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Organic Electroluminescent Devices using Organosilicon Polymers Containing Phenylene or Diethynylanthracene Units

Akira Adachi,[1]* Joji Ohshita,[2] Takahiro Ohno,[2] Atsutaka Kunai,[2]
Stefan A. Manhart,[1] Koichi Okita[1] and Junji Kido[1]
[1]Advanced Materials Laboratory, Japan Chemical Innovation Institute, 2-1-6 Sengen, Tsukuba 304-0047, Japan
[2]Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan
[3]Graduate School of Engineering, Yamagata University, Yonezawa 992-8510, Japan

Double-layer electroluminescent (EL) devices composed of an alternating polymer with mono-, di-, or tri-silanylene and phenylene units, $[(\mathrm{Si\ R})_m\ (\mathrm{C_6H_4})]_n$ (R = alkyl, $m = 1$–3) as a hole-transporting layer, and tris(8-quinolinolato) aluminium(III) complex (Alq) as an electron-transporting–emitting layer were fabricated. The longer silanylene chain lengths in the polymer, on going from $m = 1$ to $m = 2$ and 3, result in better electrical properties for the EL devices, implying that the σ–π conjugation in the polymers plays an important role in the hole-transporting properties, including the hole-injection efficiency from an anode. This is in marked contrast to the improved hole-transporting properties that occur in response to reducing the silanylene chain length of silanylene-diethynylanthracene polymers previously reported. The UV absorption maxima of silanylene-phenylene polymers shift to longer wavelengths with increasing *m*, and their oxidation peak potentials in cyclic voltammograms shift to lower potential with increasing *m*, in accordance with the improved electrical properties of the device that are observed with the polymers containing the longer silanylene chain. A triple-layer EL device with a hole-transporting layer of monosilanylene-diethynylanthracene polymer, an electron-transporting–emitting layer of Alq, and an electron-blocking layer of *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) exhibited a maximum efficiency of 1.0 lm $\mathrm{W^{-1}}$ and a maximum luminance of 14750 cd $\mathrm{m^{-2}}$, both of which are much higher than the values obtained from a conventional EL device with TPD/Alq.

Keywords: electroluminescence; aluminum complex; hole transport; organosilicon polymer; diethynylanthracene; phenylene; silanylene

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INTRODUCTION

A great deal of interest has recently been focused on polysilanes with relatively high hole mobility due to the σ-conjugation in the polymer backbone, which can be used for various functional systems such as electroluminescent (EL) devices.[1–7] In particular, soluble polysilanes such as poly(methylphenylsilane) (PMPS) have been actively studied in this respect.[2–7] On the other hand, polymers composed of an alternating arrangement of π-electron systems and Si–Si σ-bonds in the main chain represent a new class of conjugated polymers due to the σ–π conjugation, and the properties of these polymers are interesting in connection with their potential utility as photoresists, semiconductors and photoconductors.[8–12] However, there have been only a few reports thus far regarding the optical emission of this type of polymer. Fang *et al.* have recently studied the emission spectra of a series of σ–π-conjugated organosilicon polymers with an alternating arrangement of oligosilanylene units and π-electron system,[13–17] demonstrating that the emission changes from the type from a σ-

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* Correspondence to: Akira Adachi, Advanced Materials Laboratory, Japan Chemical Innovation Institute, 2-1-6 Sengen, Tsukuba 304-0047, Japan.

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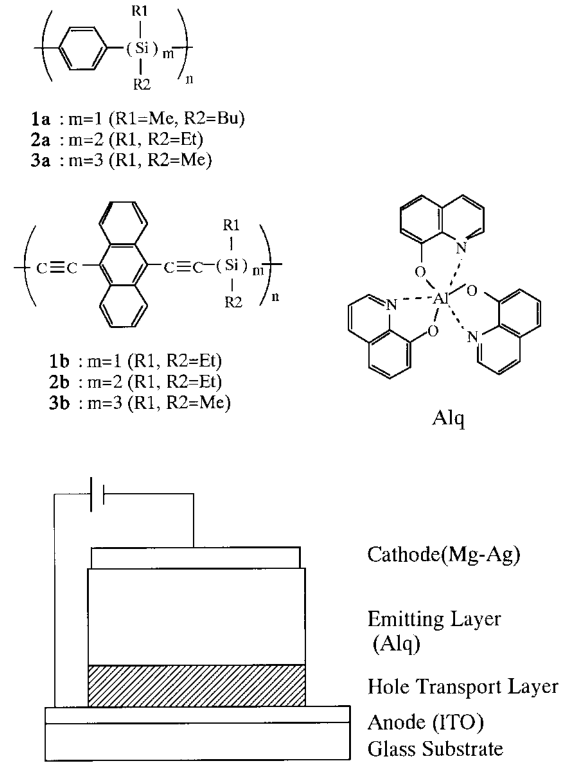

