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Synthesis and properties of σ–π conjugated alternating polymers consisting of carbazole and organosilicon units

Koichi Sakamaki,[1]* Joji Ohshita,[2] Atsutaka Kunai,[2]* Hidenobu Nakao,[1] Akira Adachi[1] and Koichi Okita[1]

[1]Japan Chemical Innovation Institute, Advanced Materials Laboratory, Tsukuba Research Center, 2-1-6 Sengen, Tsukuba, Ibaraki 305-0047, Japan

[2]Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima, Hiroshima 739-8527, Japan

We have synthesized novel σ–π conjugated polymers with an alternating organosilanylene and π-electron system, intending to utilize them for hole-transporting materials of electroluminescent (EL) devices. 3,6-Di(lithioethynyl)carbazoles were co-polymerized with organodichlorosilanes to give the corresponding polymers with molecular weights of M_W = 2000–5000. Another type of polymer with a thienylene unit was also synthesized by the nickel-catalyzed reaction of the di-Grignard reagent of 1,2-bis[2-(5-bromothienyl)]tetraethyldisilane with 3,6-dibromocarbazole, the molecular weight being M_n = 3100. The EL devices with a double-layer system composed of tris(8-quinolinolato)aluminum(III) and the present polymers as the emitting-electron-transporting and hole-transporting layers, respectively, emit green EL with a maximum intensity of the order of 10^3 cd m^{-2}. Of these, the device with the thienylene–carbazole polymers exhibited the highest luminance of 1480 cd m^{-2}.

Keywords: organosilicon polymer; 3,6-diethynylcarbazole; 3,6-dithienylcarbazole; hole transport; electroluminescence

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* Correspondence to: K. Sakamaki and A. Kunai, Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima, Hiroshima 739-8527, Japan.
E-mail: sakamaki@hiroshima-u.ac.jp; akunai@hiroshima-u.ac.jp
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INTRODUCTION

Recently, organosilicon compounds and polymers have received much attention, because of their potential utility as electrically and optically functional materials. For example, siloles are expected to be used as carrier-transporting materials of electroluminescent (EL) devices, and it has been reported that devices having a silole layer for electron transport show high performance.[1–11] In addition, σ–π conjugated polymers, with a regular alternating arrangement of an organosilicon unit —(SiR_2)— and an aromatic π-system (Ar), also exhibit unique electrical and electro-optical properties due to the σ–π conjugation and can be used as hole-transporting materials for EL devices because of their high hole-drift mobility.[1,2,4,7–12]

Recently, we have reported the preparation of such σ–π conjugated polymers having a 9,10-diethynylanthracene unit as the π-system and demonstrated the high performance of double-layer EL devices, in which the polymer is used as the hole-transporting layer, and tris(8-quinolinolato)aluminum(III) complex (Alq) as the electron-transporting-emitting layer. The devices showed superior voltage–current characteristics, compared with the devices with polymers having a phenylene, biphenylene, or naphthylene π-unit in place of the diethynylanthracene unit. These facts imply that the expansion of the aromatic π-system in the polymer enhances the hole transport in the EL device.[9–11] However, in general, too much expansion of the aromatic π-system causes low processibility, arising from low solubility in the solvents and poor film quality of the polymers.

We therefore chose a heteroaromatic system, with diethynylcarbazole as the π-system. Carbazole is known as a typical compound used for hole-transporting materials, as is seen in polyvinylcar-

bazole (PVK).[13] We synthesized organosilanylene–diethynylcarbazole alternating polymers and fabricated double-layer EL devices composed of these polymers and Alq as the hole-transporting and electron-transporting-emitting layer respectively. In this paper, we report the synthesis and device performance of the polymers, together with the optical, electrical and conducting properties.

