

## SHORT COMMUNICATIONS

## Preparation and Spectroelectrochemical Properties of Poly(*N*-phenylphenazasiline)

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Phenazasiline-containing polymers are expectable as functional materials because phenazasiline contains both diphenylamine and diphenylsilane structure. Phenazasiline-containing polyesters and polyamides possess high thermal stability.<sup>1a</sup> Phenazasiline homopolymers were prepared by electrochemical oxidation, and resulting polymers showed interesting electrochromic properties.<sup>1b</sup> We reported the preparation of phenazasiline-containing  $\pi$ -conjugated polymers.<sup>2</sup> The resulting polymers displayed interesting electrochromism and high efficiency as hole transporting polymeric material. However, these phenazasiline-containing polymers had only methyl substituent on the N atom.<sup>1,2</sup> Recently, poly(phenazasiline)s with arylmethyl and H substituent on the N atom (see Scheme 1) were prepared and compared with poly(*N*-methylphenazasiline)s.<sup>3</sup> The previous report suggested that the substituent on the N atom is essential for electrochemical and optical properties of poly(phenazasiline).

We also reported the effect of Si unit of monosilanylene- and disilanylene- bridged diphenylamines by spectroelectrochemical measurement.<sup>2b,4</sup> From the reports, the Si unit exerts influence on the electronic structure of diphenylamine. Interestingly, the spectroelectrochemical properties of poly[*N*-(pentamethylphenyl)phenazasiline] were different from those of both poly(*N*-methylphenazasiline)<sup>2</sup> and poly(phenazasiline).<sup>3</sup> Observed effect of the substituent on the N atom on poly(phenazasiline) is different from previous report.<sup>3</sup> This paper reports

preparation and spectroelectrochemical properties of poly[*N*-(pentamethylphenyl)phenazasiline] which is poly(phenazasiline) derivatives with phenyl substituent on the N atom.

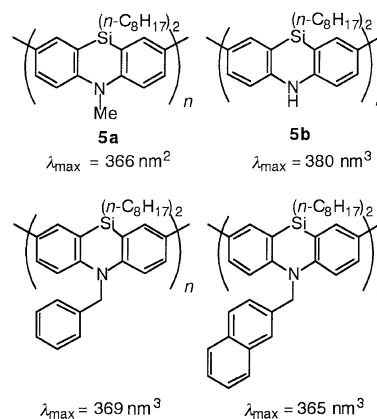
## EXPERIMENTAL

*Reagent*

Bromopentamethylbenzene was prepared by reported method.<sup>5a</sup> Other chemicals were used as purchased.

*Measurement*

IR spectra were recorded on a JASCO FT-IR 610 spectrometer. NMR spectra in solution were taken using a Bruker ARX-300 spectrometer. UV-visible spectra were measured with a Shimadzu UV-3100 and Hitachi U-3500 spectrometers.



Scheme 1.

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Cyclic voltammeteries (CV) of the polymers were measured as follows. Electrochemical control of the experiments was achieved using a BAS electrochemical analyzer model 660. A three-electrode system was used, consisting of a Glassy Carbon (GC) electrode (BAS, 3 nm in diameter) or ITO electrode as the working electrode, a platinum wire counter electrode, and an Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) reference electrode. Tetra-butylammonium perchlorate (TBAP) was used for electrolyte. *In situ* spectroelectrochemical measurements were carried out by the reported method.<sup>4</sup>

#### Preparation of 2,3,4,5,6-Pentamethyltriphenylamine (1)

Under nitrogen, a three-necked flask containing 200 cm<sup>3</sup> toluene was charged with bis(dibenzylideneacetone)palladium(0) Pd(dba)<sub>2</sub> (0.80 g, 1.4 mmol), tri(*t*-butyl)phosphine (0.43 g, 2.1 mmol), sodium *t*-butoxide (19.3 g, 0.2 mol), bromopentamethylbenzene (45.63 g, 0.23 mol), and diphenylamine (34.03 g, 0.2 mol). The reaction mixture was stirred at 90°C for 1 week. After filtration to remove precipitation, the solvent was removed by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent = hexane) to give 34.77 g of **1**. Yield was 55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>); 6.7–7.3 (m, 10), 2.34 (s, 3), 2.28 (s, 6), and 2.09 ppm (s, 6). mp: 148–150°C. *Anal.* Calcd for C<sub>23</sub>H<sub>15</sub>N·0.1 H<sub>2</sub>O: C, 87.1%; H, 8.0%; N, 4.4%. Found: C, 86.8%; H, 8.0%; N, 4.5%.

