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Synthesis and properties of novel σ–π alternating polymers with triphenylamine and organosilicon units

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We have synthesized novel σ–π conjugated polymers with *N*,*N*-bis(*p*-ethynylphenyl)-*N*-(*p*-tolyl)amine as the π-unit. The electroluminescent devices, with a double-layer system composed of Alq and the present polymers as the emitting-electron-transporting and hole-transporting layers respectively, emit green electroluminescence with a maximum intensity of 760 cd m^{-2}. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Recently, organosilicon compounds and polymers have received much attention because of their potential utilities in electrical and optical functionality materials.[1,2] In particular, polymers with a regular alternating arrangement of an organosilicon unit —(SiR_2)— and an aromatic π-system exhibit unique electrical and electro-optical properties,[3] and can be used as photoresists,[3] organic semiconductors,[4] and photoconducting materials.[5] In addition, the use of these types of polymer as precursors of silicon-based ceramics may be noted.[6–12]

Recently, we have reported the preparation of polymers with a regular alternating arrangement of an organosilicon unit and extended π-units, such as oligothienylene,[13–15] 9,10-diethynylanthracene[16–18] and 3,6-diethynylcarbazole,[19] and demonstrated the high performance of double-layer electroluminescent (EL) devices having these polymers as the hole-transporting layer and tris(8-quinolinolato)-aluminum(III) complex (Alq) as the electron-transporting-emitting layer. The devices show higher voltage–current performance than those devices with similar types of polymer that have phenylene, biphenylene, or naphthylene units as the π-system. These results indicate that the expansion of the π-system in the polymer enhances the hole-transport property of the EL device.[16–18] However, in general, expansion of the π-system causes low processibility arising from low solubility in solvents and poor film quality of the polymers.

EL devices based on organic materials are attractive for full-color display applications. Triarylamine derivatives, e.g. *N*,*N*′-diphenyl-*N*,*N*′-bis-(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) and related compounds, are of considerable interest as hole-transport materials for multilayer organic EL devices. This is due to both their relatively high hole-drift mobility and their low ionization potentials. As these materials have low glass-transition temperatures, many reports concerning the synthesis of linear oligomers and polymers, as well as of starburst-type compounds, with high thermal stability have been published to date.[20–24]

In this paper, we describe the preparation and the properties of novel σ–π polymers with a regular alternating arrangement of organosilicon and *N*, *N*-bis(*p*-ethynylphenyl)-*N*-(*p*-tolyl)amine (**2**) units, in the hope of obtaining materials with high hole-