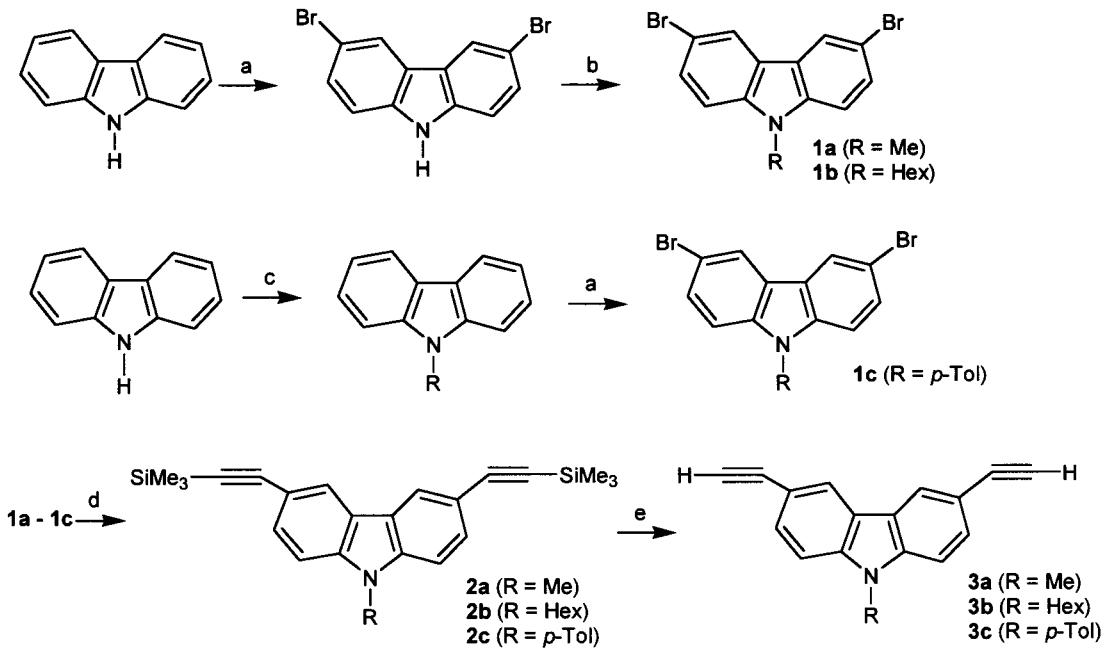
RESULTS AND DISCUSSION

Synthesis of polymers

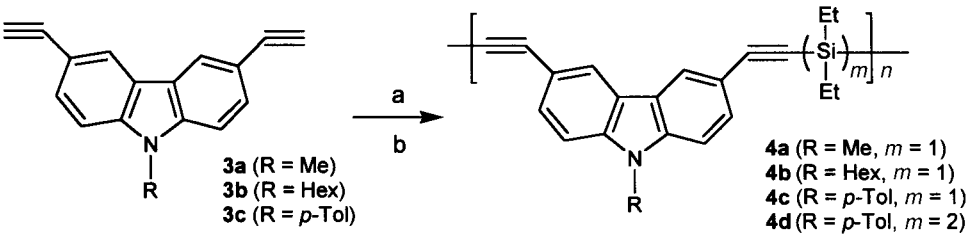
For the synthesis of polymers having a carbazole unit, we prepared 3,6-diethynylcarbazoles **3a–c**, by palladium-catalyzed reactions of 3,6-dibromocarbazoles **1a–c** with trimethylsilylacetylene, followed by desilylation of the resulting products **2a–c** (Scheme 1). Monomers **3a–c** were dilithiated by treating them with two equivalents of MeLi in diethyl ether at −80 °C, and the resulting dilithio-derivatives were reacted with dichloroorganosilanes to give polymers **4a–d** (Scheme 2). The yields and molecular weights of the polymers are listed in Table 1. The polymers were readily separated from the reaction mixture by reprecipitation from methanol or ethanol. The molecular weights of the polymers were in the range $M_W = 2000–5000$ after reprecipitation.

Another type of polymer with a thienylene unit instead of the ethynylene unit was also synthesized by the Grignard coupling reaction of *N*-methyl-3,6-dibromocarbazole (**1a**) with the di-Grignard reagent prepared from 1,2-bis[2-(5-bromothienyl)]-tetraethyldisilane in the presence of a nickel catalyst in THF at 150 °C in a sealed tube (polymer **5** in Scheme 3). The molecular weight of the polymer was $M_W = 3100$ after reprecipitation from hexane.

The polymers thus obtained are solids and soluble in aromatic solvents, halocarbons, and ethers, but they are insoluble in alcohols. Their structures were verified by ^{1}H, ^{13}C, and ^{29}Si NMR spectrometry. For example, the ^{1}H NMR spectrum for polymer **4a** reveals three kinds of signal due to the carbazole ring protons in the region of δ 8.15–7.35, a singlet signal due to *N*-methyl protons at δ 3.80, and a multiplet signal due to ethylsilyl protons at δ 1.2–0.8, in the ratio of 2:2:2:3:10. The ^{13}C NMR spectrum shows six signals for sp^2 carbon atoms, two signals for *sp* carbon atoms, and three



Scheme 1 Synthesis of compounds **3a–c**: (a) 2NBS, $CHCl_3$, CH_3COOH, r.t.; (b) NaH, RI (R =Me, Hex), DMF, r.t.; (c) *p*-iodotoluene, Cu, K_2CO_3, 18-crown-6, *o*-dichlorobenzene, 180 °C; (d) HC ≡ C-$SiMe_3$, $PdCl_2(PPh_3)_2$, NEt_3, 90 °C; (e) KOH, MeOH, Et_2O, r.t.



Scheme 2 Synthesis of polymers **4a–d**: (a) MeLi, Et_2O, −80 °C → r.t.; (b) $Cl(SiEt_2)_mCl$, −80 °C → r.t.

signals for sp^3 carbon atoms. In the ^{29}Si NMR spectrum, only a single peak was observed at δ −31.20. These facts undoubtedly support the regular alternating structure of **4a**. By combustion analysis, however, carbon and nitrogen contents were observed to be a little lower than theoretical values, probably due to the partial formation of ceramic-containing chars, as frequently observed for silicon-containing polymers.