#### Preparation of 2'', 3'', 4'', 5'', 6''-Pentamethyl-2,2',4,4'-tetrabromotriphenylamine (2)

Bromine (1.6 cm<sup>3</sup>) was added into a flask containing carbon tetrachloride (80 cm<sup>3</sup>) and **1** (2.16 g, 6.9 mmol). The reaction mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the crude product was purified by silica gel column chromatography (eluent = hexane) to give 3.71 g (6.1 mmol) of **2**. Yield was 88%. mp: 209–210.5°C. *Anal.* Calcd for C<sub>23</sub>H<sub>21</sub>Br<sub>4</sub>N: C, 43.8%; H, 3.4%; N, 2.2%. Found: C, 44.4%; H, 3.5%; N, 2.3%.

#### Preparation of 2,8-Dibromo-10,10-di-*n*-octyl-*N*-(pentamethylphenyl)phenazasiline (3)

Under nitrogen, to a dispersion of **2** (0.32 g, 0.50 mmol) in dry ether (5 cm<sup>3</sup>) were added 1.6 M hexane solution of *n*-butyllithium (0.7 cm<sup>3</sup>, 1.0 mmol) at 0°C. After the reaction mixture became homogeneous, di-*n*-octyldichlorosilane (0.17 g, 0.5 mmol) was added at 0°C and stirred overnight at room temperature. The reaction mixture was purified by silica gel column chromatography (eluent = hexane) to give 0.29 g (0.41 mmol, 82%) of **3**. <sup>1</sup>H NMR (CDCl<sub>3</sub>); 7.58

(d, 2), 7.16 (dd, 2), 6.05 (d, 2), 2.35 (s, 6), 2.29 (s, 3), 1.83 (s, 6), and 0.7–1.5 ppm (m, 34); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 146.92, 137.35, 136.38, 135.20, 134.77, 133.12, 132.41, 118.97, 117.76, 112.59, 33.20, 31.85, 29.16, 29.07, 23.91, 22.65, 16.94, 16.78, 15.44, 14.42, and 14.09 ppm; <sup>29</sup>Si NMR (CDCl<sub>3</sub>): –20.72 ppm. *Anal.* Calcd for C<sub>39</sub>H<sub>55</sub>Br<sub>2</sub>NSi: C, 64.5%; H, 7.6%; N, 1.9%. Found: C, 64.8%; H, 7.8%; N, 2.0%.

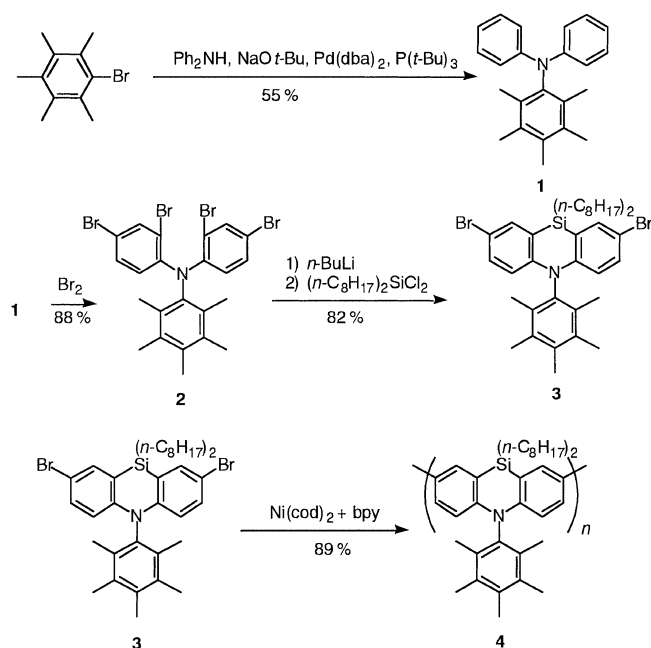
#### Preparation of Poly[10,10-di-*n*-octyl-*N*-(pentamethylphenyl)phenazasiline-2,8-diyl] (4)