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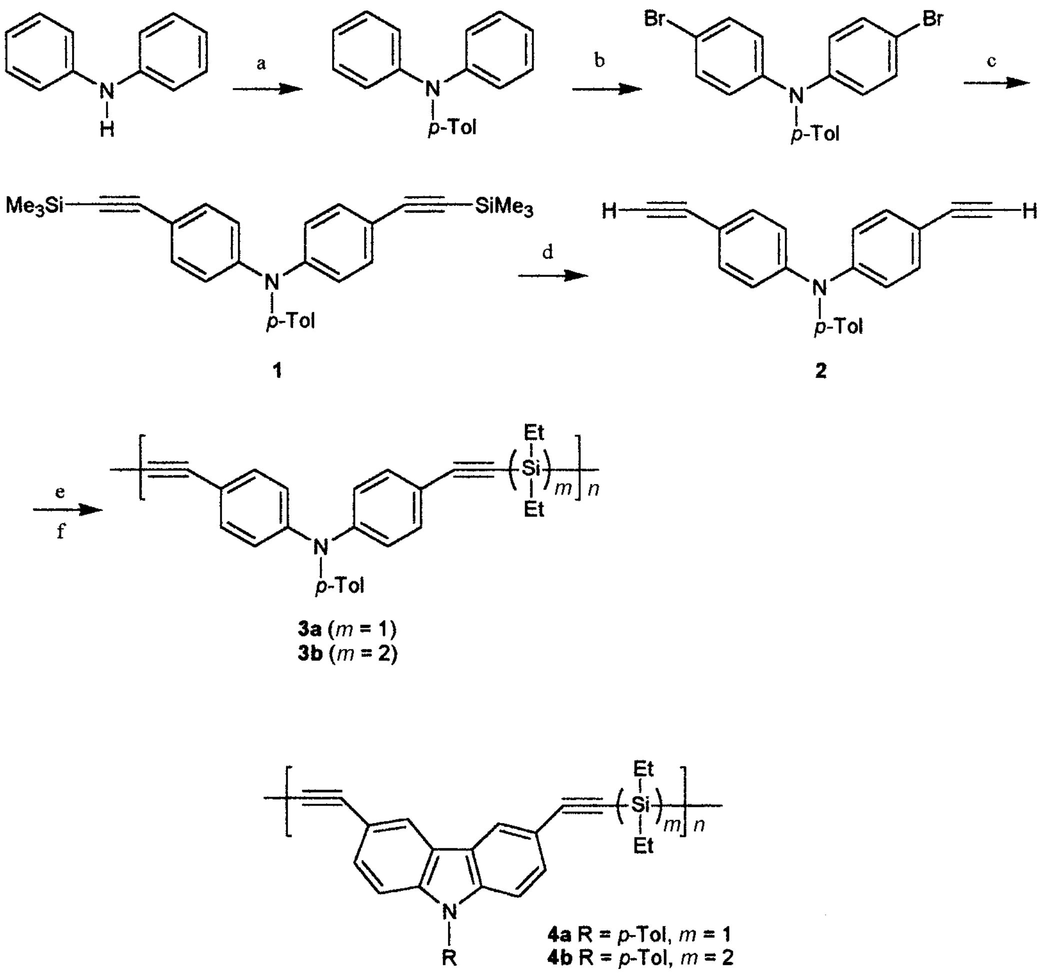

Scheme 1 Synthesis of polymers **3a**,**b** and molecular structure of polymers **4a**,**b**: (a) *p*-iodotoluene, Cu, K_2CO_3, 18-crown-6, *o*-dichlorobenzene, 180 °C; (b) 2NBS, $CHCl_3$, CH_3COOH, r.t.; (c) $HC{\equiv}C{-}SiMe_3$, $PdCl_2(PPh_3)_2$, NEt_3, 90 °C; (d) KOH, H_2O, MeOH, Et_2O, r.t.; (e) MeLi, Et_2O, THF, −80 °C → r.t.; (f) $Cl(SiEt_2)_mCl$, −80 °C → r.t.

transport properties and high thermal stability. We also describe the EL performance of devices composed of these polymers and Alq as hole-transporting and electron-transporting-emitting layer respectively.

RESULTS AND DISCUSSION

Polymerization

For the synthesis of polymers having a triarylamine unit, we prepared **2** by palladium-catalyzed reaction of *N*,*N*-bis(*p*-bromophenyl)-*N*-(*p*-tolyl)amine with trimethylsilylacetylene, followed by desilylation of the resulting product **1** (Scheme 1). Monomer **2** was di-lithiated by treating it with two equivalents of MeLi in diethyl ether at −80 °C, and the resulting dilithio-reagent was treated with dichloroorganosilanes to give the corresponding polymers **3a, b** (Scheme 1).[17–19] The polymers were soluble in common organic solvents, such as chloroform, THF and benzene, but insoluble in alcohols, and the polymers were readily separated from the reaction mixtures by reprecipitation from alcohols. The chemical structures of the products were verified by ^1H, ^{13}C, and ^{29}Si NMR spectrometry. The ^{29}Si NMR spectra revealed sharp signals at −31.14 ppm and −29.45 ppm for **3a** and **3b** respectively.

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Table 1 Preparation and thermal properties of polymers **3a**,**b**

Polymer	Yield/%[a]	M_w (M_w/M_n)[b]	M.p./ °C	Td_5/ °C[c]	Wt loss/%[d]
3a	11	5800 (1.7)	132–135	477	36
3b	17	9700 (1.5)	107–110	489	29
4a	17	3100 (1.3)	149–153	524	19
4b	9	1900 (1.2)	135–138	469	28

[a] After reprecipitation.
[b] Determined by gel-permeation chromatography, relative to polystyrene standards.
[c] Temperature of 5% weight loss.
[d] Weight loss at 1000 °C.

