White Light-Emitting Diodes from Novel Silicon-Based Copolymers Containing Both Electron-Transport Oxadiazole and Hole-Transport Carbazole Moieties in the Main Chain[†]

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ABSTRACT: Silicon-based alternating copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties in the main chain (SiHMOXD/Cz 10−01) were synthesized by means of the Heck coupling reaction. The resulting polymers exhibit a strong UV−visible absorption band in the range of 345−356 nm in chloroform solution and in film state. Their PL spectra show a maximum band around 435−485 nm in the blue region. The light-emitting diodes of Al (200 nm)/Ca (50 nm)/EL polymer (80 nm)/PEDOT (50 nm)/ITO were successfully fabricated. And, $J-V$ curves show a turn-on voltage of 6−7 V. Their EL properties depend strongly on both the applied voltage and the loading amount of hole-transport carbazole moieties in the present copolymers. With the applied voltage, these emissive EL bands were red-shifted from blue region to red region. Also, the intensity of a blue EL band at the relatively high operating voltages increases with the loading amount of carbazole units. The LED device with the copolymer of SiHMOXD/Cz 19 exhibits the almost same intensity of two bands, like two crests, giving a strong white color. The blue EL color comes from the carbazole units in these silicon-based copolymers. The latter red EL color comes from a specific charge complex with oxadiazole (and carbazole moieties). The new red band is exhibited only in EL but not in PL spectra. The EL device based on SiHMOXD/Cz 19 has a luminescence efficiency of 0.052 lm/W and a power efficiency of 0.13 cd/A at an applied voltage of 9 V. And, the maximum luminance of the white emissive color was 6.04 cd/m^2 at an applied voltage of 17 V. In this paper, from the photophysical studies, a specific intramolecular charge complex was proposed.

Introduction

Since electroluminescence from π-conjugated polymers was discovered,[1] polymeric light-emitting diodes (PLEDs) have attracted much attention because of their academic interests and potential utility of this technology in a wide variety of applications such as flat-panel displays and light-emitting diodes.[2,3] The strong scientific and commercial interest in π-conjugated electroluminescent polymers has been driven by the estimate of the huge market potential of this novel large area flat-panel display technology, while small molecule-based full color EL devices are beginning to emerge.[3] EL polymeric materials offer a number of advantages, such as three primary R/G/B colors with control of $\pi-\pi^*$ energy gap through the manipulation of the molecular structure, fast response time, high quality of display, and ease of device processability with semiconductor technologies, compared to inorganic EL materials and organic dye molecules.[4,5] They have also been considered potential candidates for a large area flat-panel displays, which are fabricated just by casting the luminescent polymer layer from a solution, due to ease of processability.

However, the realization of potential uses is limited by their low quantum and luminescence efficiency. The light emission from a polymer LED comes from the radiative decay of singlet excitons resulting from the recombination of electrons and holes injected from the cathodic and anodic electrodes. Thus, a more efficient EL device requires the balanced charge injection and transport of both electrons and holes. However, most of the π-conjugated polymers developed so far transport electrons much less efficiently than holes, leading to a decrease of the luminescence efficiency.[1,6] Two approaches have been mainly applied to maintain the balanced charge injection and transport of both electrons and holes. The first one is to fabricate a multilayered LED device, comprised of an emissive polymer layer and separate layers to facilitate electron and hole transport.[7,8] An alternative approach is to introduce oxadiazole units, which are well-known as electron transporting materials, into π-conjugated electroluminescent polymers to successfully develop a more efficient EL device.[9,10]

In our previous works, to make a more efficient EL device, we have reported the development of a novel class of silicon-based alternating copolymers having a thiophene, carbazole, or fluorene unit, etc., by a Heck reaction for blue light-emitting diodes.[11−13] These silicon-based copolymers with a relatively short π-conjugation length exhibited blue light-emitting diodes operating at

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[†] This paper is dedicated to Prof. J. I. Jin on the occasion of his 60th birthday.

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low voltages of less than 9 V, due to the lowering of the LUMO level in luminescent polymers and d-orbital participation of silicon atoms. Furthermore, to balance the hole-electron charges injected and improve the quantum efficiency, we have synthesized novel silicon-based EL copolymers containing oxadiazole units.[14]

Very recently, we have been interested in white LED devices because they have important applications such as illumination light sources, which are particularly useful for paper-thin light sources such as lightweight illumination devices in aircraft and space shuttles or a backlight for liquid crystal displays.[15] Compared with the conventional displays fabricated with three primary red, green, and blue emitters, a full color display can be realized more easily by using a white light-emitting material in combination with a micropatterned color filter.

There are three main methods that have been proposed to produce white LED devices using polymers or organic small molecules. One way is to dope the single host emissive layer with some laser dyes that emit at different color ranges from the host material or blending two different emissive materials.[16−19] An alternative one is to use a microcavity structure to get two or three emissions simultaneously from one emissive layer.[20] The third one is to use a multilayered device structure to get different emission at the same time from different emissive layers.[21,22] Kido et al. developed a device with three emitting layers, each layer emitting light in a different range to the visible spectrum to generate white light.[23] However, all of these methods have both merits and demerits: (1) Multilayered devices are especially difficult and tedious to produce from polymers, as the layers are typically deposited by spin-coating, and only in unsusual cases it is possible to choose a proper solvent that will dissolve the material being deposited layers and yet will not dissolve the previously deposited layers. (2) The immiscibility of different components in the doping systems often results in phase separation and reduces the device lifetime.

In this paper, we have designed and synthesized novel silicon-based copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties in the main chain for the two following reasons: (1) Both electron-transport oxadiazole and hole-transport carbazole moieties have directly been incorporated into silicon-based copolymers so that the balanced charge injection and transport of both electrons and holes for a more efficient LED device could be maintained. Thus, their luminescent properties could be enhanced. (2) The introduction of a carbazole unit with a bulky ethylhexyl alkyl group in the resulting copolymers containing oxadiazole units should reduce their crystallinity and improve the solubility of the final copolymer, while novel silicon-based EL copolymers containing oxadiazole units have a poor solubility, due to the high crystallinity arising from the rigid oxadiazole units.

Experimental Section

Materials. 4-Chlorostyrene, 4-bromobenzoic acid hydrazide, 4-bromobenzoyl chloride, phosphorus trichloride, 2-ethylhexyl bromide, 3,6-dibromocarbazole, and palladium(II) acetate were purchased from Aldrich and used without further purification. Hexylmethyldichlorosilane was purchased from Huls, Inc. Tri(*o*-tolyl)phosphine (TOP) was purchased from Tokyo Kasei organic chemicals. All of the solvents and other chemicals were used after purification, according to conventional methods when required.

