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Hole-transporting properties of organosilanylene–diethynylpyrene and diethynylanthracene alternating polymers. Applications to patterning of light-emitting images

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Abstract

Diethylsilanylene- and tetramethyldisilanylene-1,6-diethynylpyrene alternating polymers (**1** and **2**) were prepared by the reactions of 1,6-di(lithioethynyl)pyrene and the respective dichloroorganosilanes. The hole-transporting properties of the resulting polymers were evaluated by the performance of electroluminescent (EL) devices with the structure of indium–tin–oxide/polymer/Alq/Mg–Ag, in comparison with those of an organosilanylene-9,10-diethynylanthracene alternating polymer (**3**), reported previously. Among them, the device with polymer **1** exhibited the best performance with a maximum luminescence of 6000 cd m^{-2}, which increased to 16 000 cd m^{-2} when electron-blocking TPD layer was introduced between the polymer and Alq layers. Polymers **1**–**3** were found to be photoactive and irradiation of the polymer films with a UV lamp led to a drastic drop of the luminance of the device, being applicable to the patterning of EL images.

Keywords: EL; Hole-transport; Silicon polymer; Patterning

1. Introduction

Current interest has been focused on organic electroluminescent (EL) devices, because of their brightness and the availability of a wide range of emission, being applicable to full-color flat panel displays. Many papers concerning the synthesis of π-conjugated polymers and their utilities as the EL materials have been published to date [1]. Recently, we have demonstrated that polymers, in which extended π-conjugated systems are linked by an organosilanylene bridge, are potentially useful as efficient hole-transporting materials in multi-layer EL devices [2–5]. Interestingly, the hole-transporting properties of the polymer films, evaluated by the performance of the EL devices having the polymer film as the hole-transport, are improved by the expansion of the π-conjugated systems in the order of phenylene < biphenylene < naphthylene < 9,10-diethynylanthracene [4]. Among them, the best performance was realized from the device having diethylsilanylene-9,10-diethynylanthracene polymer **3** (Plate 1). To obtain such Si-π alternating polymers with even better hole-transporting properties, we synthesized polymers bearing a diethynylpyrene unit as the π-conjugated system.

It has been also reported that Si-π alternating polymers are usually photoactive being applicable to submicron order photoresists [2]. In the present study, we report the patterning of light-emitting images in EL devices by utilizing the bifunctionality of the polymers, i.e. hole-transporting properties and photoactivities. Some methodologies for patterning EL images, such as those by ink-jet printing of emitting materials and by morphology changes of the device layer by thermal treatment, have been reported. However, patterning by chemical modifications of the molecular structures in

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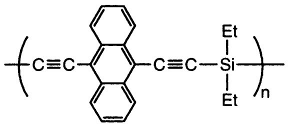

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Plate 1.

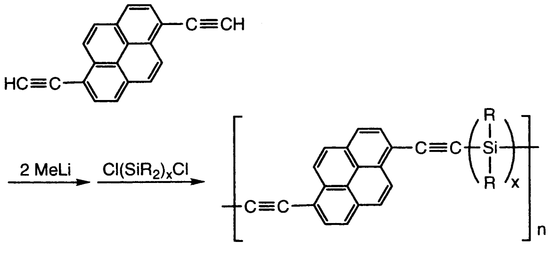
the device materials would provide the novel and readily accessible process leading to finely patterned images, which seems to be of importance for display applications [6].

2. Results and discussion

2.1. Synthesis and properties of organosilanylene–diethynylpyrene polymers

Organosilanylene–diethynylpyrene polymers **1** and **2** were obtained as shown in Scheme 1. Thus, treatment of diethynylpyrene with two equivalents of methyllithium, followed by the reactions of the resulting dilithiated reagent with dichloromono- and disilanes gave the respective polymers. Yields and molecular weights of the polymers determined by GPC after reprecipitation from chloroform/hexane for **1** and chloroform/methanol for **2** are presented in Scheme 1. As shown in Scheme 1, polymer **1** was obtained in moderate yield, while the yield of polymer **2** was rather low. For **2**, the formation of cyclic oligomers with low molecular weights that were removed by reprecipitation was observed by the GPC analysis of the reaction mixture. Both polymers were obtained as yellow solids and are soluble in organic solvents, like ethers, aromatic solvents, and chlorocarbons. They did not melt up to 300 °C. This is probably due to the cross-linking reactions concerning the ethynyl bonds, as observed for other ethynylene-containing Si-π alternating polymers that undergo cross-linking at 200–250 °C [5,7].