Although an additional signal was observed at −12.9 ppm in the spectrum of **3a**, the intensity of the signal was less than 1/10 of the major signal at −31.14 ppm. Probably, the concomitant signal is due to the MeEtSi— end group, which would be formed from the reaction of Cl—Si bonds both in the polymer ends or the monomer with excess MeLi. The IR spectra showed broad absorption bands at 1005 cm^{-1} for **3a** and 1008 cm^{-1} for **3b**, presumably due to the siloxane units formed from the hydrolysis of the remaining Cl—Si bonds, during the work-up. However, the approximate intensity ratios of these bands relative to those of the C≡C stretching at 2154 cm^{-1} were only 1/10 for **3a** and 1/4 for **3b**. The carbon contents of the polymers were determined by combustion elemental analysis as being slightly lower than the theoretical values. This is probably due to both the presence of the siloxane units in the polymers and the formation of carbon-containing ceramics during the analysis, which is often observed for silicon-containing polymers.[6,7]

The yields and molecular weights of the polymers are listed in Table 1. The yields of polymers **3a** and **3b** after reprecipitation from ethanol or isopropyl alcohol are 11% and 17% respectively, and the weight-average molecular weights M_w are 5.8×10^3 for **3a** and 9.7×10^3 for **3b**. The rather low yields of **3a** and **3b** may be due to the formation of oligomers with low molecular weight which were separated from the polymers by reprecipitation. The molecular weights are slightly higher than those of the previously reported polymers containing 3,6-diethynylcarbazole-silanylene alternating units (**4a**, **4b**).[19]

Thermal properties of polymers

The thermal stability of the polymers was ascertained by noting the melting points and the results of thermogravimetric analysis (TGA); see Table 1. As can be seen in Table 1, polymers **3a** and **3b** melt at lower temperatures than the corresponding carbazole polymers **4a** and **4b**. This may be due to the relatively flexible structures of the triarylamine units in **3a** and **3b**.

TGA in a nitrogen atmosphere resulted in a 5% weight loss based on the initial weight (Td_5) at around 477 °C for **3a** and 489 °C for **3b**. As shown in Fig. 1, a large weight loss occurred at 550–600 °C, and the total weight loss at 1000 °C was 36% and 29% for **3a** and **3b** respectively. Exothermic peaks, which may correspond to the temperature of the cross-link reactions of ethynylene units, appeared at 295 °C for **3a** and 360 °C for **3b**. These values are comparable or slightly higher than those of the previously reported polymers **4a** and **4b** (250 °C and 360 °C respectively).

Optical, electrical conducting, and electrochemical properties

The optical and electrical conducting properties of

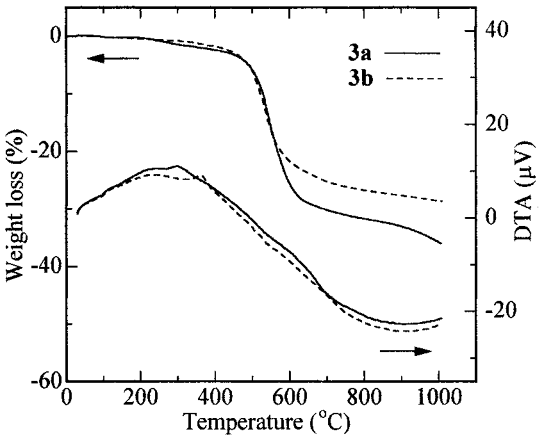

Figure 1 Thermogravimetric differential thermal analysis profiles for polymers **3a** (—) and **3b** (---) in N_2.

Table 2 Melting point, UV absorption data and conductivities of polymers **3a** and **3b**

Polymer	Absorption[a] λ_{max}/nm ($\varepsilon \times 10^{-3}$)	Conductivity[b]/ S cm^{-1}
1	355 (55), 324 (44),[c] 300 (24),[c] 246 (26)	
2	343 (30), 324 (35),[c] 300 (19)[c]	
3a	361 (31), 326 (23),[c] 246 (17)	5.6×10^{-4}
3b	362 (41), 331 (29),[c] 242 (29)[c]	7.2×10^{-4}

[a] In THF.

[b] On polymer films doped with I_2 vapor at room temperature, determined by two-probe method.