Under nitrogen, to a mixture of Ni(cod)<sub>2</sub> (0.28 g, 1.0 mmol, cod = 1,5-cyclooctadiene), cod (1 cm<sup>3</sup>) and 2,2'-bipyridyl (0.16 g, 1.0 mmol) in toluene (5 cm<sup>3</sup>) was added phenazasiline **3** (0.42 g, 0.7 mmol), and the mixture was heated at 60°C for 48 h. A black powder precipitated upon pouring the mixture into methanol was successively washed with 2 M aqueous hydrochloric acid, methanol, and was dissolved in chloroform. Reprecipitation into methanol afforded 0.27 g (0.6 mmol monomer unit, 87%) of **4** as an orange powder. *M<sub>w</sub>* = 13000, *M<sub>n</sub>* = 5000 (GPC (THF, polystyrene standard)). <sup>1</sup>H NMR (CDCl<sub>3</sub>); 7.75 (d, 2), 7.36 (dd, 2), 6.23 (d, 2), 2.36 (s, 3), 2.30 (s, 6), 1.91 (s, 6), and 0.7–1.5 (m, 34) ppm; <sup>13</sup>C NMR(CDCl<sub>3</sub>): 134.63, 134.42, 132.97, 132.03, 128.21, 115.88, 33.72, 31.86, 29.72, 29.02, 24.24, 22.63, 16.88, 15.81, 14.68, and 14.07 ppm; <sup>29</sup>Si NMR (CDCl<sub>3</sub>): –21.77 ppm. *Anal.* Calcd for (C<sub>39</sub>H<sub>55</sub>NSi·H<sub>2</sub>O)<sub>*n*</sub>: C, 80.2%; H, 9.8%; N, 2.4%. Found: C, 80.3%; H, 10.0%; N, 2.5%.

## RESULTS AND DISCUSSION

Scheme 2 illustrates the preparation of the polymer **4**. Triphenylamine derivative **1** was prepared by palladium-catalyzed amination of diphenylamine and bromopentamethylbenzene.<sup>5b</sup> Dilithiation of compound **2** using *n*-butyllithium in ether followed by addition of dichlorosilane produced monomer **3**.<sup>5c,5d</sup> Polymer **4** was prepared through dehalogenative polycondensation<sup>2a,3,6</sup> of **3**. The polymer was soluble in the general organic solvents like THF, CH<sub>2</sub>Cl<sub>2</sub>, and toluene.

UV λ<sub>max</sub> of CHCl<sub>3</sub> solution of **4** at room temperature was about 380 nm. UV λ<sub>max</sub> shown in Scheme 1 was the data of CHCl<sub>3</sub> solution of the polymers at the room temperature. Although **4** have bulky substituent on the N atom, UV λ<sub>max</sub> of **4** was longer than that of poly(10,10-dioctyl-*N*-methylphenazasiline) **5a**,<sup>2</sup> and almost the same wavelength as that of poly(10,10-dioctylphenazasiline) **5b**.<sup>3</sup> This result suggests that the electronic effect on the N atom is larger than the steric effect around the N atom for UV λ<sub>max</sub> of



Scheme 2.

poly(phenazasiline) derivative. According to our earlier report, the substituent on the Si atom of reported poly(phenazasiline) did not change UV  $\lambda_{\max}$  of the polymer,<sup>2</sup> in spite of different dihedral angles between two benzene atoms from X-Ray analysis of related monomers.<sup>5c</sup> From these results, UV  $\lambda_{\max}$  was not changed by steric effect of the substituent not only on Si atom but also on N atom.