Figure 1 Configuration of the EL device and molecular structure of the materials used.

conjugation unit such as silanylene to the that from a π-conjugation unit response to increasing the chain length of the oligosilanylene units, as well as in response to reducing the extension of the π-electron system.[17] The emission lifetime and the quantum yield also depend on the dimethylsilanylene chain length. Fang *et al.* have also reported that the emission from the polymers having π-electron systems such as phenylene or biphenylene are solvatochromic, and the maxima are red-shifted in polar solvents, which can be explained by the CT (charge transfer)-type excited states between oligosilanylene and the aromatic units. In studies relating to the EL of organosilicon polymers, a single-layer EL device with PMPS containing 3% anthracene units, which was prepared from a Wurtz-type co-condensation of dichloromethylphenylsilane and bis(chloromethylphenylsilyl)anthracene with sodium, has been studied by Suzuki and co worker.[18,19] The polymer exhibits strong photoluminescence (PL) with a high quantum efficiency (87%) based on the π–π* emission from the anthracene units. In contrast, a single-layer EL device based on the anthracene-containing polymer shows a quite low external quantum yield (0.01%) probably due to the low electron-transporting properties of this polymer.

In order to obtain more information about EL devices using σ–π conjugated polymers, we have prepared EL devices composed of a polymer alternating with the disilanylene unit and various π-electron systems in the main chain as the hole-transporting layer, and tris(8-quinolinolato)aluminium(III) (Alq) as the electron-transporting–emitting layer of these devices were then examined the voltage–current density and the voltage–luminance characteristics.[20] The EL device with the most extended π-electron system, diethynylanthracene, exhibited the best electrical properties and provided the highest luminance. Moreover, we have synthesized the diethynylanthracene polymers with various silanylene chain lengths from mono-to trisilanylene and examined their hole-transporting properties; as a result, we found that reducing the silanylene chain length leads to improved electrical properties, and the device with the monosilanylene-diethynylanthracene polymer hole-transporting layer exhibits the lowest turn-on voltage and the highest luminance. (S. A. Manhart, A. Adachi, K. Sakamaki, K. Okita, J. Ohshita, T. Ohno, T. Hamaguchi, A. Kunai and J. Kido, *J. Organometal. Chem.*, in press)

In this paper we compare the properties of EL devices that involve a polymer with a relatively small π-electron system, phenylene, and silanylene units of various chain lengths as the hole-transporting layer, with the properties of the devices based on diethynylanthracene polymers. We correlate the results of the EL device performance with the oxidation potential, UV absorption and molecular orbitals (MOs) of model compounds calculated by the semiempirical MNDO method.

EXPERIMENTAL

EL device fabrication and measurements

Figure 1 shows the configuration of EL device and the molecular structure of the materials used in the present study. The anode was indium–tin oxide (ITO) that was coated on a glass substrate, having a sheet resistance of 15 Ω (Asahi Glass Company). Mono- and di-silanylene-phenylene polymers (**1a**[21] and **2a**[22,23]) and silanylene-diethynylanthracene

Table 1 Molecular weights of the organosilicon polymers used

Polymer	M_w[a]	M_n[a]
1a	31 000	17 000
2a	14 000	6 400
3a	8 800	5 100
1b	3 200	2 100
2b	16 300	2 000
3b	8 200	3 800