[c] Shoulder.

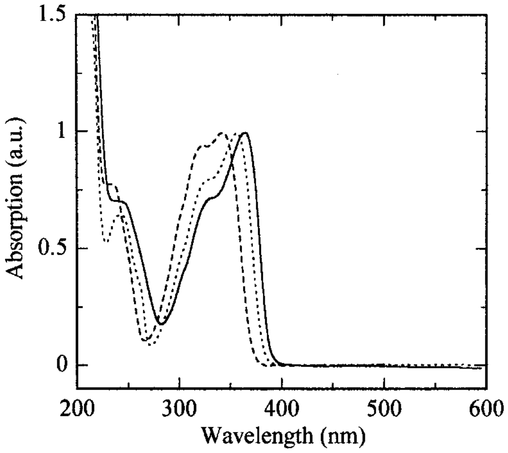

Figure 2 UV absorption spectra of compounds **1** (....), **2** (---) and polymer **3b** (—).

the polymers are summarized in Table 2. The absorption spectra of polymers **3a** and **3b** exhibit almost identical shapes, with the absorption maxima around 360 nm, independent of the silicon chain length. The absorption maxima are red-shifted by about 20 nm from that of the corresponding monomer **2** (λ_{max} = 343 nm) and by 6–7 nm from that of the model compound **1** (λ_{max} = 355 nm), as shown in Fig. 2. The absorption edge of the polymers is around 390 nm (3.2 eV), which is at a lower energy than those of the polymers with 3,6-diethynylcarbazole units, **4a** (295 nm) and **4b** (297 nm).[19]

The electrical conductivities of the present polymers are also listed in Table 2. The conductivities were measured by the two-probe method after the spin-cast films were exposed to I_2 vapor under reduced pressure. The conductivities of the present polymers are slightly higher than those of **4a** and **4b**.

The electrochemical properties of the solid films of the polymers were studied by cyclic voltammetry. The oxidation onset potentials of polymers **3a** and **3b** are 0.65 V and 0.68 V respectively versus Ag/Ag^+, which are lower than those of **4a** (0.99 V) and **4b** (0.87 V). This indicates that the present polymers are more readily oxidized, from which better hole-injecting properties are expected. On the voltammograms, oxidation peaks were clearly observed, but the anodic process was irreversible and no cathodic counter peaks were observed even in the first scan. This is probably due to the decomposition of the polymer films on electrochemical oxidation, as often observed for organosilicon polymers.[25,26]

EL properties

We also examined the hole-transporting properties of the present polymers in a double-layer EL system. The devices have a configuration of indium–tin-oxide (ITO)/polymer (30–40 nm)/Alq (60–70 nm)/Mg–Ag, in which Alq is used as the electron-transporting-emitting layer, and ITO and Mg–Ag are the anode and cathode respectively, as shown Fig. 3. We also prepared a device having a **PVK** film as the typical hole-transporting material instead of the present polymers for comparison. The performance of the EL devices thus prepared was examined in air at room temperature.

Figure 4 shows the relationships between the current density and bias voltage (*I*–*V*) of the devices with polymers **3a**, **3b**, and **PVK**. Although the device with **PVK** shows the lowest turn-on voltage (*ca* 4 V), among the devices examined the device having a **3b** film shows the highest maximum current density of 10^3 mA cm^{-2}. The value is also higher than those of the devices with **4a** and **4b** as the hole-transport material, as reported previously.[19]

Figure 5 shows the dependence of the EL intensity on the bias voltage (*L*–*V*) for the devices. Of these, the device having **PVK** shows the highest luminance of over 6000 cd m^{-2}. The device with polymer **3b**, which is superior to the other devices in *I*–*V* characteristics, shows a rather low maximum emission, *ca* 200 cd m^{-2} at most, whereas the device with **3a** shows a maximum luminance of 760 cd m^{-2}.