Monomer Synthesis. The synthesis of monomers was carried out as follows (see Scheme 1).

Distyrylhexylmethylsilane (DSHMS) (1).[11−14] A mixture of *p*-chlorostyrene (10 g, 0.072 mol) and magnesium turnings (3.5 g, 0.144 mol) in dry THF (70 mL) was stirred at room temperature for 6 h under a nitrogen atmosphere. If the reaction becomes too violent, an ice bath is used to cool it down. A solution of hexylmethyldichlorosilane (5.77 g, 0.029 mol) in dry THF (20 mL) was added dropwise during stirring, and then stirring is continued at room temperature for 5 h. An aqueous solution of 0.1 M HCl was added until precipitation occurred. The reaction mixture was filtered off the precipitate and extracted with diethyl ether. The ether layer was washed with water, dried over anhydrous magnesium sulfate, and filtered and the solvent removed by evaporation. Purification of the crude product by column chromatography (silica gel, with hexane/ethyl acetate (4/1) as an eluent) gave the product as a yellow liquid (5.04 g). The product yield was 52%. ^{1}H NMR ($CDCl_3$, ppm): 0.3 (s, $Si{-}CH_3$, 6H); 0.8−1.3 (m, Si−aliphatic, 13H); 5.2 (d, $CH{=}CH_2$, 2H); 5.7 (d, $CH{=}CH_2$, 2H); 6.7 (q, $CH{=}CH_2$, 2H); 7.4−7.5 (d; aryl CH, 8H). ^{13}C NMR ($CDCl_3$, ppm): −1.52, 14.21, 16.64, 22.65, 23.09, 31.58, 33.15, 114.34, 125.51, 133.39, 136.65, 137.94, 138.47. Anal. Calcd for $C_{28}H_{40}Si$: C, 83.10; H, 9.96; Si, 6.94. Found: C, 83.16; H, 9.93; Si, 6.91.

2,5-Bis(4-bromophenyl)-1,3,4-oxadiazole (2).[10,24] 2,5-Bis-(4-bromophenyl)-1,3,4-oxadiazole was prepared as described in the previous literature: 4-Bromobenzoic acid *N*′-(4-bromobenzoyl) hydrazide was refluxed in $POCl_3$ under a nitrogen atomosphere for 8 h. After the residue of unreacted $POCl_3$ was distilled off, the reaction mixture was cooled to 50 °C and then poured into ice/water. The white precipitate was collected by filtration and washed with water. Recrystallization from ethanol afforded the white crystal. The product yield was 92%. ^{1}H NMR ($CDCl_3$, ppm): 7.7 (d, 4H, aromatic proton); 8.07 (d, 4H, aromatic proton).

3,6-Dibromo-*N*-(2-ethylhexyl)carbazole (3).[12] To a stirred mixture of 3,6-dibromocarbazole (2 g, 6.15 mmol) and potassium carbonate (1.7 g, 12.3 mmol) in dry DMF (30 mL) was added 2-ethylhexyl bromide (1.78 g, 9.22 mmol) at room temperature. It was heated to reflux for 60 h. It was poured into ice/water (150 mL) and then extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. It was purified by silica gel column chromatography (hexane/ethyl acetate = 3/1) to give a yellow oil. The product yield was 82% (3.3 g). IR (KBr pellet, cm^{-1}): 1337 (ν_{C-N}); 748, 723 (ν_{C-H} carbazole ring out of plane). ^{1}H NMR ($CDCl_3$, ppm): 0.82−0.89 (m, 6H, 2-CH_3); 1.21−1.31 (m, 8H, 4-CH_2); 2.02 (m, 1H, −CH−); 4.07 (d, 2H, −NCH_2−); 7.2−8.1 (m, 6H, aromatic protons of carbazole).

Polymerization. The synthesis of silicon-based copolymers were carried out using well-known Heck reaction between distyrylsilane monomer and aromatic or heteroaromatic dibromides, as described in the previous procedures.[12] Results are given in Table 1.

Poly(phenylene-hexylmethylsilylene-phenylene-vinylene-oxadiazolyl-phenylene-vinylene) (SiHMOXD/Cz 10). 2,5-Bis(4-bromophenyl)-1,3,4-oxadiazole (0.5679 g, 1.494 mmol) was dissolved in 20 mL of dry DMF and 15 mL of dry acetonitrile at 80 °C under a nitrogen atmosphere. $Pd(OAc)_2$ (16.77 mg, 0.07455 mmol), tri(*o*-tolyl)phosphine (TOP: 0.1365 g, 0.447 mmol) was dissolved and stirred for 1 h. Distyrylhexylmethylsilane (0.5 g, 1.494 mmol), $(C_2H_5)_3N$ (3.324 g, 17.89 mmol) was dissolved and heated overnight to 100 °C with stirring. After 24 h, the reaction mixture was cooled to room temperature and poured into a large amount of methanol. The resulting precipitate was stirred for 1 h in methanol. The crude polymeric product was filtered off and dissolved in hot chloroform (100 mL). The solution was filtered through a glass filter to remove residual catalyst particles, and precipitated in methanol. The obtained polymer was dried in a vacuum oven at 40 °C for 2 days, yielding 52% of a yellow polymeric product.

Scheme 1. Synthetic Routes to Distyrylsilane, the Monomers of Oxadiazole Dibromide and Carbazole Dibromide, and Silicon-Based Copolymers with Different Compositions