Optical, electrical conduction and electrochemical properties

The optical properties and electrical conductivities of the polymers are summarized in Table 2. The absorption spectra of polymers **4a–d** are almost identical in shape and position, and independent of the length of the silicon chain and the substituents on the nitrogen atom of the carbazole unit. The wavelengths of the absorption maxima of **4a–d** are around 295 nm, which are slightly red-shifted (5–8 nm) relative to those of the corresponding monomers **3a–c**, as illustrated in Fig. 1. However, the degree of red-shift is smaller than that observed for the other alternating polymers composed of organosilicon units and rather smaller π-electron systems.[1] Furthermore, the UV spectra of the polymers are quite similar to those of the corresponding model compounds **2a–c**, as shown in Fig. 2. These results indicate that no significant delocalization of the π-electrons along the polymer chain takes place and the carbazole unit is electronically rather isolated, and the optical properties originate mainly from the π-electron systems in the main chain. As can be seen in Fig. 2, both the present polymers **4a–c** and model compound **3c** exhibit two absorption maxima at around 260 and 295 nm, ascribed to carbazole π–π^* transition bands. Since the UV absorption spectrum of bis(*p*-ethynylphenyl)-*p*-tolylamine shows a broad π–π^* absorption band between 260 and 420 nm, the shorter band at around 260 nm in the diethynylcarbazole derivatives may originate from the π–π^* transition but not from σ–σ^*-type transition.

Table 1 Synthesis of diethynylcarbazole polymers

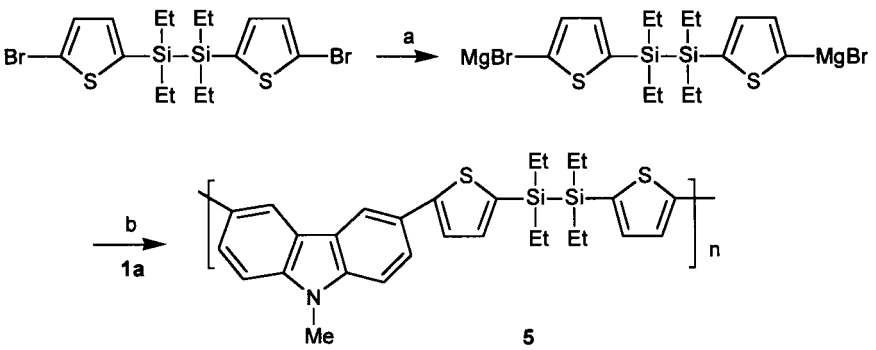
Polymer	Yield (%)[a]	M_n[b]	M_w[b] (M_w/M_n)	M.p. (°C)
4a	26	1300	2300 (1.8)	178–182
4b	41	2600	5100 (2.0)	106–109
4c	17	2400	3100 (1.3)	149–153
4d	9	1600	1900 (1.2)	135–138
5	26	1700	3100 (1.8)	131–135

[a] After reprecipitation.
[b] Determined by GPC, relative to polystyrene standards.

Polymer **5** exhibits the most red-shifted UV absorption among the present polymers; this is due to the extended π-system, as shown in Fig. 1. Polymer **5** also has the smallest band gap, as indicated by the longest absorption edge.

The electrical conductivities of the present polymers are listed in Table 2. The conductivities were measured by the two-probe method after thin solid films of the polymers were exposed to I_2 vapor under reduced pressure. The conductivities of the present polymers are at the level of semiconductors. Polymers **4a–d** exhibited conductivities of (1.7–8.6) × 10^{-5} S cm^{-1}, which are comparable to those of the I_2-doped disilanylene polymers with an oligothienylene group as the π-unit.[1,2] Of these, polymer **4b**, which has a hexyl group at the carbazole nitrogen atom, showed slightly lower conductivity than that of **4a** having a methyl group. Polymer **5** showed the highest conductivity (4.0×10^{-3} S cm^{-1}) among the present polymers, reflecting the extended π-conjugation.

The electrochemical properties of solid films of the polymers were studied by cyclic voltammetry. For this purpose, the solid films were prepared by casting of the polymer solution in 1,2-dichloroethane onto a glassy-carbon working electrode. An



Scheme 3 Synthesis of polymer **5**: (a) Mg, THF; (b) $NiCl_2$(dppe), 150 °C in a sealed tube.

Ag/Ag^+ electrode and a platinum plate were used as the reference and counter electrodes respectively. Measurements were conducted in an acetonitrile solution containing tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte in the range −0.3 to 1.5 V versus Ag/Ag^+. 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.

The oxidation onset potentials of the polymers are listed in Table 3. The potential of polymer **5** (0.6 V versus Ag/Ag^+) is lower than those of the other polymers **4a–d** (0.8–1.0 V versus Ag/Ag^+). This indicates that polymer **5** is more readily oxidized, from which better hole-injecting properties can be expected for **5** than for polymers **4a–d**.

Electroluminescence properties

We also examined the hole-transporting properties of the present polymers by the performance of double-layer EL devices with the 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 in Fig. 3. Polymer **4a** could not be used for fabricating EL devices because of its poor film quality. We also prepared a device having a PVK film instead of the present polymer films for comparison.