When the performances of the devices with **3a**,**b**

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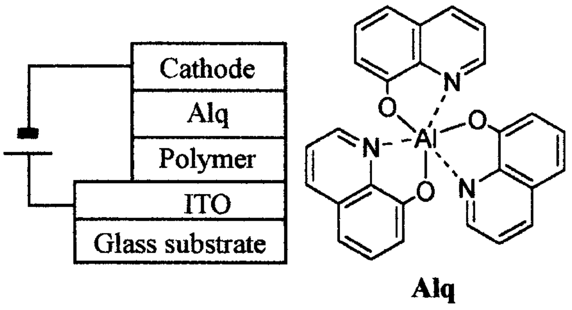

Figure 3 Schematic structure of the double-layer EL device.

and **4a**,**b** are compared at 10–12.5 V with respect to the applied bias voltage, the current density tends to diminish in the order of **3b**, **PVK** > **4b**, **3a** > **4a**. The luminance, however, decreases following the order of **PVK** > **3a**, **3b**, **4b** > **4a**. Although, at present, we cannot explain why the luminance is low for **3b**, despite the higher current density, there may be some factors operating such as low blocking ability for electrons from the Alq layer.

CONCLUSION

We have synthesized novel σ–π conjugated alternating polymers, **3a** and **3b**, having triphenylamine and organosilicon units. The absorption spectra of the polymers **3a** and **3b** were slightly red-shifted, compared with the corresponding monomer **2**, by 20 nm. The UV absorption spectra and the oxidation potential of the polymers are almost identical, but the EL device with polymer **3a** shows a higher external efficiency of EL emission than **3b**. The maximum luminance of the device with **3a** amounted to 760 cd m^{-2}.

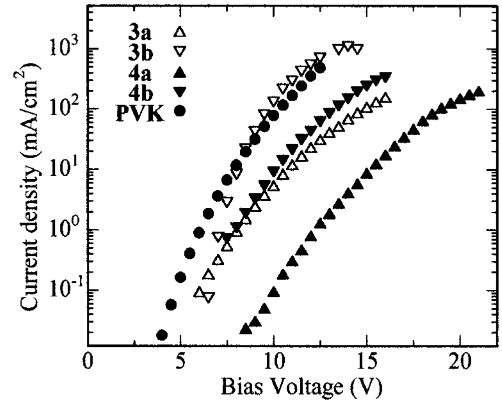

Figure 4 Plots of current densities as a function of bias voltage for the devices with **PVK** (●), **3a** (△), **3b** (▽), **4a** (▲), **4b** (▼).

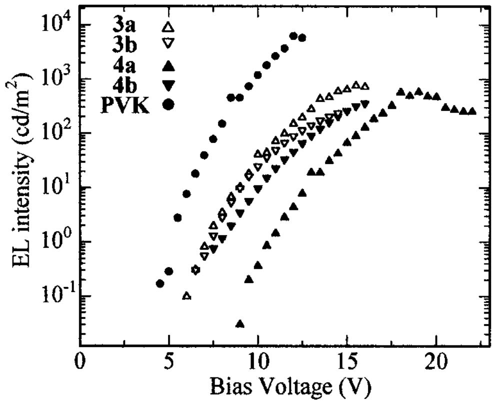

Figure 5 Plots of EL intensities as a function of bias voltage for the devices with **PVK** (●), **3a** (△), **3b** (▽), **4a** (▲), **4b** (▼).

EXPERIMENTAL

General

All reactions were carried out under a dry nitrogen atmosphere. Solvents were purified by distillation from appropriate drying agents under argon. ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL Model JNM-EX 270 spectrometer. UV spectra were measured with a Hitachi U-3210 spectrophotometer. IR spectra were measured on a Perkin–Elmer 1600-FT infrared spectrometer. Molecular weights of the polymers were determined with Shodex GPC columns, using tetrahydrofuran (THF) as the eluent, and are relative to polystyrene standards.

Materials

N,*N*-Diphenyl-*N*-(*p*-tolyl)amine was prepared in a similar fashion to that in the literature.[27]

Preparation of *N*,*N*-bis(p-bromophenyl)-*N*-(*p*-tolyl)amine

In a 300 ml three-necked flask were placed 5.61 g (21.6 mmol) of *N*,*N*-diphenyl-*N*-(*p*-tolyl)amine, 7.70 g (43.2 mmol) of *N*-bromosuccinimide and 100 ml of chloroform. After the mixture was stirred for 1 h at room temperature, 50 ml of acetic acid was added to the mixture, and the mixture was stirred for an additional 5 h. The resulting mixture was poured into 200 ml of water. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer and the extracts were dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on a silica gel column with hexane as eluent to afford 8.50 g (20.4 mmol, 94% yield) of *N,N*-bis(*p*-bromophenyl)-*N*-(*p*-tolyl) amine as a colorless solid.