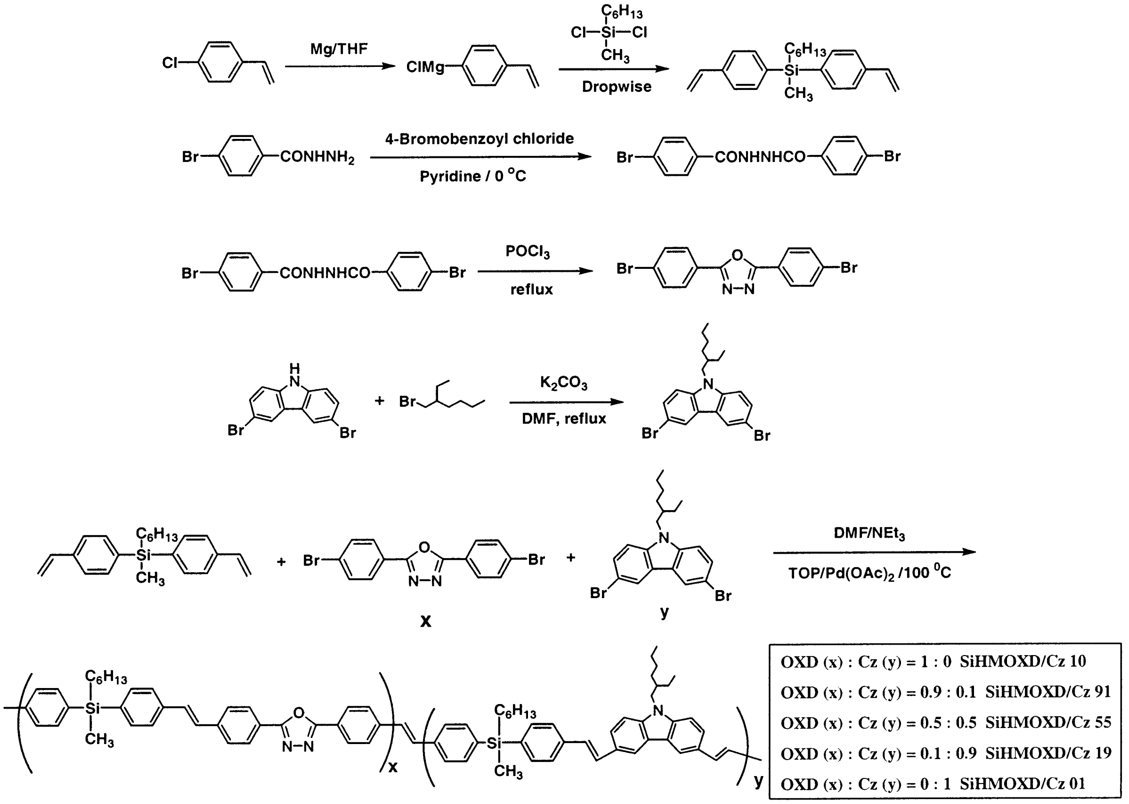


Table 1. Polymerization Results and Physical and Optical Properties of Silicon-Based Alternating Copolymers Containing Both Electron-Transport Oxadiazole and Hole-Transport Carbazole Moieties in the Main Chain

					UV λ_{max} (nm)		PL λ_{max} (nm)	
polymers	yield (%)	M_w[a] ($\times 10^3$)	T_g (°C)	T_D[b] (°C)	solution[c]	film[d]	solution[c]	film[d]
SiHMOXD/Cz 10	52	5.8	105	315	355	357	435	451
SiHMOXD/Cz 91	48	4.3	115	391	354	357	428	455
SiHMOXD/Cz 55	57	8.1	116	428	356	360	430	483
SiHMOXD/Cz 19	65	5.1	108	454	345	349	422, 442	475
SiHMOXD/Cz 01	51	2.3	106	305	322, 356		440	

[a] M_w values of the resulting copolymers were determined by gel permeation chromatography using polystyrene standards. [b] Temperature at which the initial 5 wt % loss of mass was observed. [c] Concentration = ~10^{-4}–10^{-5} mol/L in $CHCl_3$. [d] By spin-coating on quartz.

Also, poly[*n*-hexylmethylsilylene/bis(phenylenevinylene)/3,6-*N*-2-ethylhexylcarbazolediyl]] **(SiHMOXD/Cz 01)** and poly[(phenlene-hexylmethylsilylene-phenylene-vinylene-oxadiazolyl-phenylene-vinylene)-*co*-[(phenlene-hexylmethylsilylene-phenylene-vinylene-carbazolyl-phenylene-vinylene)] **(SiHMOXD/Cz *xy*)** were synthesized by previously synthetic methods.[11-14]

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded with the use of Varian Oxford 300 spectrometers, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Chloroform ($CDCl_3$) was mainly used as a solvent for recording NMR spectra. Infrared spectra were measured as neat oil or KBr pellets on a Perkin-Elmer spectrometer. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standards calibration (Water high-pressure GPC assembly model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, a refractive index detector, solvent: DMF). UV–visible absorption spectra were obtained in chloroform or in the thin film on a Perkin-Elmer Lambda 14 spectrophotometer. The photoluminescence spectra were recorded on an Edinburgh FS920 steady-state fluorometer, in which a 450 W xenon arc lamp as the excitation source and a S900-R photomultiplier as a detector system were installed. The polymer films were excited with either 300 or 350 nm of ultraviolet light from the Xenon arc lamp. Shimadzu TGA 50 and TA instruments DSC 2091 were used to record thermal gravimetric analysis and differential scanning calorimetry (DSC), respectively. For the measurement of EL, the polymer light emitting diode was constructed as follows: The glass substrate coated with transparent ITO electrode was thoroughly cleaned by successive ultrasonic treatments in acetone and isopropyl alcohol, dried with nitrogen gas, and heated for drying. The surface resistivity of the ITO glass used was ca. 10 ohm/cm^2 (from Samsung Corning, Co.). Before spin coating the polymers, the surface of the precleaned ITO-coated glass substrate was treated with UV–ozone at room temperature for 10 min. For the double layer device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrenesulfonate) (PSS) (ca. 50 nm, Bayer AG, Leverkusen, Germany) as a hole-injection/transport layer was spin-coated on the surface-treated ITO substrate and baked at 110 °C for 5 mim. The polymer film was prepared by spin casting the polymer solution containing 1 wt % in chlorobenzene. Uniform and pinhole free films with a thickness around 80 nm were easily obtained from the resulting polymer solution. The films were baked at 70 °C for 60 min. For all devices, metal contact (Ca, 50 nm) with additional encapsulating layer of Al (~200 nm) was thermally evaporated on the top of the polymer film through a mask by vacuum evaporation at pressure below 4×10^{-6} Torr, yielding active areas of 4 mm^2. After the deposition of cathode Ca/Al, the fabricated devices were sealed with a cover glass/UV curing agent in a drybox under a N_2 atmosphere. For the measurements of device characteristics, current−voltage (*I*−*V*) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). All processes and measurements mentioned above were carried out in air at room temperature.