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

polymers (**1b, 2b** and **3b**) (S. A. Manhart, A. Adachi, K. Sakamaki, K. Okita, J. Ohshita, T. Ohno, T. Hamaguchi, A. Kunai and J. Kido, *J. Organometal. Chem.*, in press) with the molecular weights listed in Table 1 were prepared as described in the literature and the trisilanylene-phenylene polymer was obtained as described below. The polymer layer was prepared by spin-coating from a dichloroethane or toluene solution of polymers. The thickness (30–40 nm) of the polymer layer was controlled by adjusting the solution concentration and the spin rate. The electron-transporting–emitting material was Alq, which was purified by the train sublimation method. Alq (thickness 60–70 nm) was vacuum deposited at 1×10^{-5} torr on the polymer layer. 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. During the evaporation process, the thickness and evaporation rate were monitored with a thickness monitor (Ulvac CRTM 5000) having a quartz oscillator. The actual thickness of each layer was measured with a Sloan Dektak 3030 surface profiler. The emitting area was 0.5×0.5 cm^2. Luminance was measured with a Topcon BM-7 luminance meter at room temperature. EL spectra were taken with an optical multichannel analyzer (Otsuka Electronics, IMUC-7000). Cyclic voltammetric measurements for polymers were carried out using a three-electrode system in an acetonitrile solution containing 100 mM tetraethylammonium tetrafluoroborate as the supporting electrode. Thin solid films of the polymers were prepared by spin-coating of the polymer solution in chloroform on ITO working electrodes. An Ag/0.1 M $AgClO_4$ electrode and a platinum plate were used as the reference and counter-electrode, respectively. Peak potential was determined in a sweep rate of 50 mV s^{-1}. The current–voltage curve was recorded on a Hokuto Denko HAB-151 potentiostat/galvanostat.

Synthesis of poly[(hexamethyltrisilanylene)phenylene]

To a solution of 0.94 g (4.00 mmol) of 1,4-dibromobenzene in 7 ml of dry hexane was added 6.33 ml (10.0 mmol) of a 1.58 M solution of butyllithium in hexane and the mixture was heated to reflux for 1 h. The solvent was decanted off and the resulting white precipitates containing dilithiobenzene and lithium chloride were washed twice with dry hexane. To this were added 8 ml of dry ether and 0.93 g (3.80 mmol) of dichlorohexamethyltrisilane at −80 °C. The mixture was then warmed to room temperature and stirred for 36 h. After hydrolysis of the mixture, the organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was reprecipitated from acetone/chloroform to give 70.0 mg (7% yield) of the title polymer as white solids: $M_w = 8800$ ($M_w/M_n = 1.7$); ^{1}H NMR (δ in $CDCl_3$) 0.04 (6H, MeSi), 0.24 (s, 12H, MeSi), 7.33 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −6.6, −3.4 (MeSi), 133.0, 139.7 (phenylene).

RESULTS AND DISCUSSION

EL device performance

As shown in Fig. 2, the EL spectra of all the EL devices with various hole-transporting materials are identical to the photoluminescent (PL) spectrum of Alq in the solid state, indicating that the electroluminescence originates from Alq. The spectral profile is independent of the hole-transporting materials used as well as the current density, implying that the recombination of injected holes and electrons takes place almost entirely in the Alq layer.

Figure 3 shows the current density–voltage (*I*–*V*) characteristics of the double-layer devices with silanylene-phenylene polymers (**1a** and **2a**). The plots depict different functional dependences between the applied voltage and current of the two devices with different hole-transporting layers. The current density of the disilanylene polymer-based device is always larger than that of the monosilanylene polymer (**1a**) device at any applied

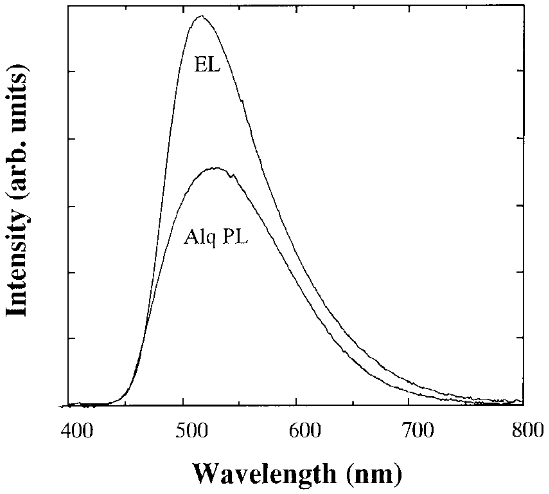

Figure 2 Electroluminescent spectrum of EL devices using various hole-transporting materials and photoluminescent spectrum of Alq in the solid state.