Figure 4 shows the relationship between the current density and bias voltage of the devices. The device with polymer **5** exhibited the lowest turn-on voltage (*ca* 6 V) and the highest current density, which are slightly inferior but comparable to that of the device having a PVK film. This seems to be due to the relatively low energy barrier for hole injection from the ITO anode to the polymer layer. The device with polymer **4d** shows better *I–V*

Table 2 Optical and electrical properties of the present polymers

Polymer	Absorption[a] λ_{max}/nm ($\varepsilon \times 10^{-2}$)	Conductivity[b]/ S cm^{-1}
4a	258 (514), 295 (529)	3.3×10^{-5}
4b	263 (249), 294 (261)	1.7×10^{-5}
4c	258 (612), 295 (662)	8.6×10^{-5}
4d	259 (676), 297 (710)	4.3×10^{-5}
5	318 (348), 348 (274)	4.0×10^{-3}

[a] THF solution.
[b] Determined by the two-probe method on polymer films doped with I_2 vapor at room temperature.

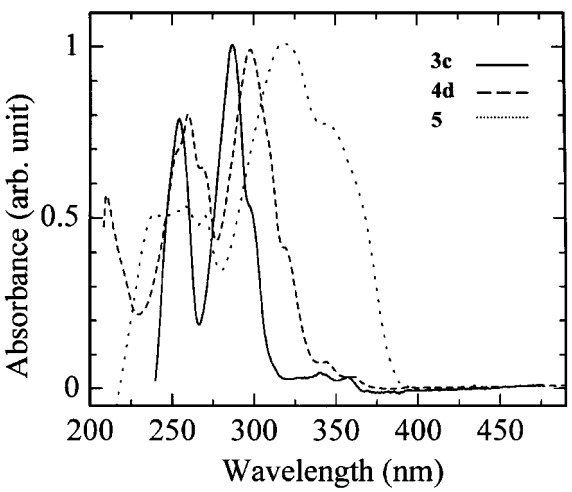


Figure 1 UV spectra of polymers **3c, 4d**, and **5**.

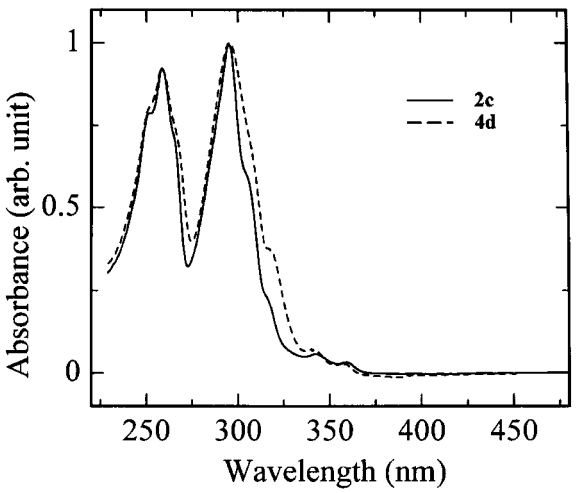


Figure 2 UV spectra of polymers **2c** and **4d**.

properties than that of the device with polymer **4c**. The improved hole injection properties of the device with polymer **4d** may be due to the relatively low oxidation potential. Although polymer **4b** has an equivalent oxidation onset to polymer **4d**, the device with polymer **4b** exhibits the lowest *I–V* performance. This may be caused by other factors, such as film morphology and hole mobility.

The EL spectra of the devices with the present polymers are identical, in shape, to the photoluminescent spectrum of Alq in the solid state, indicating that the electroluminescence originates from Alq emission.[11] The maximum EL intensities of the devices are listed in Table 3. Figure 5 shows the relationship between the EL intensity and the bias voltage (*L–V*) of the EL devices. The maximum luminance of the devices increases in the order **4b** < **4c** < **4d** < **5**, in accordance with the

Table 3 Oxidation potentials and EL properties of the present polymers

Polymer	Onset potential[a]/V	Maximum EL intensity/cd m^{-2}
4a	0.91	–[b]
4b	0.86	180 (at 25.0 V)
4c	0.99	580 (at 19.0 V)
4d	0.87	860 (at 15.5 V)
5	0.61	1480 (at 14.0 V)
PVK	0.67	6250 (at 12.0 V)

[a] Versus Ag/Ag^+.
[b] EL device cannot be fabricated because of poor film processibility of **4a**.

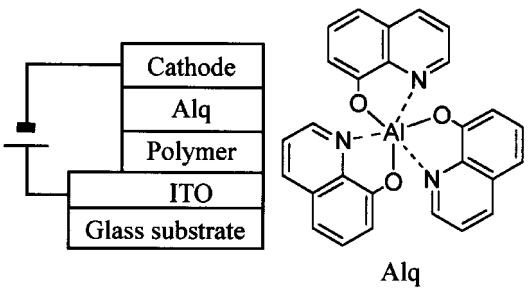


Figure 3 Schematic structure of the double-layer EL device.

improved *I–V* characteristics in the same order. Among the various devices, that with polymer **5** shows the highest EL intensity of 1480 cd m^{-2} at 14 V. The hole injection properties of polymer **5** seem comparable to that of PVK, as suggested by the oxidation onset potential in Cyclic Voltammetry and the turn-on voltage in *I–V* curves. As for the lower *L–V* feature of polymer **5** than that of PVK, there might be other factors operating, such as hole-drift mobility, film quality, and/or blocking of electrons from Alq, to reduce the EL performance for polymer **5**.