Results and Discussion

The Grignard reaction between *p*-styrylmagnesium chloride and dialkyl dichlorosilane yields alkyl substituted silane synthetic products with high conversion, as shown in Scheme 1. The chemical structure of the final monomer was identified by FT-IR, ^{1}H and ^{13}C NMR, and elemental analysis, etc. These results indicate that the distyrylsilane monomer (1) and oxadiazole dibromide (2) were successfully synthesized. As the reaction proceeded, the broad singlet peaks of −NHNH in the hydrazide group present around at 10.73 ppm disappeared. It indicates the formation of oxadiazole dibromide.

The synthesis of silicon-based alternating copolymers was carried out using well-known Heck reaction (see Scheme 1). Instead of the Wittig method, the Heck synthetic route to the preparation of the silicon-based alternating copolymers was used mainly for the following reasons: (1) The Heck route could overcome the problem of low quantum efficiency due to the formation of the triplet state from the unreacted or remained aldehyde functional groups in the same silicon-based copolymers obtained from the Wittig reaction. (2) The Heck reaction directly produces the desired polymers with trans configuration, which is important to optimize the luminescence efficiency and the emissive wavelength. To obtain quantitatively a trans-double bond from a cis-double bond, the Wittig reaction requires a further postreaction of the isomerization step, achieved by heating the crude polymers with a trace of iodine in toluene.

The chemical structure and purity of the resulting polymer are investigated by means of FT-IR, ^{1}H NMR, gel permeation chromatography (GPC), UV−visible, and photoluminescence (PL) and excitation spectroscopies. The polymerization reaction was monitored by the ^{1}H NMR spectroscopy.[12] As the polymerization proceeded, the terminal vinyl peak of the monomer present at 5.2 and 5.7 ppm disappeared, and a newly vinyl proton peak in the polymer overlapped with 7.0−7.5 ppm in aromatic units. Also, the broad peaks around 0.2−2.0 ppm were assigned to the alkyl protons adjacent to the silicon atom. The weight-average molecular weights (M_w) of the SiHMOXD/Cz *xy*, as determined by gel permeation chromatography using polystyrene standards, were in the range 2.1×10^3 to 8.1×10^3. In the typical FT-IR spectrum of SiHMOXD/Cz 10, vinyl C=C bonds in the monomer showed vanishingly a weak absorption at 1600 cm^{-1}. On the other hand, the out-of-plane bending mode of the trans vinylene groups in the polymer showed a newly weak and sharp absorption peak at 960 cm^{-1}. It indicates the formation of the silicon-based alternating polymers with trans double bonds.

The thermal behavior of the silicon-based copolymers was evaluated by means of DSC and TGA. The synthesized copolymers did not show any definite melting point, implying that the silicon-based copolymers could be amorphous. The SiHMOXD/Cz 10 had the glass transition temperature (T_g) of 105 °C. It shows good thermal stability up to 315 °C, but a small amount of weight loss began to occur at 230 °C under atmospheric conditions.

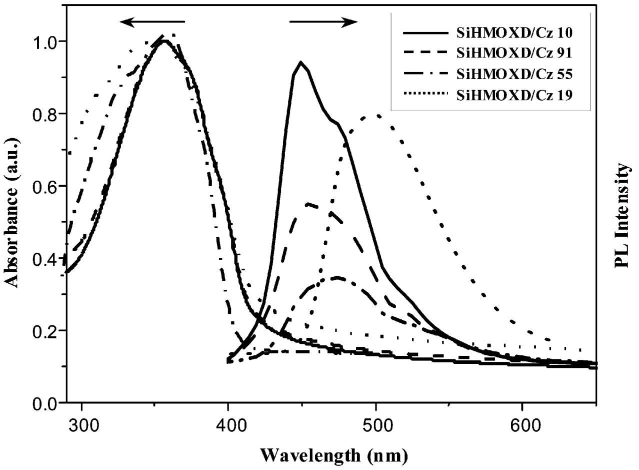


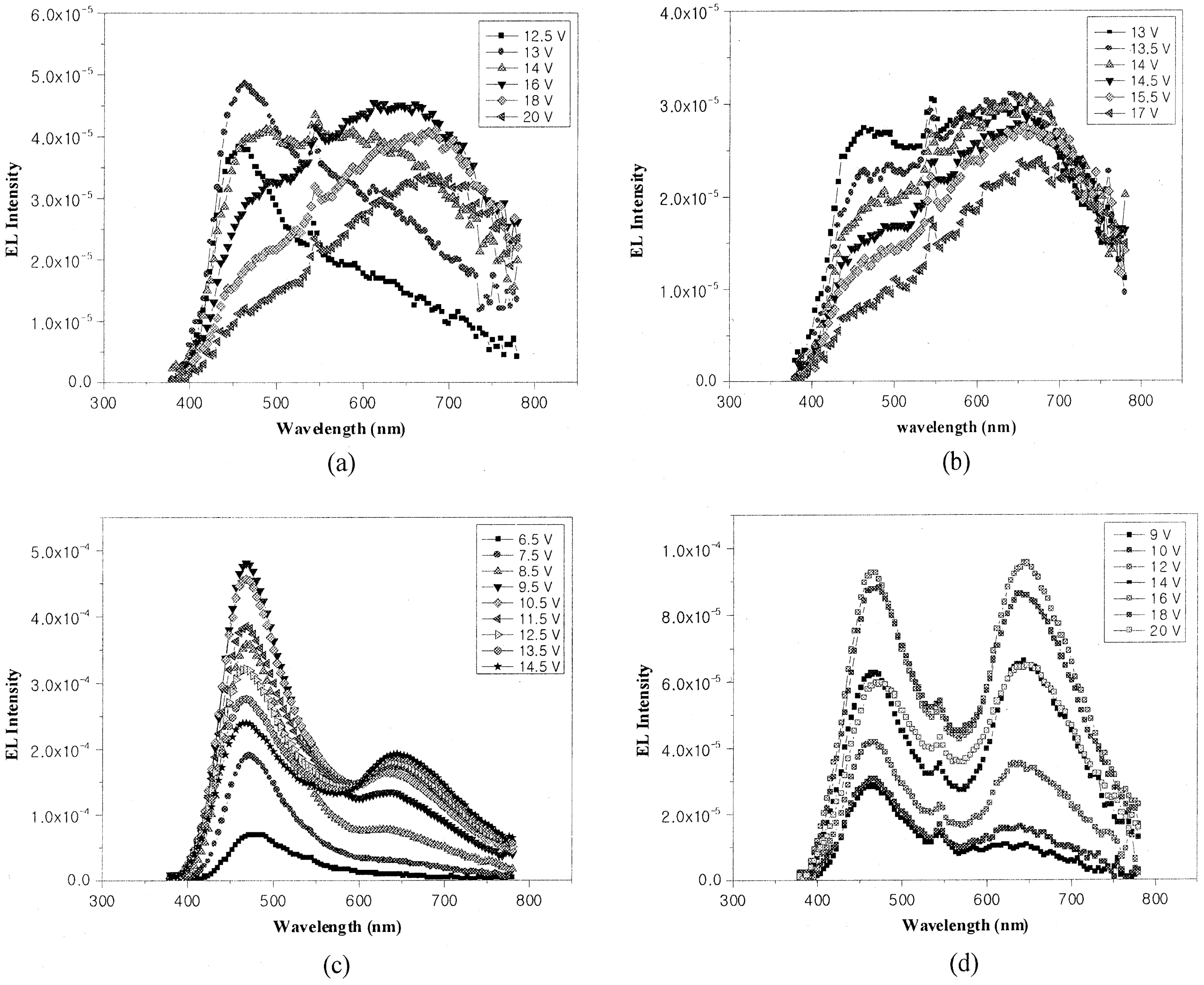
Figure 1. UV−visible absorption and photoluminescence spectra of SiHMOXD/Cz 10, SiHMOXD/Cz 91, SiHMOXD/Cz 55, and SiHMOXD/Cz 19 in the thin film state.