UV absorption maxima of polymers **1** and **2** in THF appeared around 400 nm, which were slightly blue shifted from that of **3** (Plate 1, $\lambda_{max} = 448$ nm). The cyclic voltammograms (CVs) of the polymer films prepared on indium–tin–oxide (ITO) electrodes by spin-coating revealed irreversible oxidation peaks at 0.80 V (sh) and 1.06 V vs Ag/Ag$^+$ for **1**, and 0.80 V for **2**, similar to that of **3** (0.80 V (sh), 1.02 V) [3b].



	R	x	yield	Mw	Mn
1	Et	1	57%	10 600	4300
2	Me	2	17%	24 000	6300

Scheme 1.

2.2. EL device performance based on organosilanylene–diethynylpyrene polymers

We examined hole-transporting properties of the present polymers in a double-layer EL system with the structure of ITO/polymer **1** or **2**/Alq (60 nm)/Mg–Ag (devices **I-1** and **I-2**). In this device system, Alq (tris(8-quinolinolato) aluminum (III)) was used as the electron-transporting-emitter, and ITO and Mg–Ag are the anode and cathode, respectively. First, we studied the influence of the polymer film thickness on the device performance, using polymer **1** as the example. Thus, when devices I having spin-coated films of polymer **1** with different thicknesses of 40, 70, 120, and 200 nm were fabricated and their EL performance was examined, the device with a film of 70 nm exhibited the best results with the highest maximum luminance and high reproducibility of the data. The following experiments, therefore, were carried out employing the polymer films with the thickness of 70–80 nm.

Fig. 1 represents current density–voltage ($I-V$) and luminance–voltage ($L-V$) plots for the present devices. For comparison, those of device **I-3** having a film of polymer **3** that exhibited the best hole-transporting properties among the Si-π alternating polymers reported previously [4], are also shown in Fig. 1.

As can be seen in Fig. 1(A), device **I-1** exhibited an $I-V$ profile similar to device **I-3**, while $I-V$ characteristics of device **I-2** were inferior to devices **I-1** and **I-3**. The maximum current densities obtained from the present devices **I-1** and **I-2** were about 500 and 400 mA cm^{-2}, respectively. This seems to indicate the effects of length of the silanylene bridge in polymers **1** and **2**, that is, EL performance was improved by reducing the number of silicon atoms in the silanylene unit. This is presumably due to the favored inter- and intramolecular π–π interaction in the solid states by reducing the volume of the silicon unit. Similar tendency has been already found for other Si-π alternating polymers [4]. In the $L-V$ plots shown in Fig. 1(B), device **I-1** exhibited higher luminance in the whole range of the applied voltage than device **I-3**, leading to the maximum luminance of 6000 cd m^{-2}, indicating higher efficiency of $I-L$ energy conversion in device **I-1** than in **I-3**. In accordance with the $I-V$ characteristics, device **I-2** always showed lower luminance than **I-1** and **I-3**.

Recently, we found that the performance of device **I-3** can be improved by introducing a TPD (*N*,*N*′-diphenyl-*N*,*N*′-di(*m*-tolyl)-1,1-biphenyl-4,4′-diamine) layer as the