As shown in Figure 1, cyclic voltammogram of dichloromethane solution of **4** showed two reversible oxidation peaks which were typical for poly(diphenylamine) type polymers.<sup>2, 3, 6b</sup> Spectroelectrochemical properties of the polymer **4** were shown in Figures 2a and 2b. Absorption spectral changes of **5a** were also shown in Figures 2c and 2d for comparison. As shown in Figure 2a, absorption bands assigned as polaron of **4** were observed at about 500 and 1950 nm at lower potential. At higher potential ( $> 0.6$  V), polaron states in **4** were transformed to bipolaron states indicating the absorption band at about 850 nm (Figure 2b).

Generally, the mechanism of the electrochemical oxidation of poly(diphenylamine) derivative was explained as shown in Scheme 3.<sup>2b</sup> When the polaron is formed by electrochemical oxidation (step 1 in Scheme 3), the absorption based on the neutral state decreases, and the absorption based on the polaron increases. When the polymer is oxidized further, diradical dication intermediate is formed (step 2 in Scheme 3), and then, diradical dication changes to bipolaron (step 3 in Scheme 3). When bipolaron is formed, the absorption based on the polaron decreases, and then, the absorption based on the bipolaron in-

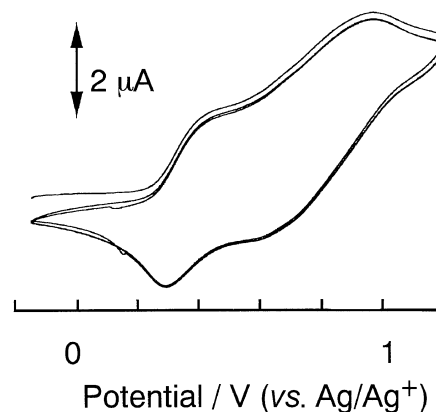
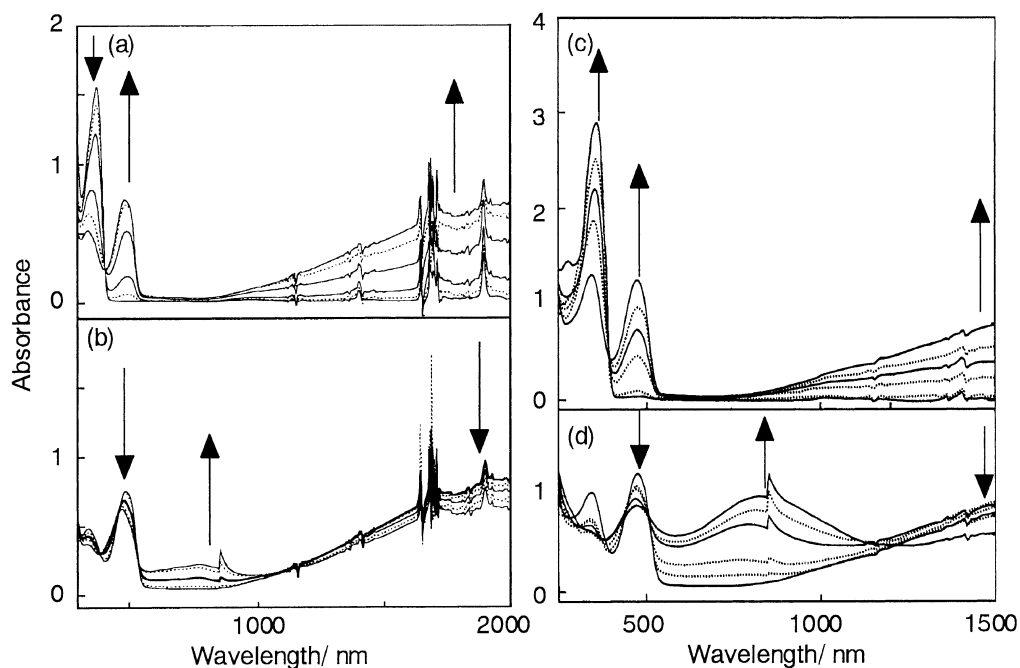


Figure 1. CV curve of  $\text{CH}_2\text{Cl}_2$  solution of **4** containing TBAP (0.1 M) at  $50 \text{ mVs}^{-1}$ .