In the UV−visible spectra, the absorption maximum wavelength (λ_{max}) of SiHMOXD/Cz 10 appears at 355 and 357 nm in chloroform solution and thin film, respectively. Also, the PL spectra show a strong band around 435 and 451 nm in chloroform and thin film, respectively. Its UV−visible and PL spectra are shown in Figure 1.

The multilayered light emitting diode of Al (200 nm)/Ca (50 nm)/SiHMOXD/Cz 10 (80 nm)/PEDOT (50 nm)/ITO glass was fabricated. The *J*−*V* curve shows the turn-on voltage of 7 V. Its EL spectrum, as shown in Figure 2, exhibits a broad band around 460 nm in the blue region at the operating voltage of 12.5 V. With the applied voltage, the emissive EL bands were red-shifted from blue region to red region. When the higher voltage was applied, however, the broad band in the blue region decreases and a new broad band in red region increases. The broad shoulder band in the blue region and the new peak at about 676 nm can be assigned to emissions from the individual lumophore and a specific charge complex like excimer, exciplex, or electroplex, respectively. The new red EL peak is generated only by electric field as shown in Figure 2, since this new red band is exhibited only in EL but not in PL spectra. In other word, a specific charge complex cannot be produced by photoexcitation. However, it is formed, more like an electroplex, under a strong electric field inside the device. A similar phenomenon has been reported in an oxadiazole-containing conjugated polymer.[25] Therefore, two broad emissive bands combine to produce the white emissive color above 13 V. Also, the maximum luminance of the white emissive color was 3.71 cd/m^2 at the applied voltage of 12 V.

To overcome the relatively poor solubility of the resulting polymer containing only an oxadiazole unit, due to the rigidity of a fully aromatized oxadiazole unit and to improve the quantum efficiency and luminescent properties, we introduce the carbazole units into the SiHMOXD/Cz 10 with various molar ratios, yielding novel silicon-based copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties in the main chain. Scheme 1 shows the chemical structures of the present silicon-based alternating copolymers (SiHMOXD/Cz *xy*).

The chemical structures and purity of the resulting polymers have been characterized by FT-IR, ^{1}H NMR, gel permeation chromatography (GPC), UV−vis, pho-



(a) (b)

(c) (d)

Figure 2. EL spectra of SiHMOXD/Cz 10 (a), SiHMOXD/Cz 91 (b), SiHMOXD/Cz 55 (c), and SiHMOXD/Cz 19 (d).

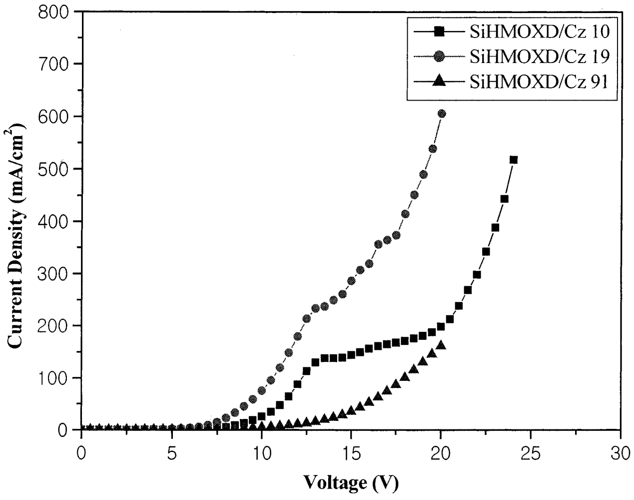


Figure 3. *J*−*V* curves of SiHMOXD/Cz 10, SiHMOXD/Cz 91, and SiHMOXD/Cz 19.

toluminescence (PL) and excitation spectroscopies, etc. FT-IR and ^{1}H NMR results of SiHMOXD/Cz *xy* are silimar to those of SiHMOXD 10. The maximum absorption wavelength (λ_{max}) of SiHMOXD/Cz 91, 55, and 19 appears at wavelengths of 357, 360, and 349 nm in the film state, respectively (see Figure 1). The PL spectra of these polymers exhibit strong bands around 455, 483, and 475 nm in the blue region, respectively.

Multilayered light-emitting diodes with the same device structure of SiHMOXD/Cz *xy* were fabricated (see Figure 2). The turn-on voltage is in the range of 6−7 V from *J*−*V* curves (see Figure 3). It should be noted that two out of three *J*−*V* curves look unusual, having several shoulders in the range 12−18 V. Sometimes, we observed that an unusual *J*−*V* feature has resulted from the interfacial phenomena between a EL polymer and an electrode. When the EL device with this unusual *J*−*V* curve was annealed at elevated temperatures, the normal *J*−*V* curve was obtained.[13] Also, in EL measurement, we observed the unusual electroluminescent properties and the different electrophysical behaviors along with the applied voltage.