Data for *N,N*-bis(*p*-bromophenyl)-*N*-(*p*-tolyl) amine: m.p. 74–79 °C. ^{1}H NMR ($CDCl_3$) δ (ppm) 2.37 (3H, s), 6.98 (4H, d, $J = 8.9$ Hz), 7.03 (2H, d, $J = 8.5$ Hz), 7.14 (2H, d, $J = 8.5$ Hz), 7.35 (4H, d, $J = 8.9$ Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) 20.83, 114.90, 124.78, 125.09, 130.17, 132.13, 133.78, 144.15, 146.54. Anal. Found: C, 54.74; H, 3.52; N, 3.32. Calc. for $C_{19}H_{15}Br_2N$: C, 54.71; H, 3.62; N, 3.36%.

Preparation of *N,N*-bis(*p*-trimethylsilylethynylphenyl)-*N*-(*p*-tolyl)amine (1)

In a 300 ml three-necked flask were placed 3.32 g (7.95 mmol) of *N,N*-bis(*p*-bromophenyl)-*N*-(*p*-tolyl)amine, 63 mg (0.33 mmol) of CuI, 230 mg (0.33 mmol) of $PdCl_2(PPh_3)_2$, 3.12 g (31.8 mmol) of trimethylsilylacetylene and 100 ml of triethylamine. After stirring the mixture for 24 h at reflux temperature, the inorganic salts were filtered and the solvent was evaporated. The residue was chromatographed on a silica gel column with hexane as eluent to afford 2.02 g (56% yield) of **1** as a yellow powder.

Data for **1**: m.p. 69–71 °C. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.25 (18H, s), 2.33 (3H, s), 6.95 (6H, m), 7.10 (2H, d, $J = 8.4$ Hz), 7.32 (4H, d, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) 0.04, 20.86, 93.33, 105.19, 116.59, 122.70, 125.77, 130.19, 132.96, 134.16, 143.95, 147.46. UV (λ_{max}/nm in THF) 355 (ε 55 200), 324 (43 500, sh), 300 (24 400, sh), 246 (25 500). IR (KBr) = 2154 cm^{-1}. Anal. Found: C, 76.85; H, 7.13; N, 3.10. Calc. for $C_{29}H_{33}NSi_2$: C, 77.10; H, 7.36; N, 3.16%.

N,N-Bis(*p*-ethynylphenyl)-*N*-(*p*-tolyl)amine (2)

N,N-Bis(*p*-ethynylphenyl)-*N*-(*p*-tolyl)amine (**2**) was prepared in a similar fashion to that in the literature.[19]

Data for **2**: glassy yellow solid. ^{1}H NMR ($CDCl_3$) δ (ppm) 2.34 (3H, s), 3.03 (2H, s), 6.97 (4H, d, $J = 8.6$ Hz), 7.00 (2H, d, $J = 8.3$ Hz), 7.11 (2H, d, $J = 8.3$ Hz), 7.34 (4H, d, $J = 8.6$ Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) 20.88, 76.46, 83.33, 115.53, 122.71, 126.00, 130.30, 133.12, 134.43, 143.88, 147.73. UV (λ_{max}/nm in THF) 343 (ε 30 100), 324 (34 900, sh), 300 (19 000, sh). IR (KBr) = 2104, 3287 cm^{-1}. Anal. Found: C, 88.62; H, 5.70; N, 4.49. Calc. for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56%.

Compound **2** was soluble in most of the common organic solvents, just after the purification by silica gel column chromatography. However, standing it for a few days led to the formation of an insoluble dark brown solid, even in an argon atmosphere, although the IR spectrum was consistent with that of **2** as prepared. Therefore, we used **2** for the following polymerization without further purification.