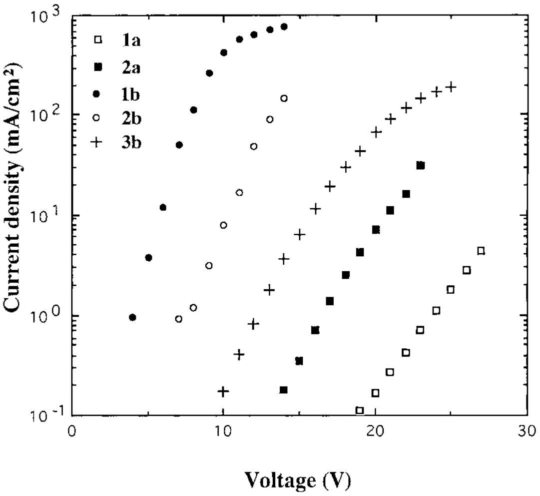

Figure 3 *I–V* characteristics of EL devices with silanylene-phenylene polymers (**1a–3a**) or silanylene-diethynylanthracene polymers (**1b–3b**).

voltage. The *I–V* characteristic of the EL device with trisilanylene polymer (**3a**) was almost equal to that of the disilanylene polymer. However, the detailed data for the trisilanylene polymer are not described in this paper because of their low reproducibility, resulting from the quality of the trisilanylene polymer film. The maximum current density of the disilanylene polymer-based device was 30 mA cm^{-2} at 23 V.

We have already reported that polymer **2a** is electrochemically active and its cyclic voltammogram (CV) in the solid state reveals an irreversible peak due to anodic oxidation (J. Ohshita, K. Sugimoto, A. Kunai, Y. Harima and K. Yamashita, *J. Organometal. Chem.*, 580, (1999)). Similarly, the anodic oxidation peak was observed in the CV on the thin solid film of polymer **3a**, prepared by spin-coating of a $CHCl_3$ solution of the polymer on an ITO working electrode, in CH_3CN. The anodic oxidation occurred irreversibly, as was observed for polymer **2a**. After one cycle of CV scanning in the range 0.0–2.0 V vs Ag/Ag$^+$, the polymer was wholly dissolved in the CH_3CN solution and no longer remained on the electrode, probably due to the decomposition of the polymer main chain. In contrast, polymer **1a** was found to be inactive towards electrochemical oxidation. No oxidation peaks were observed in its CV in the range 0.0–2.0 V vs Ag/Ag$^+$, and the polymer film remained unchanged on the ITO electrode after the potential scanning.

As shown in Table 2, the oxidation potentials of polymers **1a–3a** were >2, 1.58 and 1.45 V, respectively. The oxidation potential was significantly reduced when the silanylene chain length changed from mono- to di-silanylene. With trisilanylene polymer, the oxidation occurred at essentially the same, but a slightly lower, potential compared with the disilanylene polymer.

Disilanylene polymer **2a** exhibits remarkably red-shifted UV absorption compared with that of polymer **1a**, implying the existence of expanded σ–π conjugation along the polymer chain. In contrast, the UV absorption of the trisilanylene polymer appears in the same region as that of the disilanylene polymer **2a**. The improvement in the *I–V* characteristics for di- and tri-silanylene polymers **2a** and **3a** relative to **1a** may be a result of the expansion of the conjugation through σ–π interaction in the polymer main chain, which strongly influences the oxidation potential and the UV λ_{max}. From these results, it is most likely that the σ–π conjugation of these silanylene-phenylene polymers, which would elevate the HOMO level of the polymers, plays an important role in producing the better electrical properties of EL devices with polymers **2a** and **3a**.

In Fig. 4, the luminance–voltage (*L–V*) characteristics of the devices with the silanylene-phenylene polymers are given. As suggested from the *I–V* characteristics, the devices with the disilanylene-phenylene polymer **2a** exhibited a higher lumi-

Table 2 UV absorption and oxidation peak potentials of phenylene-silanylene polymers

Polymer	Absorption, λ_{max} (nm)	Oxidation peak potential vs. Ag/Ag$^+$ (V)
1a	238	>2.0
2a	260	1.58
3a	264	1.45

nance than those with the monosilanylene-phenylene polymer **1a**, and a maximum luminance of 17 cd m^{-2} was achieved at 23 V.