Figure 2d and 4 shows the EL spectra of SiHMOXD/Cz 19. The EL spectra obtained from the LED device with SiHMOXD/Cz 19 are quite different from those of SiHMOXD/Cz 10. Also, we observed that the intensity of two emissive peaks increases with the increment of the operating voltage. Below 10 V, the device has two bands: a relatively strong blue EL band and a relatively weak red EL band. At the applied voltage of 9 V, the

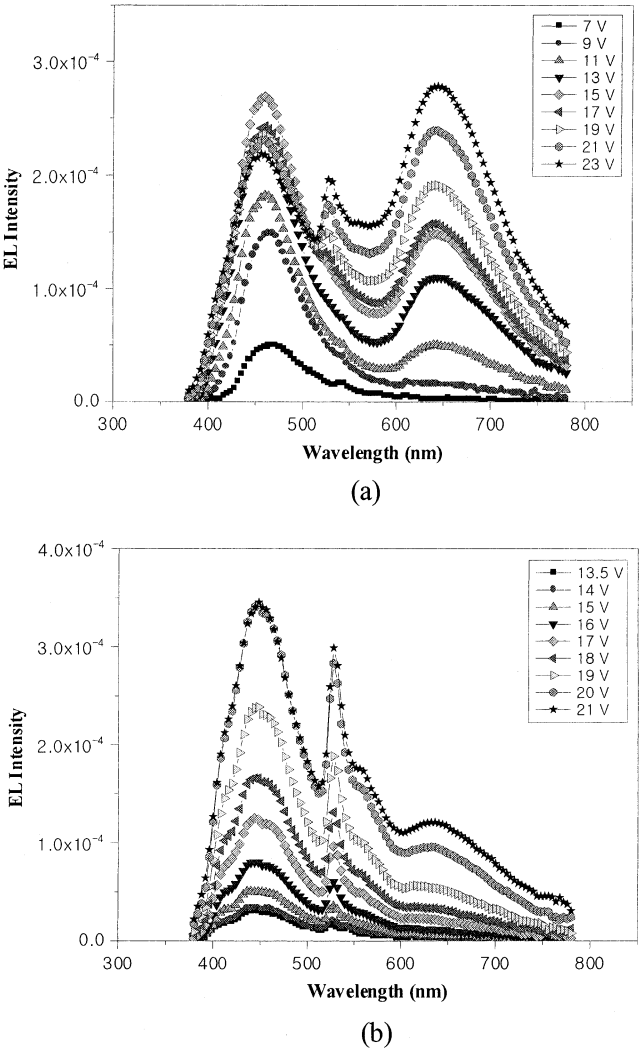


Figure 4. EL spectra of SiHMOXD/Cz 19 with PS (copolymer: PS = 5:5 (a) and 8:2 (b).

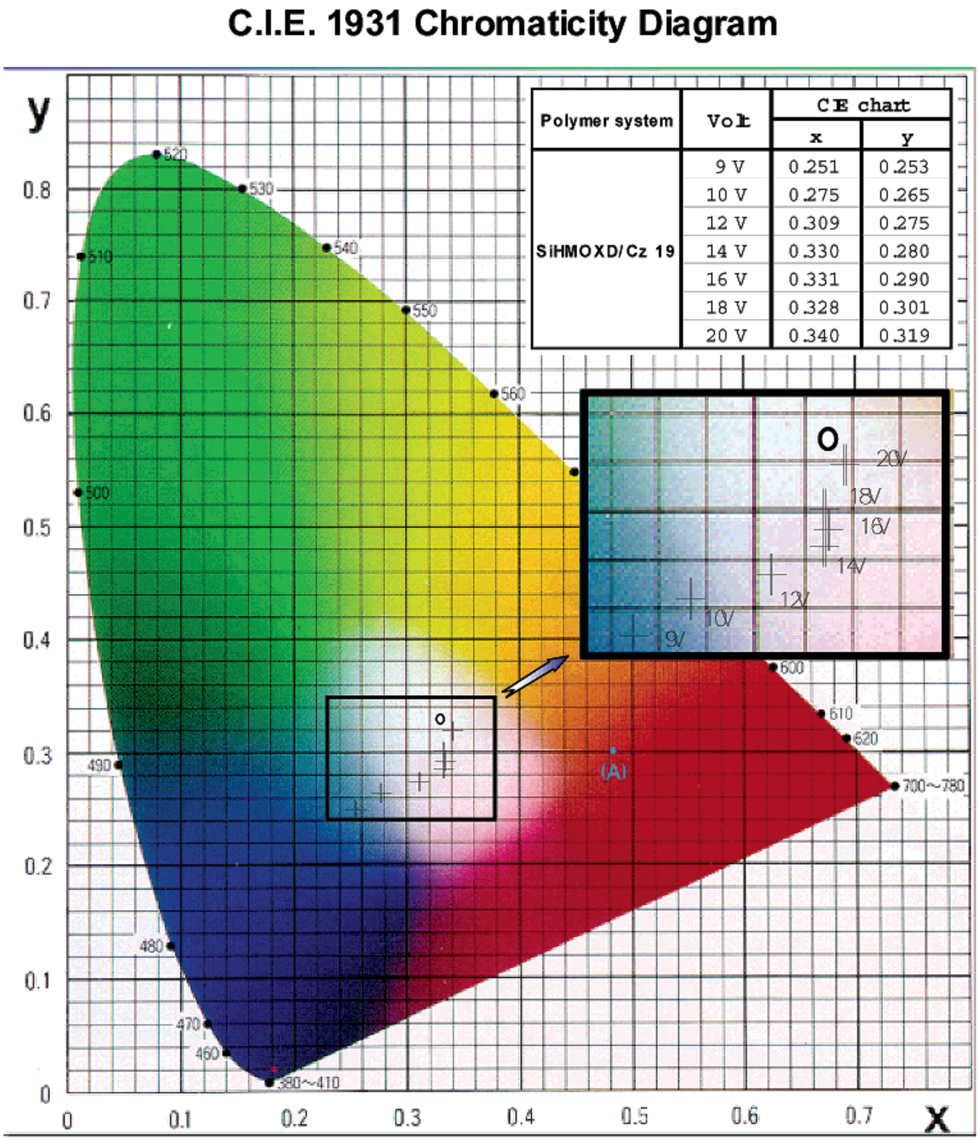
EL device based on SiHMOXD/Cz 19 has a luminescence efficiency of 0.052 lm/W and a power efficiency of 0.13 cd/A. Surprisingly, the intensity of two emissive EL bands increases concomitantly with an applied voltage of higher than 12 V, showing two strong emissive bands, like two crests. They combine together and emit a strong white color. Figure 5 shows the CIE chromaticity diagram as a function of the applied voltages. The purity of a white color increases with the applied voltages, and the maximum luminance of the white emissive color was 6.04 cd/m^2 at the applied voltage of 17 V.