Preparation of polymers

Polymers **3a** and **3b** were prepared in a similar fashion to that in the literature.[19]

In a 300 ml three-necked flask were placed 0.60 g (2.0 mmol) of **2** and 40 ml of diethyl ether. To this was added 2.8 ml (4.0 mmol) of a 1.4 M MeLi–diethyl ether solution at −80 °C. The reaction mixture was allowed to warm to room temperature. After stirring the mixture for 2 h, 40 ml of THF was added to the mixture, and the mixture was cooled to −80 °C again, then 0.32 g (2.0 mmol) of dichlorodiethylsilane was added dropwise. The mixture was allowed to warm to room temperature and stirred for 12 h at this temperature. After hydrolysis with water, the organic layer was separated and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined and dried over $MgSO_4$. After evaporation of the solvent, the residue was reprecipitated from methanol–chloroform, then from ethanol–chloroform to give 84 mg (11% yield) of **3a** as a yellow powder: m.p. 132–135 °C. $M_w = 5800$ ($M_w/M_n = 1.7$). ^{1}H NMR ($CDCl_3$) δ (ppm) 0.8–1.0 (4H, m), 1.0–1.4 (6H, m), 2.33 (3H, s), 6.9–7.0 (6H, m), 7.10 (2H, d, $J = 8.3$ Hz), 7.36 (4H, d, $J = 8.3$ Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) 6.69, 7.37, 20.90, 88.30, 106.70, 116.30, 122.62, 125.91, 130.24, 133.23, 134.36, 143.85, 147.65. ^{29}Si NMR ($CDCl_3$) δ (ppm) −31.14. IR (KBr) = 2154 cm^{-1}. Anal. Found: C, 80.29; H, 6.55; N, 3.30. Calc. for $C_{27}H_{25}NSi$: C, 82.82; H, 6.44; N, 3.58%.

Polymer **3b** was prepared as above. Data for **3b**: yellow powder, m.p. 107–110 °C. $M_w = 9700$ ($M_w/M_n = 1.5$). ^{1}H NMR ($CDCl_3$) δ (ppm) 0.8–1.0 (8 H, m), 1.0–1.4 (12 H, m), 2.34 (3H, s), 6.9–7.0 (6H, m), 7.10 (2H, d, $J = 7.9$ Hz), 7.32 (4H, d,

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$J = 8.6$ Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) 5.05, 8.43, 20.88, 90.12, 108.64, 117.05, 122.67, 125.75, 130.17, 132.90, 134.12, 143.97, 147.33. ^{29}Si NMR ($CDCl_3$) δ (ppm) −29.45. IR (KBr) = 2154 cm^{-1}. Anal. Found: C, 77.22; H, 7.37; N, 2.85. Calc. for $C_{31}H_{35}NSi_2$: C, 77.93; H, 7.38; N, 2.93%.

TGA of the polymers

On a platinum plate was placed 3–5 mg of a polymer, and the plate was heated from room temperature to 1000 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere.

Measurements of conductivities of polymer films doped with I_2

Solid films of polymers prepared by spin-coating of polymer–chloroform solutions on glass plates were held over granular iodine, which was placed in the bottom of a glass vessel. Doping was performed under reduced pressure at room temperature until the conductivities reached the maximum values.

Cyclic voltammetric measurements of polymer films

Thin solid films of the polymers were prepared by casting of the polymer solution in 1,2-dichloroethane on glassy-carbon working electrodes, and the cyclic voltammetric behavior of the films was examined using a three-electrode system in an acetonitrile solution containing tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. An Ag/Ag^{+} electrode and a platinum plate were used as the reference and counter electrode respectively. Oxidation potentials were determined at a sweep rate of 50 m V s^{-1}. The current–voltage curves were recorded on a BAS Model 660 electrochemical analyzer.

Preparation of EL devices

A thin film (30–40 nm) of these polymers was prepared by spin-coating from a solution of the polymer in dichloroethane on an anode, ITO coated on a glass substrate with a sheet resistance of 15 Ω cm^{-1} (Asahi Glass company). An electron-transporting-emitting layer was then prepared by vacuum deposition of Alq at 1×10^{-5} Torr with a thickness of 60–70 nm on the polymer films. Finally, a layer of magnesium–silver alloy with an atomic ratio of 10:1 was deposited on the Alq layer surface as the top electrode at 1×10^{-5} Torr.

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