and dried in vacuum at room temperature for 24 h. Polyaniline (4.77 g) was obtained as a black powder. The elemental analysis is shown in Table 1.

Poly(*o*-anisidine), Poly(*o*-toluidine), and Poly(*N*-methyl-aniline) Polymerized with Ammonium Peroxodisulfate. A typical procedure for polymerization is as follows. Poly(*o*-anisidine) was prepared by chemical oxidation of *o*-anisidine with ammonium peroxodisulfate in an acidic medium.⁵ A solution of *o*-anisidine (5.46 g, 44.3 mmol) in 1 M HCl (150 mL) was placed in an ice/water bath and cooled. A solution of ammonium peroxodisulfate (2.52 g, 11.1 mmol) in 1 M HCl (100 mL) cooled in an ice/water bath was added dropwise to the solution of *o*-anisidine over about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned dark green and the salt of poly(*o*-anisidine) began to precipitate. After the addition of ammonium peroxodisulfate was completed, the mixture was stirred for additional 2 h. Workup and isolation of the polymer were carried out similarly as mentioned above. Poly(*o*-anisidine) (0.99 g) was obtained as a black powder. The elemental analyses are shown in Table 1.

Dedoping of Polyaniline. The polyaniline obtained above was treated with an aqueous solution of 0.1 M sodium hydroxide at room temperature for 24 h with stirring in order to convert it to the undoped base, which was filtered using a Büchner funnel, washed with deionized water (300 mL), acetonitrile (300 mL), and then ether (300 mL), and dried in vacuum at room temperature for 24 h. The elemental analyses are shown in Table 1.

Polypyrrole. A solution of pyrrole (3.35 g, 50.0 mmol) in 1 M HCl (150 mL) was placed in an ice/water bath and cooled. A solution of ammonium peroxodisulfate (2.85 g, 12.5 mmol) in 1 M HCl (100 mL) cooled in an ice/water bath was added dropwise to the solution of pyrrole over about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned black and the salt of polypyrrole began to precipitate. After the addition of ammonium peroxodisulfate was completed, the mixture was stirred for additional 2 h. Polypyrrole was filtered using a Büchner funnel, washed with 1 M HCl (300 mL), acetonitrile (300 mL), and then ether (300 mL), and dried in vacuum at room temperature for 24 h. Polypyrrole (0.88 g) was obtained as a black powder. The elemental analysis is shown in Table 1.

Poly(*N*-methylpyrrole). A solution of *N*-methylpyrrole (2.03 g, 25.0 mmol) in 1 M HCl (150 mL) was placed in an ice/water bath and cooled. A solution of ammonium peroxodisulfate (5.71 g, 25.0 mmol) in 1 M HCl (100 mL) cooled in an ice/water bath was added dropwise to the solution of

N-methylpyrrole over about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned black and the salt of poly(*N*-methylpyrrole) began to precipitate. After the addition of ammonium peroxodisulfate was completed, the mixture was stirred for additional 2 h. Workup and isolation of the polymer were carried out similarly as mentioned above. Poly(*N*-methylpyrrole) (1.00 g) was obtained as a black powder. The elemental analysis is shown in Table 1.

Polyaniline-Catalyzed Dehydrogenative Oxidation of Benzylamine. A typical experimental procedure for the oxidation reaction of benzylamine is as follows. Polyaniline (10 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) was dried in vacuum in a reaction vessel. Benzylamine (107 mg, 1.00 mmol) in acetonitrile (1.0 mL) was added under oxygen. The mixture was stirred under oxygen at 80 °C for 50 h. Ether (2 mL) was added to the reaction mixture at room temperature. After stirring for 10 min, the mixture was filtered and concentrated. Yields of **2a** were determined by GLC (PEG 20M 10% 2.1 m, 200 °C).

Polyaniline-Catalyzed Dehydrogenative Oxidation of Aminodiphenylmethane. Polyaniline (10 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) was dried in vacuum in a reaction vessel. Aminodiphenylmethane (183 mg, 1.00 mmol) in DMF (1.0 mL) was added under oxygen. The mixture was stirred under oxygen at 80 °C for 10 h. Ether (2 mL) was added to the reaction mixture at room temperature. After stirring for 10 min, the mixture was filtered and concentrated. Ethanol (2 mL), deionized water (0.2 mL), and SiO₂ (1.0 g) were added to the mixture, which was stirred for 24 h. The mixture was filtered and concentrated. The yield of benzophenone was determined by GLC (PEG 20M 10% 2.1 m, 200 °C).

Polyaniline-Catalyzed Dehydrogenative Oxidation of 2-Phenylglycine. A typical experimental procedure for the oxidation reaction of 2-phenylglycine is as follows. Polyaniline (10 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) was dried in vacuum in a reaction vessel. 2-Phenylglycine (151 mg, 1.00 mmol) in DMF (1.0 mL) was added under oxygen. The mixture was stirred under oxygen at 80 °C for 20 h. Ether (2 mL) was added to the reaction mixture at room temperature. After stirring for 10 min, the mixture was filtered and concentrated. The yield of **2a** was determined by GLC (PEG 20M 10% 2.1 m, 200 °C).