CONCLUSION

We have synthesized σ–π conjugated alternating polymers, **4a–d** and **5**. The absorption spectra of polymers **4a–d** were slightly red-shifted compared

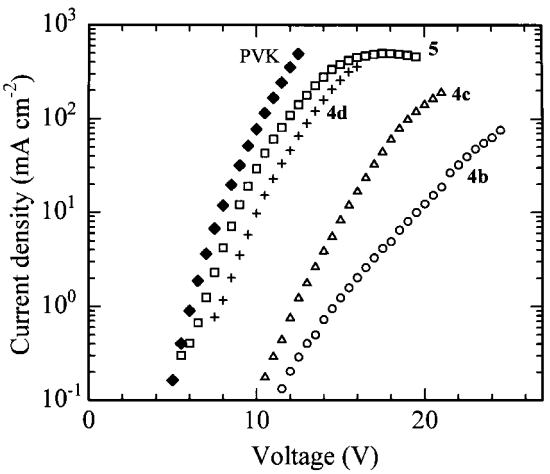


Figure 4 Plots of current densities as a function of bias voltage for the devices with PVK (◆), **4b** (○), **4c** (△), **4d** (+), and **5** (□).

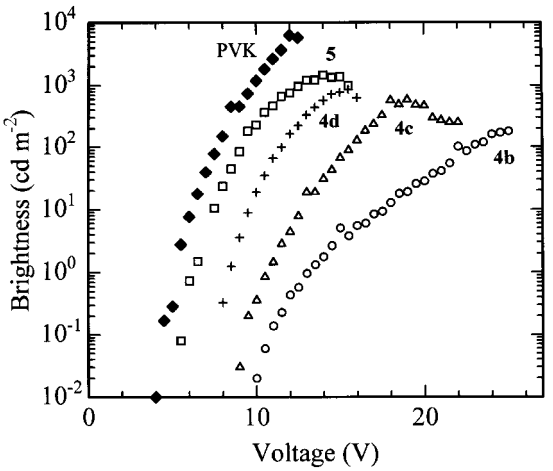


Figure 5 Plots of EL intensities as a function of bias voltage for the devices with PVK (◆), **4b** (○), **4c** (△), **4d** (+), and **5** (□).

with the corresponding monomers **3a**–**c**, but they were almost the same as the model compounds **2a**–**c**. Polymer **5** has the smallest HOMO–LUMO gap among the present polymers, as estimated by the UV absorption edge. Reflecting this, the device with polymer **5** showed the higher *I*–*V* and *L*–*V* performance.

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. The molecular weights of the polymers were determined with Shodex GPC columns, using THF as the eluent, and are relative to polystyrene standards.

Materials

Preparation of 1a, b

Compounds **1a** and **1b** were prepared as reported in the literature.[14]

Preparation of 2a and 2b

Compound **2a**, 3,6-bis(trimethilsilylethynyl)-*N*-methylcarbazole, was synthesized as follows. Compound **2b** was synthesized by the same procedure.

In a 200 ml three-necked flask were placed 0.68 g (2.0 mmol) of **1a**, 15 mg (0.16 mmol) of CuI, 57 mg (0.08 mmol) of $PdCl_2(PPh_3)_2$, 0.78 g (8.0 mmol) of trimethylsilylacetylene, and 20 ml of triethylamine. After stirring the mixture for 12 h at reflux temperature, the mixture was filtered and the solvent was evaporated. The residue was chromatographed on a silica gel column with hexane as eluent to give 0.66 g (1.8 mmol, 90% yield) of **2a** as a yellow powder.

Data for **2a**: yellow solid, m.p. 65–69 °C. ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d, J = 1.54 Hz), 7.47 (2H, dd, J = 8.50, 1.54 Hz), 7.01 (2H, br d, J = 8.50 Hz), 3.47 (3H, s), 0.04 (18H, s) ppm. ^{13}C NMR ($CDCl_3$) δ 140.61, 129.74, 124.21, 121.85, 113.59, 108.30, 106.51, 91.84, 28.70, 0.22 ppm. IR (KBr) 2152 cm^{-1}. UV (λ_{max} in THF) 362 (ε 1600), 345 (2800), 318 (13 800), 295 (55 200), 260 (46 000), 250 (34 400 s)nm. Anal. Calc. for $C_{23}H_{27}NSi_2$: C, 73.93; H, 7.28; N, 3.75. Found: C, 73.80; H, 7.21; N, 3.55%.

Data for **2b**: yellow powder, m.p. 36–41 °C. ^{1}H NMR ($CDCl_3$) δ 8.19 (2H, d, J = 1.57 Hz), 7.56 (2H, dd, J = 8.49, 1.57 Hz), 7.28 (2H, br d, J = 8.49 Hz,), 0.8–1.9 (13H, m), 0.29 (18H) ppm. ^{13}C NMR ($CDCl_3$): δ 140.63, 129.96, 124.65, 122.32, 113.77, 108.75, 106.40, 92.02, 43.27, 31.47, 28.84, 26.85, 22.48, 13.91, 0.15 ppm. ^{29}Si NMR ($CDCl_3$) δ −18.22 ppm. IR (KBr) 2152 cm^{-1}. UV (λ_{max} in THF) 364 (ε 1700), 347 (3100), 320 (20 600), 296 (8250), 261 (77 900), 250 (63 000) nm. Anal. Found: C, 75.64; H, 8.37; N, 3.37. Calc. for $C_{28}H_{37}NSi_2$: C, 75.78; H, 8.40; N, 3.16%.