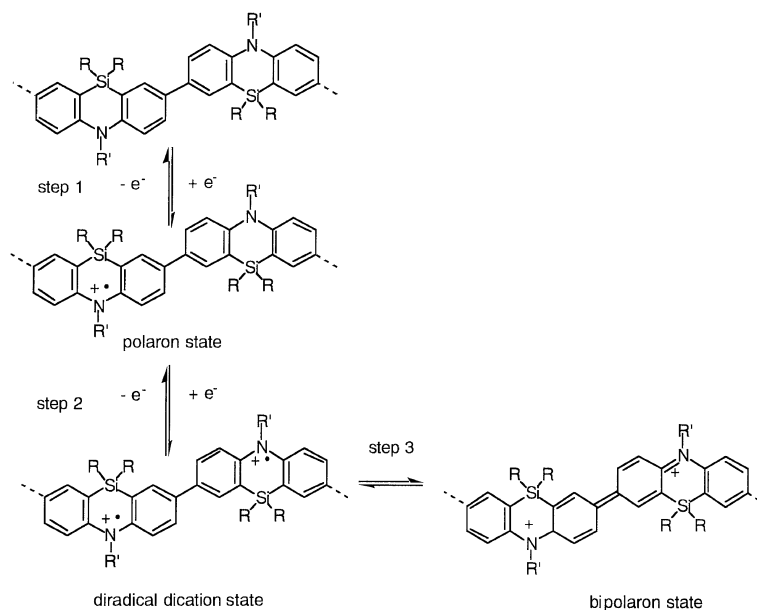
creases. Figures 2c and Figure 2d were typical for the description. As shown in Figure 2d, the polaron band originated from oxidized **5a** disappears by further electrochemical oxidation because of formation of bipolaron state.

However, from comparison between Figures 2b and 2d, the ratio of the decrease of the absorption based on polaron band of the polymer **4** is very smaller than that of polymer **5a**. The increase of the absorption based on the bipolaron band of the polymer **4** is also very smaller than that of **5a**. These results seem to suggest that the electrochemically two-electron oxidized **4** exist as diradical dication state rather than dication state.

In order to understand the effect of the substituent on the N atom of poly(phenazasiline)s at the two-electron oxidized state, the molecular orbital calculations were performed. We calculated *N*-methylphenazasiline dimer (**6a**:  $R' = \text{Me}$  in Figure 4a) and *N*-phenylphenazasiline dimer (**6b**:  $R' = \text{Ph}$  in Figure 4a) as a model of poly(*N*-methylphenazasiline) **5a** and poly[*N*-(pentamethylphenyl)phenazasiline] **4**, respectively. Structures were optimized by the density functional theory (DFT). The DFT method employed in this study is Beck's three-parameter hybrid model<sup>7</sup> using the Lee–Yang–Parr correlation functional<sup>8</sup> (B3LYP) with 3-21G basis set (denoted B3LYP/3-21G). In order to optimize structures at the two-electrons oxidized state as Scheme 3, the unrestricted B3LYP/3-21G calculations were performed for singlet dication (bipolaron state in Scheme 3) and the triplet diradical dication (diradical dication state in Scheme 3) of phenazasilines. For reasons of using large size molecules, vibrational analysis could not be carried out. The DFT calculations were carried out by the Gaussian 98 program package<sup>9</sup> on Visual Technology VT-Alpha600 and SGI Origin 2000/256. Figure 3b shows optimized structures of phenazasilines. The energetic data is presented in Table I. In **6a**, the triplet



