Synthesis of Bis(phenazasiline) Compounds and Their Application for TFT as a Model of Phenazasiline-Containing Polymers

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New bis(phenazasiline) compounds were prepared and a thin film transistor (TFT) device containing bis(phenazasiline) derivatives was fabricated. The bis(phenazasiline)s, prepared from 2-bromo-8-methylphenazasiline, were effective materials for TFT. Obtained bis(phenazasiline) derivatives were considered to be model compounds of phenazasiline-containing polymers in the prediction of TFT properties.

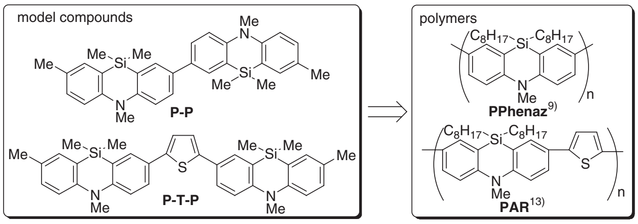
Diphenylamines with a bridging structure are interesting as functional materials. Phenazasiline (=9,10-dihydro-9-aza-10-silaanthracene), which has a Si-bridged diphenylamine framework, is one of these materials. Phenazasiline derivatives are potentially useful as a hole transporting layer for electroluminescent (EL) devices[1] and antioxidants.[2] Phenazasiline-containing polyesters and polyamides possess high thermal stability.[3] Previously, Casalbore-Miceli and co-workers have synthesized phenazasiline homopolymers by electrochemical oxidation of trimethylphenazasiline, and examined their electrochromic behavior.[4–8] Although several phenazasiline-containing polymers have been reported, they had only methyl substituent on the N atom and phenyl[3] or methyl[4–8] substituents on the Si atom.

Recently, we have prepared phenazasiline-containing polymers with various substituents on the N and Si atoms by organometallic polycondensation using the corresponding dibromophenazasiline to obtain structurally well-defined π-conjugated polymers.[9–11] We have also investigated their application as hole transport layers of EL devices,[9] electrochromic devices,[12] functional additives for resin,[13] and substrates for the extension fixation of DNA.[14] However, it seems that there have been no reports about the transistor properties of phenazasiline-containing compounds.

We therefore planned to make thin film transistor (TFT) devices using a phenazasiline-containing polymer by a solution casting method. However, solubility of the polymer sometimes becomes a problem when the devices are prepared by casting. In order to investigate the effect of the polymer's phenazasiline unit on transistor properties, we synthesized two new bis(phenazasiline) derivatives, (bis(7,9,10,10-tetramethyl-9,10-dihydro-9-aza-10-silaanthracen-2-yl) (**P-P**) and 2,5-bis(7,9,10,10-tetramethyl-9,10-dihydro-9-aza-10-silaanthracen-2-yl)thiophene (**P-T-P**)), which are model compounds of phenazasiline-containing polymers (poly(9-methyl-10,10-dioctyl-9,10-dihydro-9-aza-10-silaanthracene-2,7-diyl) (**PPhenaz**)[9] and poly(9-methyl-10,10-dioctyl-9,10-dihydro-9-aza-10-silaanthracene-2,7-diyl-*alt*-thiophene-2,5-diyl) (**PAR**)[13]) as shown in Scheme 1. Herein we report the chemical and TFT properties of **P-P** and **P-T-P**. In addition, we describe the transistor properties of the films made of the phenazasiline-containing polymers.

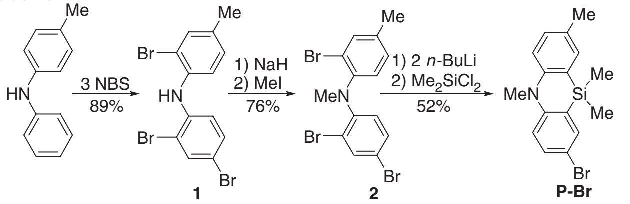
Bis(phenazasiline) derivatives, **P-P** and **P-T-P**, were synthesized by the coupling reaction of monobromophenazasiline, **P-Br**, as shown in Scheme 2.