We have recently described the performance of EL devices with a double-layer system consisting of a hole-transporting layer of alternating polymers with mono-, di- or tri-silanylene and diethynylanthracene units (**1b–3b**), and an electron-transporting–emitting layer of Alq (S.A. Manhart, A. Adachi, K. Sakamaki, K. Okita, J. Ohshita, T. Ohno, T. Hamaguchi, A. Kunai and J. Kido, *J. Organometal. Chem.*, in press). In marked contrast to the present EL devices having silanylene-phenylene polymers, the electrical properties of the EL devices with polymers **1b–3b** were improved by reducing the silanylene chain length from $m = 3$ to 1 (Fig. 3). The turn-on voltages of the devices were at much lower energies than those of the devices with polymers **1a–3a**, and these voltages shifted to higher values with increases in m (4 V for **1b**, 6 V for **2b**, and 12 V for **3b**). These characteristics are due to the favored inter- and intra-molecular π–π aggregation in the solid state for polymers with higher concentrations of aromatic units, which improves the hopping transport between π-electron systems, and the σ–π conjugation in the polymer chain seems to exert little influence on the hole-transporting properties of these diethynylanthracene polymers. In fact, the UV absorption maxima of diethynylanthracene polymers **1b–3b** appeared at almost the same wavelength (448–449 nm), regardless of the silanylene chain length. Of these, the maximum luminance, 1120 cd m^{-2}, was obtained for the device with polymer **1b** (Fig. 4), and this luminance was much higher than the maximum luminance of the device with polymer **2a**, indicating that in diethynylanthracene polymer holes are transported through π–π aggregation in preference to σ–π conjugation.

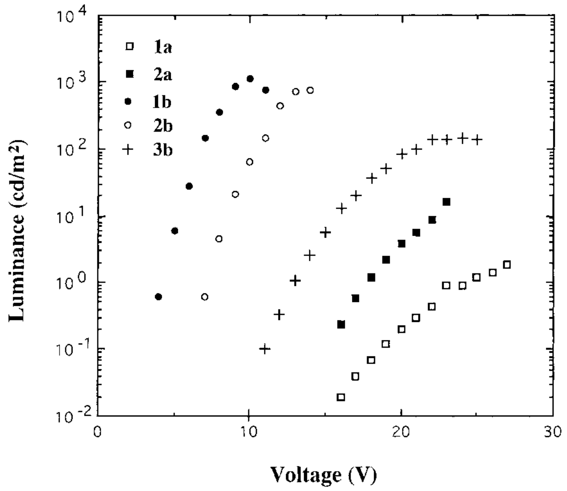

Figure 4 *L–V* characteristics of EL devices with silanylene-phenylene polymers (**1a:2a**) or silanylene-diethynylanthracene polymers (**1b–3b**).

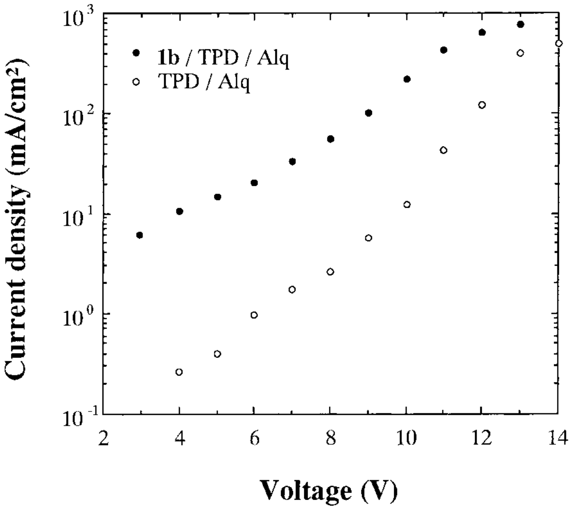

Figure 5 *I–V* characteristics of typical EL devices (TPD/Alq) with or without the monosilanylene-diethynylanthracene polymer (**1b**).