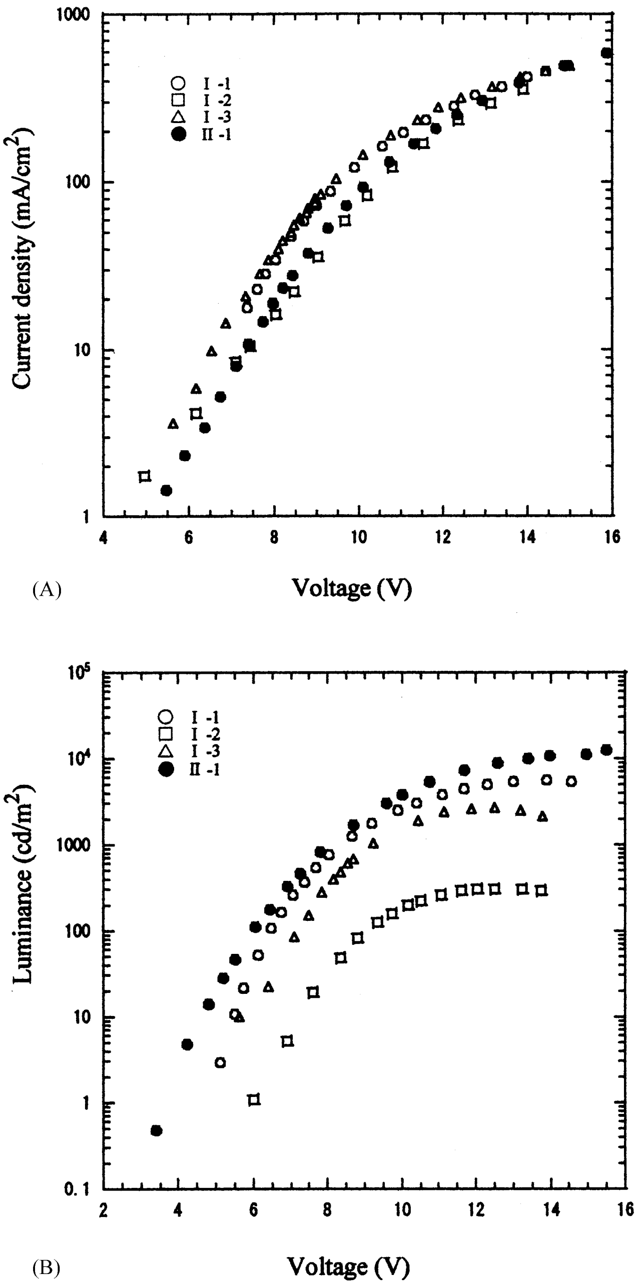


Fig. 1. (A) $I-V$ and (B) $L-V$ plots for devices, I-1, I-**2**, I-**3**, and II-**1**.

electron-block between the polymer film and the Alq vapor-deposited layer [8]. Similar improvement of the performance was realized for the present device with **1**. Thus, the device with the structure of ITO/**1** (40 nm)/TPD (10 nm)/Alq (60 nm)/Mg–Ag (device II-**1**) emitted a bright light of 16 000 cd m^{-2} at the bias voltage of 14–16 V as shown in Fig. 1(B), much higher than did device I-**1**. When compared with the device of ITO/TPD (50 nm)/Alq (60 nm)/Mg–Ag (device III), the $I-V$ plots of device II-**1** showed lower turn-on voltage (4–5 V for II-**1** and 6 V for III) and higher current density in the whole range of the applied voltage. The maximum current density was 900 mA cm^{-2} for II-**1** and 700 mA cm^{-2} for III at 17 V. Although the $L-V$ profile of device II-**1** was a little inferior to that of device III in the high voltage region, 12–17 V (maximum luminance = 27 000 cd m^{-2} at 17 V for III), II-**1** afforded higher luminance up to 12 V. These results clearly indicate the excellent hole-injecting properties of polymer **1** film. However, the efficiencies of current–luminance energy conversion of device II-**1** estimated by $I-L$ plots were a little inferior to those of III. Using a thicker polymer film of **1** (70 nm) in device II resulted in slightly inferior $I-V$ and $L-V$ characteristics (maximum current density = 800 mA cm^{-2}, luminance = 8000 cd m^{-2}).