P-Br was prepared as shown in Scheme 2a. Bromination of 4-methyldiphenylamine by *N*-bromosuccinimide (NBS) gave 2,2′,4-tribromo-4′-methyldiphenylamine (**1**). **1** was treated with NaH, and then reacted with iodomethane to give *N*-methylated compound **2**. Dilithiation of **2** using *n*-butyllithium in diethyl ether followed by the addition of dichlorodimethylsilane produced **P-Br**. Two bis(phenazasiline) derivatives, **P-P** and **P-T-P**, were synthesized by Ni(0)-promoted dehalogenative condensation and Pd-catalyzed cross-coupling reaction, respectively (Scheme 2b).

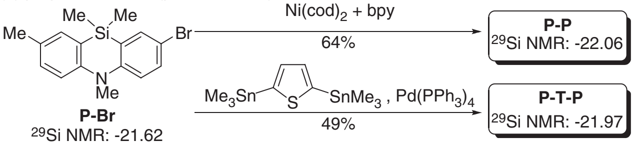


Scheme 1. Bis(phenazasiline) compounds and relative polymers.

(a) preparation of **P-Br**



(b) preparation of bis(phenazasiline)s



Scheme 2.

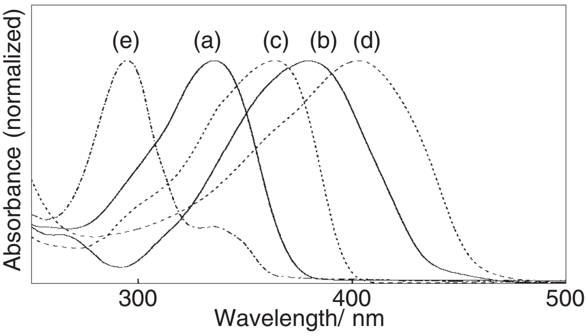


Figure 1. Absorption spectra of (a) **P-P**, (b) **P-T-P**, (c) **PPhenaz**, (d) **PAR**, and (e) **P-Br** in $CHCl_3$.

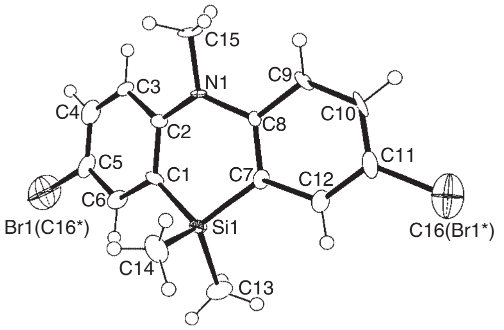


Figure 2. **P-Br** with 50% ORTEP drawing ellipsoidal level. C16 and Br1 were disordered.

As shown in Scheme 2b, the $^{29}Si\{^1H\}$ NMR spectra of **P-P** and **P-T-P** showed signals in almost the same region as that of **P-Br**. Their ^1H and $^{13}C\{^1H\}$ NMR spectra also supported these structures.

Figure 1 shows the absorption spectra of **P-P**, **P-T-P**, **PPhenaz**, **PAR**, and **P-Br** in a $CHCl_3$ solution. The λ_{max} based on π–π^* transition of **P-P** appears at 339 nm (Figure 1a), which is longer than that of monophenazasiline **P-Br** ($\lambda_{max} =$ 295 nm, Figure 1e). Similarly, the λ_{max} of **P-T-P** (379 nm, Figure 1b) is observed at a longer wavelength than that of **P-Br**. On the other hand, λ_{max} of **P-P** and **P-T-P** in $CHCl_3$ appeared at a shorter wavelength than those of corresponding polymers, **PPhenaz** (364 nm, Figure 1c) and **PAR** (405 nm, Figure 1d). These results suggest that the differences of absorption λ_{max} derive from the effective π-conjugation system. Figure 1 also suggested that from comparison between **P-P** and **P-T-P**, the introduction of a thienylene unit makes λ_{max} longer. This relationship was the same as that of the corresponding polymers **PPhenaz** and **PAR**.