**Figure 2.** Absorption spectral changes during oxidation at constant potentials. (a) The solution of **4** in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP at  $-0.15$  V,  $+0.2$  V,  $+0.3$  V,  $+0.4$  V,  $+0.5$  V, and  $+0.6$  V in the arrow direction. (b) The solution of **4** in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP at  $+0.65$  V,  $+0.7$  V,  $+0.8$  V,  $+1.0$  V, and  $+1.2$  V in the arrow direction. (c) The solution of **5a** in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP at  $-0.15$  V,  $+0.3$  V,  $+0.4$  V,  $+0.45$  V,  $+0.5$  V, and  $+0.6$  V in the arrow direction. (d) The solution of **5a** in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP at  $+0.6$  V,  $+0.65$  V,  $+0.7$  V,  $+0.75$  V,  $+0.8$  V, and  $+0.9$  V in the arrow direction.



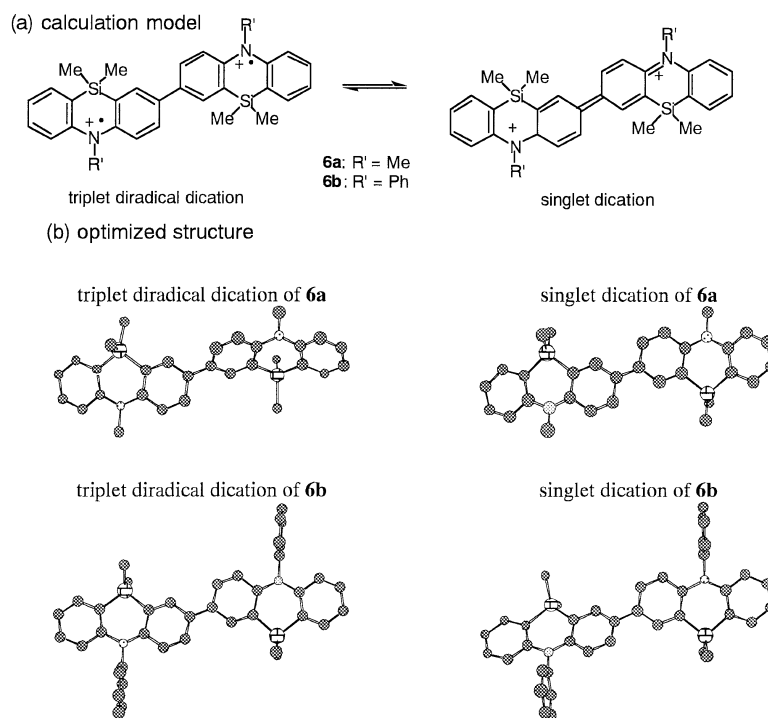
**Scheme 3.**

state is slightly stable than the singlet state ( $0.32 \text{ kcal mol}^{-1}$ ). On the other hand, in **6b**, the triplet state is more stable than the singlet state ( $1.43 \text{ kcal mol}^{-1}$ ). The result shows that in the two-electrons oxidized state, **6b** may prefer to the diradical dication state than **6a**. It is, however, difficult task to calculate more quantity calculation with any accuracy within a finite system. Therefore, we still need to carry out further MO calculations.

Further experimental and theoretical studies of the

radicals from **4** are now in progress to explain the two-electrons oxidized state of the effect of the substituent on the N atom of poly(phenazasiline)s.

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**Figure 3.** The result of DFT calculations. (a) Calculated chemical structure. (b) Optimized chemical structure.

**Table I.** The result of DFT calculations by the unrestricted B3LYP/3-21G

	State	Total energy (Hartree)	$\Delta E$ kcal mol <sup>-1</sup>
<i>N</i> -Methylphenazasiline dimer	singlet	-1840.52667	-0.32
(6a)	triplet	-1840.52616	0.00
<i>N</i> -Phenylphenazasiline dimer	singlet	-2221.91117	-1.43
(6b)	triplet	-2221.90968	0.00

use the SGI Origin 2000.

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