2.3. Patterning of EL images

Polymers **1**–**3** were found to be photoactive. Thus, when the polymer films were irradiated with a 6 W low-pressure mercury lamp (254 nm) in air, the intensity of the UV absorption decreased with increasing the time of irradiation. The intensities of absorption bands after 5 h irradiation were about 1/5 and 1/10 of the original values, for **1** and **2** (λ_{max} = ca. 400 nm) and for **3** (λ_{max} = ca. 450 nm), respectively, as illustrated for polymer **1** in Fig. 2. This would indicate the decomposition of the chromophores, diethynylpyrene and diethynylanthracene units. The IR spectra of the photolyzed polymer films revealed broad absorption bands due to the stretching frequencies of Si–O (1100 cm^{-1}) and SiO–H (3300 cm^{-1}) bonds. In addition, absorptions at 3050–3080 cm^{-1} and 2130 cm^{-1} ascribed to stretching of C(sp^2)–H and C≡C bonds of **3** decreased on irradiation, although the decrease of the corresponding IR bands for **1** and **2** by irradiation was not so clear as for **3**. Irradiation of the films also affected the CVs. For example, the anodic current decreased to less than 1% of that of the non-irradiated film, after 5 h irradiation of polymer film of **1** on an ITO electrode.

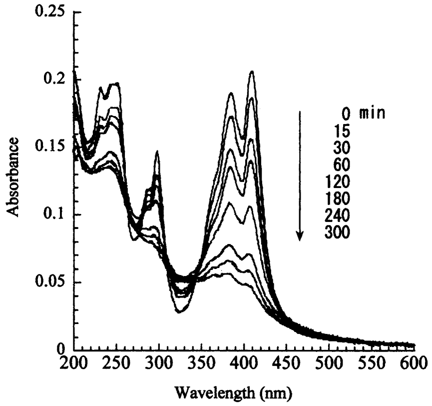


Fig. 2. UV spectral changes of a polymer **1** film prepared by spin-coating on a quartz plate upon irradiation of the film in air for 0–300 min.

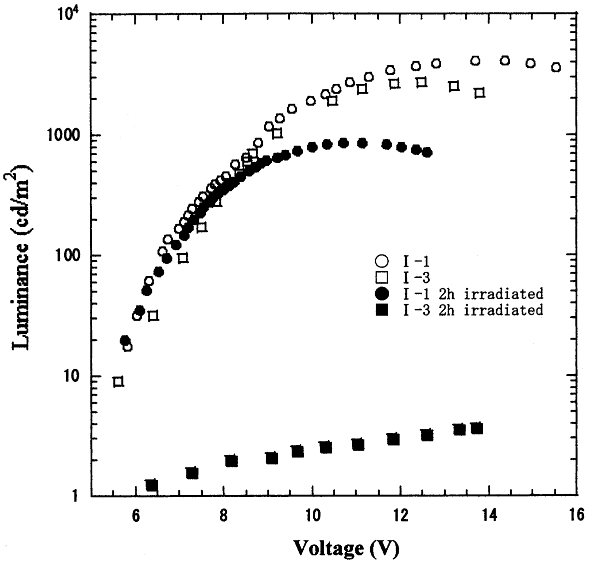


Fig. 3. Changes of $L-V$ characteristics depending on the irradiation period for devices **I-1** and **I-3**.

Reflecting the decomposition of the chromophores, the hole-transporting ability of the polymer films was markedly suppressed by the photolysis. Fig. 3 shows the changes of $L-V$ characteristics for devices **I-1** and **I-3**, depending on the irradiation time. For these experiments, a film of **1** or **3** on an ITO plate was irradiated for a certain period in air, then Alq and Mg–Ag were vapor-deposited in this order. The device with a polymer **1** film irradiated for 2 h, emitted a tiny light, whose luminance corresponded to ca. 1/5 of the original value. Polymer **3** was found to be more sensitive toward the photolysis in the solid state and 2 h irradiation in air led to a decrease in luminance of the resulting device to ca. 1/1000 of the non-irradiated one. Based on the above mentioned optical behaviors of the polymer films, we applied the polymers **1** and **3** to the patterning of EL images. Thus, irradiation of the polymer films through a photo mask in air led to the formation of patterned hole-transport layers. Successive fabrication of the emitting Alq layer and the cathode produced EL images as shown in Fig. 4. As can be seen in Fig. 4, a clear patterned image was produced by using polymer **3**, in which only the non-irradiated area emitted a visible light. On the other hand, the contrast of the image of polymer **1**-based device was rather low. Polymer **1** may be useful for fine-tuning of the luminance.