To investigate the structure of phenazasiline unit of **P-P** and **P-T-P**, the molecular structure of **P-Br** was determined by X-ray crystallography. Figure 2 shows the ORTEP drawing of **P-Br**, showing **P-Br**'s bent structure between two benzene units whose dihedral angle is 154.7(3)°. On the other hand, the sum of the angles around N1 of **P-Br** is 358.6(7)°, showing that the surroundings of the N atom have a planar structure. These values are almost the same as those of dibromotrimethylphenazasiline, 151.23 and 358.5°, respectively.[15] The flatness around the N atom in **P-Br** strongly suggested the expansion of π-conjugation through the N atom, even though the two benzene rings in **P-Br** form a bent structure.

Table 1. Transistor Properties of the Devices

Run No.	Compound	Device type[a)]	Method of film formation[b)]	Mobility /$cm^2\,V^{-1}\,s^{-1}$	ON–OFF ratio
1	**P-P**	bc	vacuum	2.91×10^{-5}	$10^{4.03}$
2	**P-P**	bc	cast	1.09×10^{-5}	$10^{2.73}$
3	**P-P**	tc	vacuum	1.22×10^{-4}	$10^{4.89}$
4	**P-T-P**	bc	vacuum	1.04×10^{-5}	$10^{2.17}$
5	**P-T-P**	bc	cast	1.86×10^{-6}	$10^{1.24}$
6	**P-T-P**	tc	vacuum	2.06×10^{-5}	$10^{4.42}$
7	**PPhenaz**	bc	cast	1.71×10^{-4}	$10^{2.83}$
8	**PAR**	bc	cast	—[c)]	—[c)]

a) bc: bottom-contact type, tc: top-contact type. b) vacuum: vacuum-deposited, cast: cast from 1,2-dichloroethane. c) Transistor properties were not observed.

TFT was fabricated by using bis(phenazasiline) compounds **P-P** and **P-T-P**. The transistor properties of the devices are summarized in Table 1. **P-P** and **P-T-P** showed p-type transistor properties. Comparing Runs 1 and 2 (for **P-P**) and Runs 4 and 5 (for **P-T-P**), the properties of the devices produced by vacuum deposition were better than those of the devices made by casting in both cases, and this tendency was the same as previously reported results.[16] From a comparison between Runs 1 and 3 (For **P-P**) and between Runs 4 and 6 (for **P-T-P**), the TFT properties of the top-contact device are better than those of the bottom-contact one, and this tendency was the same as previously reported.[17] As shown in Table 1, the TFT properties of the **P-P** device were better than those of the **P-T-P** device. This agreed with the tendency in conductivity of an electrochemically doped cast film of relative polymers (**PPhenaz** ($17\,S\,cm^{-1}$)[15] and **PAR** ($1.8\,S\,cm^{-1}$)[13]). As shown in Figure 3, XRD patterns of films of **P-P** and **P-T-P** suggest that crystallinity of the film seems to also affect the transistor properties in the case of bis(phenazasiline) compounds.

As described above, **P-P** and **P-T-P** showed p-type transistor properties. Accordingly, phenazasiline-containing polymers are also expected to show transistor properties. Therefore, TFT devices were fabricated using phenazasiline-containing polymers by solution casting. As shown in Figure 3c, the obtained **PPhenaz** film was amorphous.

The transistor properties of the polymer-using devices are summarized in Table 1. The **PPhenaz**-based device showed transistor properties, whereas the **PAR**-based device did not. In short, the transistor properties of the **PPhenaz** device were better than those of the **PAR** device. This difference in the transistor properties between **PPhenaz** and **PAR** agreed with the tendencies of **P-P** and **P-T-P**. Transistor properties of phenazasiline homopolymer seem to be improved by extension of π-conjugation.

In conclusion, we report the preparation of **P-P** and **P-T-P** as model compounds of phenazasiline-containing polymers. We also found that phenazasiline-containing compounds are useful materials for construction of TFT devices. We successfully investigated the relationship between the degree of polymerization and transistor properites of phenazasiline-containing materials. We believe that phenazasiline-containing materials' transistor properties could be improved by molecular design.