Polyaniline-Catalyzed Dehydrogenative Oxidation of 2,6-Di-*tert*-butylphenol. A typical experimental procedure for the oxidation reaction of 2,6-di-*tert*-butylphenol is as follows. Polyaniline (10 mg; anal. $C_{6.00}H_{4.39}N_{0.98}$) was dried in vacuum in a reaction vessel. 2,6-Di-*tert*-butylphenol (206 mg, 1.00 mmol) in DMF (1.0 mL) was added under oxygen. The mixture was stirred under oxygen at 70 °C for 40 h. Ether (2 mL) was added to the reaction mixture at room temperature. After stirring for 10 min, the mixture was filtered and concentrated. The yields of **6** and **7** were determined by GLC (SE-30 1.0 m, 50–250 °C, 10 °C/min).

Dehydrogenative Oxidation of Cinnamyl Alcohol Catalyzed by the Polyaniline–Transition Metal Complex. A typical experimental procedure for the oxidation reaction of cinnamyl alcohol is as follows. A mixture of polyaniline (10 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) and copper(II) chloride (13.4 mg, 0.10 mmol) in DMF (1.0 mL) was stirred at room temperature for 30 min. Cinnamyl alcohol (134 mg, 1.00 mmol) was added to the resulting mixture, which was stirred under oxygen at 80 °C for 10 h. Ether (2 mL) was added to the reaction mixture at room temperature. After stirring for

10 min, the mixture was filtered and concentrated. Yield of **9** was determined by GLC (PEG 20M 10% 2.1 m, 200 °C).

Dehydrogenative Oxidation of Mandelic Acid Catalyzed by the Polyaniline–Copper Complex. A typical experimental procedure for the oxidation reaction of mandelic acid is as follows. The mixture of polyaniline (10 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) and copper(II) chloride (13.4 mg, 0.10 mmol) in DMF (1.0 mL) was stirred at room temperature for 30 min. Mandelic acid (152 mg, 1.00 mmol) was added to the resulting mixture, which was stirred under oxygen at 80 °C for 50 h. Ether (2 mL) was added to the reaction mixture at room temperature. After stirring for 10 min, the mixture was filtered and concentrated. Yield of **11** was determined by GLC (PEG 20M 10% 2.1 m, 200 °C).

Chemical Redox of Polyaniline. The UV-visible spectrum of 3 mL of solution dissolved polyaniline (1.0 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) in NMP (20 mL) was measured under nitrogen at 30 °C (Figure 1a). The polyaniline (10 mg) was treated with benzylamine (107 mg, 1.00 mmol) in NMP (1.0 mL) under nitrogen at 80 °C for 2 h. A 30 μ L volume of the reaction mixture was added to NMP (3 mL) in the cell. The UV-visible spectrum of the solution was taken under nitrogen at 30 °C (Figure 1b–1). Oxygen was bubbled into the solution at room temperature for 20 min. Spectrum 1 in Figure 1b gradually changed to spectrum 2.

Complexation of Polyaniline with CuCl₂. The UV-visible spectrum of 3 mL of solution dissolved polyaniline (0.54 mg; anal. $C_{6.00}H_{4.50}N_{1.00}(BF_4)_{0.11}$) in NMP (20 mL) was measured under nitrogen at 30 °C. The solution was treated successively with 5 μ L portion of 10 mM CuCl₂ solution to give the spectra as shown in Figure 4a. Figure 4b shows plots of $\Delta\lambda$ vs the amount of CuCl₂.

Cyclic Voltammetry of Polyaniline and the Complex with CuCl₂. All electrochemical measurements were carried out under nitrogen at 25 °C. Cyclic voltammograms were obtained in the NMP solution containing 0.1 M Bu₄NClO₄ as a supporting electrolyte: polyaniline (10 mg; anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) in NMP (5 mL) in Figure 5; polyaniline (10 mg) and CuCl₂ (0.27 mg, 2.0×10^{-3} mmol) in NMP (5 mL). Potentials were determined with a three-electrode system consisting of a glassy carbon electrode, a platinum auxiliary electrode, and a KCl-saturated calomel reference electrode at 50 mV s⁻¹ scan rate.

***In Situ* UV-Visible Spectra of Polyaniline and the Complex with CuCl₂ at a Given Potential.** *In situ* UV-visible spectral measurements were carried out under nitrogen at 25 °C.¹⁷ *In situ* UV-visible spectra were obtained in the NMP solution containing 0.1 M Bu₄NClO₄ as a supporting electrolyte at an electrical potential between -0.6 V and 0.6 V vs SCE with a reported hand-made thin layer cell:¹⁷ polyaniline (8.0 mg; anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) in NMP (4 mL) in Figure 2; polyaniline (8.0 mg; anal. $C_{6.00}H_{6.34}N_{0.98}Cl_{0.57}$) in NMP (4 mL) in Figure 3; polyaniline (8.0 mg; anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) and CuCl₂ (10.8 mg, 0.08 mmol) in NMP (4 mL) in Figure 6.

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