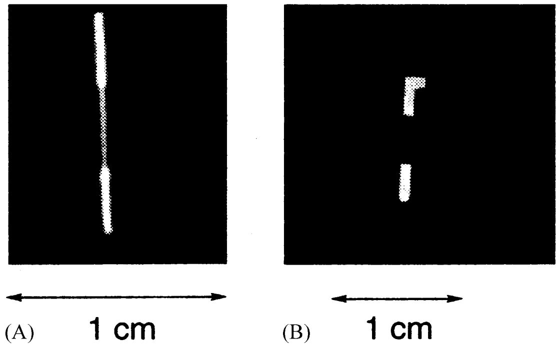


Fig. 4. Photos of patterned EL images of (A) device **I-1** and (B) device **I-3**. Dark areas between the emitting parts are the photolyzed areas. The luminance of the bright parts was about 1000 cd m^{-2}.

In conclusion, we demonstrated that the device with monosilanylene–diethynylpyrene alternating polymer **1** exhibited the best device performance among those having Si-π alternating polymers thus far examined. In addition, we developed a novel method for patterning EL images based on photochemical tuning of the hole-transporting properties of the polymer films.

3. Experimental

3.1. General

1,6-Dibromopyrene was prepared as reported in the literature [9]. Diethyl ether and triethylamine used as the solvents were dried over sodium–potassium alloy and KOH, respectively, and distilled just before use. 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 Shimadzu FT 8000 infrared spectrometer. Molecular weights of polymers were determined with two Shodex columns, using THF as the eluent, and are relative to polystyrene standards. CVs were measured for the polymer films prepared by spin-coating on ITO working electrodes in an acetonitrile solution containing 100 mM of tetraethylammonium tetrafluoroborate as the supporting electrolyte. An Ag/Ag$^+$ electrode and a Pt 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.

3.2. Preparation of 1,6-bis(trimethylsilylethynyl)pyrene

A mixture of 1,6-dibromopyrene (5.5 g, 15 mmol), trimethylsilylacethylene (6.0 g, 61 mmol), $PdCl_2(PPh_3)_2$ (0.42 g, 0.60 mmol, 2.0 mol.%), and CuI (0.24 g, 1.3 mmol, 4.0 mol.%) in triethylamine (220 ml) was heated to reflux for 6 h. The resulting precipitates were filtrated and the solvent was evaporated. The residue was chromatographed on silica gel with hexane as the eluent to give the title compound as the crude solids. Recrystallization of the crude solids from hexane gave 4.3 g

(72% yield) of 1,6-bis(trimethylsilylethynyl)pyrene as the yellow powder: m.p. 199–200 °C (in argon), b.p. 200–202 °C (in argon); IR $\nu_{C\equiv C}$ 2145 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.39 (s, 18H, MeSi), 8.09–8.12, 8.54–8.58, (m, 8H, aromatic H); ^{13}C-NMR (CDCl$_3$) δ 0.1, 100.7, 103.8, 118.3, 124.0, 125.0, 126.3, 128.2, 130.2, 131.2, 132.3. Anal. Found: C, 79.09; H, 6.54. Calc. for $C_{26}H_{26}Si_2$: C, 79.13; H, 6.64%.

3.3. Preparation of 1,6-diethynylpyrene

A mixture of 1,6-bis(trimethylsilylethynyl)pyrene (2.1 g, 5.3 mmol), diethyl ether (300 ml), methanol (200 ml), and 1 N NaOH (aq) (100 ml) was stirred at room temperature for 6 h. The organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the resulting crude solids were recrystallized from hexane–benzene to give 0.60 g (45% yield) of 1,6-diethynylpyrene as the yellow solids: IR $\nu_{C\equiv C}$ 2098 cm^{-1};ν_{C-H} 3296 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 3.63 (s, 2H, HC≡C), 8.11–8.20, 8.58–8.62 (m, 8H, aromatic H); ^{13}C-NMR (CDCl$_3$) δ 82.5, 83.0, 117.3, 123.9, 125.1, 126.3, 128.3, 130.5, 131.4, 132.5. The title compound gradually became insoluble on standing it in air at room temperature, although the IR spectra showed no obvious changes. Therefore, 1,6-diethynylpyrene thus obtained was subjected to the following polymerization immediately after the recrystallization without further purification.