It is an unusual result from π-conjugated electroluminescent polymers, to the best of our knowledge. To examine the dependence of this unusual EL property on the different copolymer compositions and the applied voltages, we fabricated the multilayered light-emitting diodes using SiHMOXD/Cz 91, 55, and 19. As seen from Figure 2, the EL property depends strongly on the loading amount of carbazole uints in the present copolymers. The intensity of a blue EL band at the relatively high operating voltages increases with the loading amount of carbazole units in these silicon-based copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties in the main chain. Eventually, the LED device from the silicon-based copolymer containing a mole ratio of electron-transport oxadiazole moiety to hole-transport carbazole moiety = 1/9 exhibits the almost same intensity of two emissive bands, giving a strong white color. Two obvious crests of the blue peak at about 464 nm and the new red peak at about 644 nm can be assigned to emissions from the individual lumophore and a specific charge complex like excimer, exciplex, or electroplex, respectively: The blue EL color comes from the carbazole units in these silicon-based copolymers, since the intensity of a blue EL band increases with the loading amount of carbazole units in these silicon-based copolymers. The latter red EL color comes from a specific charge complex with oxadiazole units. Also, in EL devices, the oxadiazole moiety emits much stronger than the carbazole moiety in the polymer backbone, because the LED device from the silicon-based copolymer containing the much less amount of electron-transport oxadiazole moiety, like SiHMOXD/Cz 19, exhibits a strong red emission.

Also, to gain further insight into the nature of the formation of the specific charge complex, we fabricated two LED devices from the blend systems of SiHMOXD/Cz 19 and polystyrene (PS) with different loading amounts of PS. With a large loading amount of PS (80%), we could eliminate the intermolecular interaction between the polymer chains in SiHMOXD/Cz 19. However, with the device from the blend system of SiHMOXD/Cz 19 with a large amount of PS (80%), in which intermolecular interaction between the polymer chains could be negligible, we still obtained two crestlike emissive bands, similar to that of SiHMOXD/Cz 19 (see Figure 4). It indicates that these unusual EL properties, originating from the formation of a specific charge complex, do not exclude intrachain interaction. In other word, a specific charge complex in EL devices can be formed by both inter- and intrachain interactions in the polymer chains.

To understand the origin of the formation of the specific charge complex in silicon-based copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties in the main chain, we measured the emission and excitation spectroscopies for silicon-based copolymers containing only the hole-transport carbazole moiety (SiHMOXD/Cz 01), the silicon-based copolymers containing only electron-transport oxadiazole moiety (SiHMOXD/Cz 10), and the silicon-based copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties (SiHMOXD/Cz *xy*) at the various wavelengths. Their PL spectra were obtained with photoexcitation at two different wavelengths corresponding to the absorption maximum positions. These two excitation wavelengths at 300 and 350 nm were chosen for the selective photoexcitation of the intrinsic carbazole unit (Cz units: D_{Cz}) or the intrinsic oxadiazole unit (OXD unit: A_{OXD}) and the π-conjugated segements with the carbazole unit (D_π) or the oxadiazole unit (A_π) (see Scheme 3).

The PL spectra of SiHMOXD/Cz 01 and the SiHMOXD/Cz 10 at the two excitation wavelengths show the same emission maximum bands around 430 nm and around 455 nm, which is attributed to photoexcitation of the carbazole unit and the oxadiazole unit, respectively (see Figure 6). However, these PL spectral features behave quite differently from those of SiPhOXD/Cz 01 (or SiPhPVK), reported in our previous paper, in which diphenylsilyl units ($SiPh_2$), instead of



Polymer system	Volt	CIE chart	
		x	y
SiHMOXD/Cz 19	9 V	0.251	0.253
	10 V	0.275	0.265
	12 V	0.309	0.275
	14 V	0.330	0.280
	16 V	0.331	0.290
	18 V	0.328	0.301
	20 V	0.340	0.319

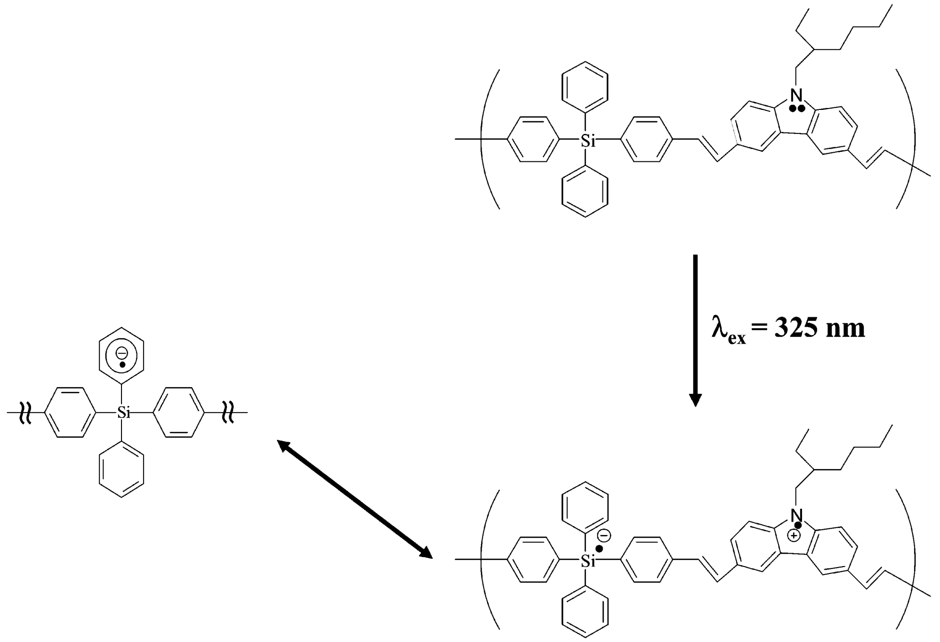
Figure 5. CIE chromaticity diagram of the EL device based on SiHMOXD/Cz 19 as a function of applied voltages.

hexylmethylsilyl (SiHexMe) units, were incorporated into organosilicon units in the main chain.[12,26] Upon photoexcitation of the carbazole unit at 300 nm, the PL spectra of SiPhOXD/Cz 01 (or SiPhPVK) show the emission maximum band around 440 nm, in addition to the emission band at 520 nm. We proposed, from time-resolved PL measurement and some photophysical studies, that the additional new band might be attributed to the formation of a specific charge-transfer complex, as shown in Scheme 2. The stable resonance structure in the excited state was formed through stabilizing it with phenyl side groups in the SiPh unit of SiPhOXD/Cz 01 (or SiPhPVK). Phenyl side groups in the SiPh unit of SiPhOXD/Cz 01 (or SiPhPVK) behave like an electron-withdrawing group. Unlike the SiPh unit in the SiPhOXD/Cz 01 (or SiPhPVK), the electron-withdrawing power of oxadiazole units in the SiHMOXD is not enough to stabilize the excited state of SiHMOXD for the formation of the stable resonance structure in the excited state, since the oxadiazole units are connected indirectly to silicon atoms via π-conjugated styryl groups.