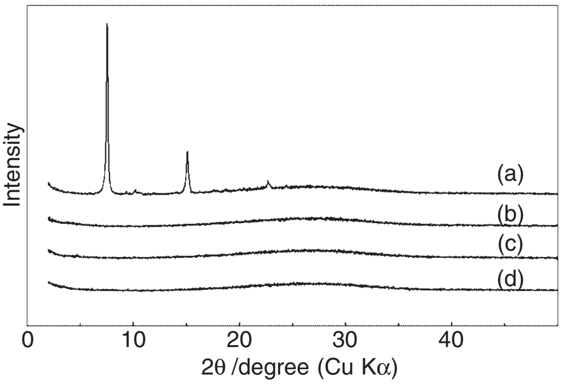


Figure 3. XRD patterns of (a) **P-P**, (b) **PPhenaz**, and (c) **P-T-P** cast film on a polyimide substrate. XRD pattern of the polyimide substrate was shown in (d) for comparison.

Experimental

Reagent. 2,5-Bis(trimethylstannyl)thiophene,[18] **PPhenaz** ($M_w = 4.3 \times 10^3$, $M_w/M_n = 1.6$),[15] and **PAR** ($M_w = 4.4 \times 10^3$, $M_w/M_n = 1.4$)[13] were prepared by the reported method. Other chemicals were used as purchased.

Measurement. NMR spectra in solutions were taken using a JEOL EX-400 spectrometer. UV–visible spectra were recorded on a JASCO V-570 spectrometer.

Preparation of P-P and P-T-P. Preparation Data of 2-Bromo-7,9,10,10-tetramethyl-9,10-dihydro-9-aza-10-sila-anthracene (P-Br): **P-Br** was obtained as colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.6–6.8 (m, 6H), 3.47 (s, 3H), 2.33 (s, 3H), 0.41 (s, 6H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 149.82, 148.41, 135.28, 133.54, 132.35, 130.82, 129.72, 126.07, 122.72, 116.69, 115.04, 113.08, 38.14, 20.42, −2.26. Anal. Found: C, 57.4; H, 5.4; N, 4.4; Br, 24.6%. Calcd for $C_{16}H_{18}BrNSi$: C, 57.8; H, 5.5; N, 4.2; Br, 24.0%. Selected bond angles from crystallographic data of **P-Br**, C_{Ar1}–N–C_{Ar2}, 122.5(6)°, C_{Ar1}–N–C_{Me}, 118.0(7)°, C_{Ar2}–N–C_{Me}, 118.1(8)°. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-752038 for **P-Br**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Preparation Data of Bis(7,9,10,10-tetramethyl-9,10-dihydro-9-aza-10-silaanthracen-2-yl) (P-P): **P-P** was obtained as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7–6.9 (m, 12H), 3.55 (s, 6H), 2.34 (s, 6H), 0.45 (s, 12H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 149.88, 148.69, 133.58, 132.71, 131.30, 130.66, 129.23, 128.32, 123.34, 122.98, 115.06, 114.86, 38.10, 20.44, −1.99. Anal. Found: C, 74.3; H, 6.9; N, 5.2%. Calcd for $C_{32}H_{36}N_2Si_2 \cdot 0.6H_2O$: C, 74.5; H, 7.3; N, 5.4%.

Preparation Data of 2,5-Bis(7,9,10,10-tetramethyl-9,10-dihydro-9-aza-10-silaanthracen-2-yl)thiophene (P-T-P): **P-T-P** was obtained as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7–6.9 (m, 14H), 3.54 (s, 6H), 2.34 (s, 6H), 0.47 (s, 12H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 150.24, 148.49, 142.71, 133.62, 130.75, 130.35, 129.52, 127.27, 126.40, 123.42, 122.90, 122.59, 115.08, 114.98, 38.19, 20.45, −1.97. Anal. Found: C, 71.4; H, 6.2; N, 4.1; S, 5.6%. Calcd for $C_{36}H_{38}N_2SSi_2 \cdot 0.9H_2O$: C, 71.7; H, 6.7; N, 4.6; S, 5.3%.

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Supporting Information

Experimental details of the preparation of **1**, **2**, **P-Br**, **P-P**, and **P-T-P**, and crystallographic data of **P-Br**, and of the fabrication of TFT with phenazasiline-containing compounds are shown. Optical data of **P-Br**, **P-P**, **P-T-P**, **PPhenaz**, and **PAR** are also shown. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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