Preparation of 3a and 3b

In a 300 ml three-necked flask were placed 0.66 g (1.8 mmol) of **2a**, 1.00 g of KOH, 60 ml of diethyl ether, 40 ml of methanol and 20 ml of water. The solution was stirred for 4 h at room temperature. Then the mixture was washed with water until *ca* pH 7. The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent, the resulting mixture was chromatographed on a silica gel column with hexane as eluent to afford 0.38 g (1.7 mmol, 94% yield) of **3a** as a yellow solid.

Data for **3a**: ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d, J = 1.55 Hz), 7.55 (2H, dd, J = 8.41, 1.55 Hz), 7.18 (2H, d, J = 8.41 Hz), 3.66 (3H, s), 3.10 (2H, s) ppm.

^{13}C NMR ($CDCl_3$) δ 140.92, 129.99, 124.47, 121.92, 112.60, 108.52, 84.73, 75.47, 28.99 ppm. IR (KBr) 3285, 2152 cm^{-1}. UV (λ_{max} in THF) 360 (ε 1300), 343 (1800), 330 (1400), 300 (18 400), 288 (46 900), 252 (44 700) nm. HRMS *m/z* found 229.0869. Calc. for $C_{17}H_{11}N$ 229.0892.

Compound **3b** was prepared in 94% yield in a similar fashion as above.

Data for **3b**: yellow solid, m.p. 57–60 °C: ^{1}H NMR ($CDCl_3$) δ 8.20 (2H, d, J = 1.32 Hz), 7.59 (2H, dd, J = 8.58, 1.32 Hz), 7.30 (2H, d, J = 8.58 Hz), 4.23 (2H, t, J = 7.26 Hz), 3.08 (2H, s), 1.75–1.80 (2H, m), 1.20–1.40 (6H, m), 0.85 (3H, t, J = 6.93 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ 140.61, 130.08, 124.71, 122.21, 112.67, 108.90, 84.73, 75.40, 42.27, 31.45, 28.83, 26.85, 22.46, 13.93 ppm. IR (KBr) 3267, 2099 cm^{-1}. UV (λ_{max} in THF) 362 (ε 2600), 345 (1900), 301 (21 800), 289 (57 600), 254 (80 500), 248 (75 600) nm. HRMS *m/z* found: 299.1671. Calc. for $C_{22}H_{21}N$: 299.1674.

Preparation of *N*-(*p*-tolyl)carbazole

In a 500 ml three-necked flask were placed 3.9 g (23.3 mmol) of carbazole, 5.20 g (23.8 mmol) of *p*-iodotoluene, 2.96 g (46.6 mmol) of copper powder, 12.88 g (93.2 mmol) of potassium carbonate, 0.62 g (2.3 mmol) of 18-crown-6-ether and 200 ml of *o*-dichlorobenzene. The mixture was heated at reflux temperature for 24 h. Then, the solvent was removed by distillation under reduced pressure, and chloroform was added to the residue. The inorganic salts were filtered off, and the filtrate was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the resulting mixture was chromatographed on a silica gel column with hexane as eluent, and recrystallized from hexane, affording 3.94 g (15.3 mmol, 66% yield) of *N*-(*p*-tolyl)carbazole as colorless crystals.

Data for *N*-(*p*-tolyl)carbazole: m.p. 109–110 °C. ^{1}H NMR ($CDCl_3$) δ 8.22 (2H, d, J = 7.79 Hz), 7.40–7.55 (8H, m), 7.3–7.4 (2H, m), 2.53 (3H, s) ppm. ^{13}C NMR ($CDCl_3$) δ 147.77, 144.04, 141.70, 137.17, 133.69, 132.55, 129.95, 126.97, 126.45, 116.49, 27.94 ppm. UV (λ_{max} in THF) 341 (ε 4000), 328 (3600), 293 (25 300), 286 (22 400), 259 (28 400), 240 (73 200), 213 (76 500) nm. Anal. Found: C, 88.63; H, 5.81; N, 5.56. Calc. for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44%.

Preparation of 1c

In a 300 ml three-necked flask were placed 3.94 g (15.3 mmol) of *N*-(*p*-tolyl)carbazole, 5.45 g (30.6 mmol) of *N*-bromosuccinimide and 100 ml of chloroform. After the solution was stirred for 3 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 recrystallized from chloroform to give 4.98 g (12 mmol, 78% yield) of **1c** as colorless crystals.