MO analysis by the MNDO method

The MO calculations for the model compounds of silanylene-phenylene and silanylene-diethinylanthracene polymers $H(SiH_2)_m(C_6H_4)(SiH_2)_mH$ and $H(SiH_2)_mC{\equiv}C(C_{14}H_8)C{\equiv}C(SiH_2)_mH$ ($m = 1, 2, 3$) were carried out by the semiempirical MNDO method[24] using a closed-shell Restricted Hartree-Fock (RHF). Plate 1 shows the highest occupied

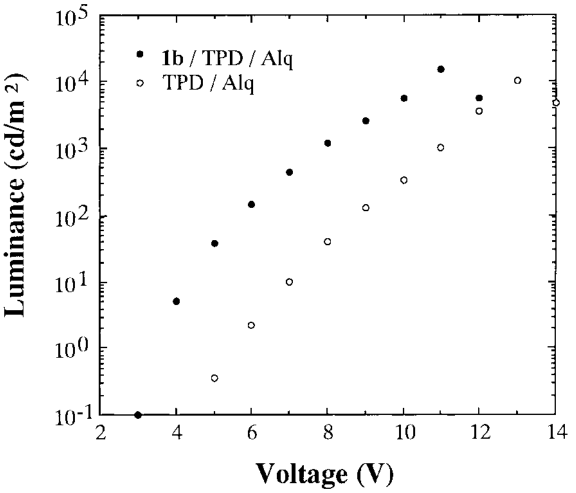

Figure 6 *L–V* characteristics of typical EL devices (TPD/Alq) with or without the monosilanylene-diethynylanthracene polymer (**1b**).

molecular orbitals (HOMOs) of model compounds of the silanylene-phenylene polymers. The HOMO of the monosilanylene model (*m* = 1) is located only on a phenylene unit, indicating that the high oxidation potential of more than 2 V for the monosilanylene-phenylene polymer **1a** may be caused only by the phenylene unit. In contrast, the HOMO of the disilanylene model (*m* = 2) is delocalized not only on a phenylene but also on silanylene units, implying that σ–π conjugation is involved in disilanylene polymer **2a**. This is in agreement with the remarkably red-shifted UV absorption and the lower oxidation potential of the disilanylene polymer **2a** as compared with the polymer **1a**. The improved *I–V* characteristics of the EL device with polymer **2a** is also in agreement with the results of the MO calculations. The HOMO of the trisilanylene model (*m* = 3) is delocalized over the molecule, resembling the disilanylene model, which is in agreement with the UV absorption and oxidation potential of the trisilanylene-phenylene polymer **3a** being almost the same as those of the disilanylene-phenylene polymer **2a**.

Plate 2 shows the HOMOs of model compounds of the silanylene-diethynylanthranylene polymers. The HOMOs of the model compounds appear to be located only on a diethynylanthranylene unit, regardless of the number of the silicon atoms (*m*). These results imply that little σ–π conjugation is involved in the corresponding polymers, which is consistent with the results of the UV spectrometry for the silanylene-diethynylanthracene polymers (**1b–3b**).

High-efficiency EL device with an electron-blocking layer

The EL device with the monosilanylene-diethynylanthracene polymer (**1b**) as the hole-transporting layer exhibited the best *I–V* characteristics and the highest luminance among the organosilicon polymer-based devices examined in the present study. However, the quantum efficiency of the EL devices was still lower (0.2%) than that observed for the devices with Poly(N-Vinylcarbazole) (PVK) or *N*,*N′*-diphenyl-*N*,*N′*-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD). These results may be due to the poor electron-blocking of the diethynylanthracene polymer.[20] Therefore, we examined an EL device with an electron-blocking layer, for which we used TPD, placed between the layer of the diethynylanthracene polymer (**1b**) and Alq. Figure 5 shows the *I–V* characteristics of the two devices with polymer **1b** (20 nm)/TPD (20 nm)/Alq (60 nm) and a conventional EL device of TPD (40 nm)/Alq (60 nm). The current density of the triple-layer device with polymer **1a** was higher than that of the conventional device at any applied voltage. As shown in Fig. 6, the luminance of the polymer **1b**-based device was observed with a turn-on voltage of 3 V, which is *ca* 1 V lower than the conventional device. The maximum luminance of 14750 cd m^{-2} was achieved at 11 V. The maximum energy efficiency (1.0 lm W^{-1}) of this device with polymer **1b** was higher than that (0.85 lm W^{-1}) of the conventional EL device without **1b**, TPD/Alq.