3.4. Preparation of poly(diethylsilanylene-1,6-diethynylpyrene) (*1*)

In a 50 ml Schlenk tube was placed 1,6-diethynylpyrene (0.30 g, 1.20 mmol) and diethyl ether (10 ml) and the tube was cooled to −80 °C. To this was added a 1.14 M MeLi–diethyl ether solution (2.30 ml, 2.62 mmol) and the resulting mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was again cooled down to −80 °C, and dichlorodiethylsilane (0.20 g, 1.27 mmol) was added drop wise to the mixture. After stirring at room temperature for 48 h, the mixture was hydrolyzed with water. The organic layer was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent and reprecipitation of the residue from chloroform–hexane gave 0.23 g of polymer **1** (57% yield) as bright yellow solids: $M_w = 10\,600$ (M_w/M_n = 2.5); IR $\nu_{C\equiv C}$ 2143 cm^{-1}; UV λ_{max} (THF) 403 nm (ε 64 000); CV oxidation peak on film 0.80 (sh), 1.06 V vs Ag/Ag$^+$; ^{1}H-NMR (CDCl$_3$) δ 1.12–1.20, 1.36–1.42 (m, 10H, EtSi), 8.11–8.26, 8.57–8.72 (m, 8H, aromatic H); ^{13}C-NMR (CDCl$_3$) δ 6.9, 7.7, 95.5, 105.7, 118.0, 124.0, 125.1, 126.5, 128.4, 130.5, 131.5, 132.6. Anal. Found: C, 79.62; H, 5.34. Calc. for $(C_{24}H_{18}Si)_n$: C, 86.18; H, 5.39%. Lower carbon content determined by combustion elemental analysis than the theoretical value is often observed for organosilicon polymers. This may be due to the formation of silicon-containing ceramics, such as β-SiC during the analysis [4b, 7c].

3.5. Preparation of poly(tetramethyldisilanylene-1,6-diethynylpyrene) (*2*)

Polymer **2** was obtained from a similar reaction to **1**, using 1,2-dichlorotetramethylsilane instead of dichlorodiethylsilane as the monomer, and was purified by reprecipitation twice from chloroform–methanol (17% yield): $M_w = 24\,000$ (M_w/M_n = 3.8); IR $\nu_{C\equiv C}$ 2137 cm^{-1}; UV λ_{max} (THF) 405 nm (ε 54 000); CV oxidation peak on film 0.80 V vs Ag/Ag$^+$; ^{1}H-NMR (δ in CDCl$_3$) 0.63 (s, 12H, MeSi), 7.77–8.03, 8.51 (br m, 8H, aromatic H); ^{13}C-NMR (δ in CDCl$_3$) −2.6, 98.7, 106.8, 118.3, 123.8, 124.8, 126.2, 128.0, 130.2, 131.0, 132.2. Anal. Calc. for $(C_{24}H_{18}Si)_n$: C, 79.06; H, 5.53. Found: C, 73.53; H, 5.63%.

3.6. Fabrication of EL devices

A thin film of the oligosilanylene polymer was prepared by spin-coating from a solution of polymer in chloroform on an anode, ITO coated on a glass substrate (Nippon Sheet Glass Co.). An electron-transporting-emitting layer was then prepared by vacuum deposition of tris(8-quinolinolato) aluminum (III) (Alq) at 1×10^{-5} on the polymer film. Finally a layer of magnesium–silver alloy (Mg–Ag) with an atomic ratio of 10:1 was deposited on the Alq layer surface as the top electrode at 1×10^{-5} Torr. For EL patterning, the polymer layer was irradiated with a 6 W mercury lamp in air through a photo mask, then Alq and Ag–Mg were vapor-deposited as above.

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