Data for **1c**: m.p. 214–215 °C. ^{1}H NMR ($CDCl_3$) δ 8.17 (2H, d, J = 1.97 Hz), 7.47 (2H, d, J = 8.90 Hz), 7.3–7.4 (4H, m), 7.21 (2H, d, J = 8.90 Hz), 2.48 (3H, s) ppm. ^{13}C NMR ($CDCl_3$) δ 139.98, 138.11, 134.03, 130.66, 129.27, 126.76, 123.77, 123.13, 112.85, 111.50, 21.22 ppm. UV (λ_{max} in THF) 358 (ε 3400), 342 (3200), 302 (20 800), 270 (36 900), 244 (66 000), 224 (48 900) nm. Anal. Found: C, 54.94; H, 3.17; N, 3.32. Calc. for $C_{19}H_{13}Br_2N$: C, 54.97; H, 3.16; N, 3.37%.

Preparation of 2c

In a 200 ml three-necked flask were placed 3.03 g (7.3 mmol) of **1c**, 110 mg (0.58 mmol) of CuI, 210 mg (0.3 mmol) of $PdCl_2(PPh_3)_2$, 2.85 g (29 mmol) of trimethylsilylacetylene and 80 ml of triethylamine. After stirring the mixture for 24 h at reflux temperature, the mixture was filtered and the solvent was evaporated. The resulting mixture was chromatographed on a silica gel column with hexane as eluent to afford 2.32 g (5.2 mmol, 71% yield) of **2c** as a yellow powder.

Data for **2c**: m.p. 95–97 °C. ^{1}H NMR ($CDCl_3$) δ 8.25 (2H, d, J = 1.23 Hz), 7.51 (2H, q, J = 8.29 Hz), 7.3–7.4 (4H, m), 7.24 (2H, d, J = 8.29 Hz), 2.48 (3H, s), 0.32 (18H, s) ppm. ^{13}C NMR ($CDCl_3$) δ 141.06, 137.97, 134.03, 130.57, 130.17, 126.76, 124.53, 122.61, 114.68, 109.83, 106.20, 92.26, 21.21, 0.13 ppm. UV (λ_{max} in THF) 359 (ε 2800), 342 (4800), 295 (80 500), 258 (74 200) nm. Anal. Found: C, 77.73; H, 6.96; N, 3.05. Calc. for $C_{29}H_{31}NSi_2$: C, 77.45; H, 6.95; N, 3.11%; IR (KBr) 2141 cm^{-1}.

Preparation of 3c

In a 300 ml three-necked flask were placed 1.0 g (2.3 mmol) of **2c**, 1.0 g of NaOH, 60 ml of diethyl ether, 40 ml of methanol and 20 ml of water. The solution was stirred for 4 h at room temperature. Then the mixture was washed with water until *ca* pH 7. The organic layer was separated and dried over $MgSO_4$. The resulting mixture was chromatographed on a silica gel column with hexane as

eluent to afford 0.69 g (95% yield) of **3c** as a yellow solid.

Data for **3c**: m.p. 143–146 °C. ^{1}H NMR ($CDCl_3$) δ 8.25 (2H, d, J = 1.38 Hz), 7.53 (2H, dd, J = 8.58, 1.38 Hz), 7.3–7.4 (4H, m), 7.27 (2H, d, J = 8.58 Hz), 3.10 (2H, s), 2.48 (3H, s) ppm. ^{13}C NMR ($CDCl_3$) 141.19, 138.04, 133.87, 130.57, 130.28, 126.72, 124.58, 122.50, 113.57, 109.97, 84.57, 75.71, 21.17 ppm. UV (λ_{max} in THF) 356 (ε 2400), 340 (3100), 287 (53 700), 254 (57 500) nm. Anal. Found: C, 90.60; H, 5.00; N, 4.37. Calc. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59%. IR (KBr) 3279, 2103 cm^{-1}.

Preparation of polymers

Preparation of 4a

In a 300 ml three-necked flask were placed 0.47 g (2.1 mmol) of **3a** and 20 ml of diethyl ether. To this was added 3.8 ml (4.2 mmol) of a 1.1 M MeLi–diethyl ether solution at −80 °C. The reaction mixture was allowed to warm up to room temperature. After stirring the mixture for 2 h, 20 ml of THF was added to the mixture, and the mixture was cooled to −80 °C again, then 0.32 g (2.1 mmol) of dichlorodiethylsilane was added dropwise. The mixture was allowed to warm to room temperature and stirred for 12 h at this temperature. The solution was washed with water, the organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and dried over $MgSO_4$. After evaporation of the solvent, the residue was reprecipitated from methanol and then from ethanol to give 0.121 g (19% yield) of **4a** as a yellow powder.

Data for **4a**: m.p. 178–182 °C. M_w = 2300 (M_w/M_n = 1.8). ^{1}H NMR ($CDCl_3$) δ 8.15–8.30 (2H, br m), 7.55–7.70 (2H, br m), 7.20–7.35 (2H, br m), 3.80 (3H, s), 1.3–0.8 (10H, m) ppm. ^{13}C NMR ($CDCl_3$) δ 141.15, 130.37, 124.89, 122.21, 113.69, 108.55, 107.87, 87.23, 29.27, 7.53, 6.88 ppm. ^{29}Si NMR δ −31.20 ppm. Anal. Found: C, 77.76; H, 6.30; N, 3.89. Calc. for $(C_{21}H_{19}NSi)_n$: C, 80.46; H, 6.11; N, 4.47%. IR (KBr) 2152 cm^{-1}.