CONCLUSIONS

We have investigated double-layer EL devices with silanylene-phenylene and silanylene-diethynylanthracene polymers as the hole-transporting layer. In the case of the phenylene polymers (**1a–3a**), the electrical properties of the EL devices were improved by increasing the silanylene chain length because of the expanded σ–π conjugation along the polymer backbone. This is in contrast to the case of the EL device with diethynylanthracene polymers, whose electrical properties were improved by decreasing the silanylene chain length, suggesting that the σ–π conjugation is no longer important in these devices. The EL device with monosilanylene-diethynylanthracene polymers and TPD as an electron-blocking layer afforded higher efficiency ($1.0\,\mathrm{lm\,W^{-1}}$) and maximum luminance ($14750\,\mathrm{cd\,m^{-2}}$) than a conventional EL device, TPD/Alq.

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REFERENCES

1. J. M. Zeigler and F. W. Gordon Fearon (Eds), *Silicon-based Polymer Science*, American Chemical Society, Washington, DC, 1990.
2. J. Kido, K. Nagai, Y. Okamoto and T. Skotheim, *Chem. Lett.* 1267 (1991).
3. J. Kido, K. Nagai, Y. Okamoto and T. Skotheim, *Appl. Phys. Lett.* **59**, 2760 (1991).
4. H. Suzuki, H. Meyer, J. Simmerer, J. Yang and D. Haarer, *Adv. Mater.* **5**, 743 (1993).
5. H. Suzuki, H. Meyer, S. Hoshino and D. Haarer, *J. Appl. Phys.* **78**, 2684 (1995).
6. H. Suzuki and S. Hoshino, *J. Appl. Phys.* **79**, 858 (1996).
7. H. Suzuki, *Adv. Mater.* **8**, 657 (1996).
8. J. Ohshita, D. Kanaya, M. Ishikawa and T. Yamanaka, *J. Organomet. Chem.* **369**, C18 (1989).
9. M. Ishikawa, Y. Hasegawa, T. Hatano, A. Kunai and T. Yamanaka, *Organometallics* **8**, 2741 (1989).
10. M. Ishikawa, Y. Hasegawa, A. Kunai and T. Yamanaka, *J. Organomet. Chem.* **381**, C57 (1990).
11. J. Ohshita, D. Kanaya, M. Ishikawa, T. Koike and T. Yamanaka, *Macromolecules* **24**, 2106 (1991).
12. J. Ohshita, H. Ohsaki and M. Ishikawa, *Bull. Chem. Soc. Jpn.* **66**, 1795 (1993).
13. M. C. Fang, A. Watanabe and M. Matsuda, *Chem. Lett.* 13 (1994).
14. M. C. Fang, A. Watanabe and M. Matsuda, *J. Organomet. Chem.* **489**, 15 (1995).
15. M. C. Fang, A. Watanabe and M. Matsuda, *Jpn. J. Appl. Phys.* **34**, Suppl. 34–1, 98 (1995).
16. M. C. Fang, A. Watanabe and M. Matsuda, *Polymer* **37**, 163 (1996).
17. M. C. Fang, A. Watanabe and M. Matsuda, *Macromolecules* **29**, 6807 (1996).
18. H. Suzuki, S. Satoh, Y. Kimata and A. Kuriyama, *Chem. Lett.* 451 (1995).
19. S. Satoh, H. Suzuki, Y. Kimata and A. Kuriyama, *Synth. Met.* **79**, 97 (1996).
20. A. Adachi, S. A. Manhart, K. Okita, J. Kido, J. Ohshita and A. Kunai, *Synth. Met.* **91** 333 (1997).
21. J. Ohshita, A. Yamashita, T. Hiraoka, A. Shinpo, A. Kunai, M. Ishikawa, *Macromolecules* **30** 1540 (1997).
22. M. Ishikawa, H. Ni, K. Matsuzaki, K. Nate, T. Inoue and H. Yokono, *J. Polym. Sci., Polym. Lett. Ed.* **22** 669 (1984).
23. K. Nate, M. Ishikawa, H. Ni, H. Watanabe and Y. Saheki, *Organometallics* **6** 1673 (1987).
24. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99** 4899 (1977).