Preparation of 4b–d

Polymers **4b, 4c**, and **4d** were prepared from **3b** or **3c** in a similar manner as above. As for **4d**, 1,2-dichlorotetraethyldisilane was used instead of dichlorodiethylsilane.

Data for **4b**: m.p. 106–109 °C. M_w = 5100 (M_w/M_n = 2.0). ^{1}H NMR ($CDCl_3$) δ 8.20–8.35 (2H, br m), 7.50–7.70 (2H, br m), 7.20–7.40 (2H, br m), 4.22 (2H, br), 1.4–0.8 (21H, m) ppm. ^{13}C NMR ($CDCl_3$) δ 140.53, 130.23, 124.91, 122.23, 113.51, 108.75, 107.85, 87.14, 43.22, 31.43, 28.81, 26.79, 22.45, 13.91, 5.91, 5.29 ppm. ^{29}Si NMR ($CDCl_3$) δ −31.78 ppm. Anal. Found: C, 78.22; H, 7.42; N, 3.37. Calc. for $(C_{26}H_{29}NSi)_n$: C, 81.41; H, 7.62; N, 3.65%. IR (KBr) 2151 cm^{-1}.

Data for **4c**: m.p. 149–153 °C. M_w = 3100 (M_w/M_n = 1.3). ^{1}H NMR ($CDCl_3$) δ 8.25–8.40 (2H, br m), 7.50–7.65 (2H, br m), 7.30–7.45 (4H, br m), 7.2–7.3 (2H, br m), 2.48 (3H, s), 1.4–0.8 (10H, br m) ppm. ^{13}C NMR ($CDCl_3$) δ 141.24, 138.02, 133.96, 130.58, 126.77, 124.83, 122.59, 114.50, 113.60, 109.87, 107.71, 87.37, 21.21, 7.40, 6.85 ppm. ^{29}Si NMR ($CDCl_3$) δ −31.14 ppm. Anal. Found: C, 81.12; H, 5.80; N, 3.46. Calc. for $(C_{27}H_{23}NSi)_n$: C, 83.24; H, 5.95; N, 3.60%. IR (KBr) 2151 cm^{-1}.

Data for **4d**: m.p. 135–138 °C. M_w = 1900 (M_w/M_n = 1.2). ^{1}H NMR ($CDCl_3$) δ 8.22 (2H, br s), 7.15–7.60 (8H, br m), 2.47 (3H, s), 0.8–1.4 (20H, br m) ppm. ^{13}C NMR ($CDCl_3$) δ 140.99, 137.92, 134.01, 130.57, 130.24, 126.79, 124.39, 122.62, 115.18, 109.81, 109.67, 89.15, 21.21, 8.52, 5.12 ppm. ^{29}Si NMR ($CDCl_3$) δ −29.43 ppm. Anal. Found. C, 76.10; H, 6.80; N, 2.72. Calc. for $(C_{31}H_{33}NSi_2)_n$: C, 78.26; H, 6.99; N, 2.94%. IR (KBr) 2151 cm^{-1}.

Preparation of 5[7]

A mixture of 24 mg (1.0 mmol) of magnesium and 0.25 g (0.5 mmol) of 1,2-bis[2-(5-bromothienyl)]-tetraethyldisilane in 1 ml of THF was stirred in a Pyrex tube (10 mm × 150 mm) at the reflux temperature until all magnesium was consumed. To the resulting mixture of di-Grignard reagent was added 0.17 g (0.5 mmol) of 3,6-dibromo-*N*-methylcarbazole (**1a**) and 3 mg (0.005 mmol) of dichloro[bis(diphenylphosphino)ethane]nickel(II), and the tube was degassed and sealed. The tube was heated at 150 °C for 78 h. After a similar work-up as above, the products were reprecipitated from ethanol to give 66 mg (26% yield) of **5** as a yellow powder.

Data for **5**: m.p. 131–135 °C. M_w = 3100 (M_w/M_n = 1.8). ^{1}H NMR ($CDCl_3$) δ 8.3–7.1 (10H, br m), 3.68 (3H, s) 1.2–0.6 (20H, br s) ppm. ^{13}C NMR ($CDCl_3$) δ 151.08, 141.54, 137.07, 135.09, 131.53, 129.09, 126.54, 124.27, 118.82, 109.66, 29.79, 9.29, 6.22 ppm. ^{29}Si NMR ($CDCl_3$) δ −18.06 ppm. Anal. Found: C, 65.06; H, 6.55; N, 2.19. Calc. for $(C_{29}H_{33}NS_2Si_2)_n$: C, 67.52; H, 6.45; N, 2.72%.

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 placed in the bottom of a glass vessel. Doping was performed under reduced pressure at room temperature until the conductivities reached the maximum value.

Cyclic voltammetric measurements of polymer films

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

Preparation of electroluminescence devices

A thin film (30–40 nm) of the polymers was prepared by spin-coating from a solution of polymer in dichloroethane on an anode of ITO coated on a glass substrate with a sheet resistance of $15\ \Omega\,cm^{-1}$ (Asahi Glass company). An electron-transporting-emitting layer with a thickness of 60–70 nm was then prepared on the polymer films by vacuum deposition of Alq at 1×10^{-5} Torr. 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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