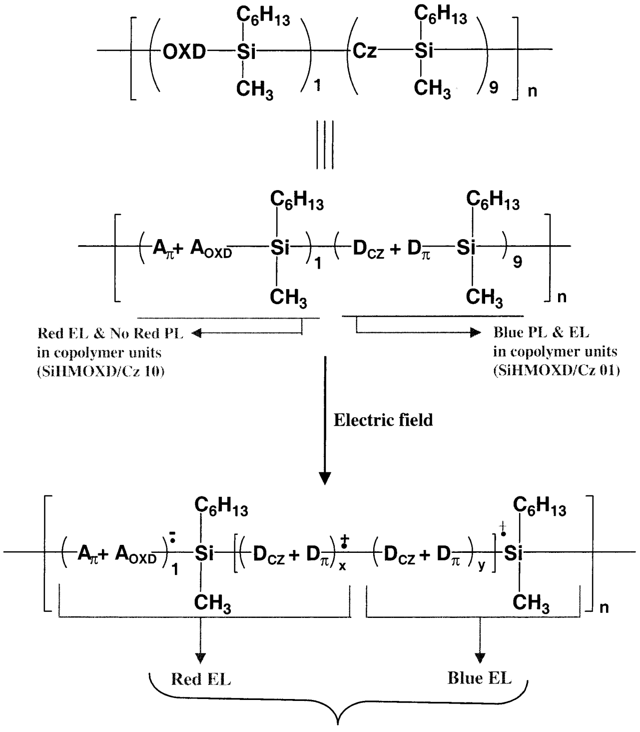
Similarly, the PL spectra of the SiHMOXD/Cz *xy* with all of the different copolymer compositions at two excitation wavelengths were obtained. Their PL spectra show the same emission maximum band around 465 nm, which is attributed to photoexcitation of the intrinsic oxadiazole unit (OXD unit: A_{OXD}) as well as the π-conjugated segements with the oxadiazole unit (A_π). Even though the carbazole units (D_{Cz}) as well as the π-conjugated segements with the carbazole unit (D_π) were photoexcited at 300 nm, the emission maximum band around 430 nm, corresponding to carbazole moieties, was not observed. It might be due to the energy transfer of the excited state of carbazole moieties to the ground state of the oxadiazole units. Thus, this energy transfer process exhibits only the emission band for the π-conjugated segements with the carbazole unit (D_π) and the oxadiazole unit (A_π). From these emission studies, we could not observe the red PL spectra, ascribed to the formation of a specific intramolecular charge complex.

Therefore, we could propose the formation of a specific intramolecular charge complex corresponding to a red color, as shown in Scheme 3. The proposed scheme for a specific intramolecular charge complex can be deduced as follows: In the LED device from the silicon-based copolymer with only the oxadiazole moiety, this new red band is exhibited only in EL but not in PL spectra. Then,

Scheme 2. Proposed Scheme for the Formation of a Certain Charge Complex in SiPhOXD/Cz 01 (or SiPhPVK)



Scheme 3. Proposed Scheme for the Formation of a Certain Charge Complex in SiHMOXD/Cz 19



in the LED device from the silicon-based copolymer with only the carbazole moiety, the blue EL band is exhibited in both EL and PL spectra. So, the blue EL color and the new red EL color come from the silicon-based copolymer with only the carbazole moiety and the silicon-based copolymer with only the oxadiazole moiety, respectively. Thus, a specific charge complex for the silicon-based copolymer containing only the oxadiazole moiety, more like an electroplex, is formed under a strong electric field inside the device and cannot be produced by photoexcitation.

On the other hand, let us compare the EL spectral features obtained from the EL device based on the SiHMOXD/Cz 10 with those obtained from the EL device based on the SiHMOXD/Cz 19. The former EL spectral features are observed to be red-shifted from blue region to red region with the applied voltages, finally exhibiting a new broad band with an emissive maximum wavelength of 676 nm in the region of blue to red. As mentioned above, it might be attributed to the formation of a specific charge complex, more like an electroplex. However, the EL device based on SiHMOXD/Cz 19 has different EL spectral features as compared with those of the EL device based on SiHMOXD/Cz 10. Its device shows two crestlike emissive bands. Two crestlike emissive bands, consisting of the blue peak at about 464 nm and the new red peak at about 644 nm, can be assigned to emissions from the individual lumophore and a specific charge complex like an electroplex, respectively. It should be noted that the maximum wavelengths and the spectral features of two EL red peaks obtained from the EL devices based on SiHMOXD/Cz 10 and SiHMOXD/Cz 19 are quietly different (see Figure 2). Thus, the electric field-induced charge complexes could be different from each other. In the case of the silicon-based copolymer with the electron-transporting oxadiazole and hole-transporting carbazole moieties in the main chain (SiHMOXD/Cz 19), the presence of the crestlike EL band at around 644 nm suggests the existence of a stabilized, trapping energy level, which is responsible for the formation of a specific stabilized charge complex. Also, the blending study indicates that the specific stabilized charge complex can be formed by intramolecular interaction between the oxadiazole units and the cabazole units, as proposed in Scheme 3. When the voltage was applied, the electrons can inject from the cathodic electrode into the oxadiazole units (A_{OXD}) and π-conjugated segements with the oxadiazole unit (A_π), yielding the negative polarons in the oxadiazole units (A_{OXD}) and π-conjugated segments with the oxadiazole unit (A_π). Alternatively, the holes can inject from the anodic electrode into the carbazole units (D_{Cz}) as well as the π-conjugated segments with the carbazole unit (D_π), forming the positive polaron in the carbazole units (D_{Cz}) as well as the π-conjugated

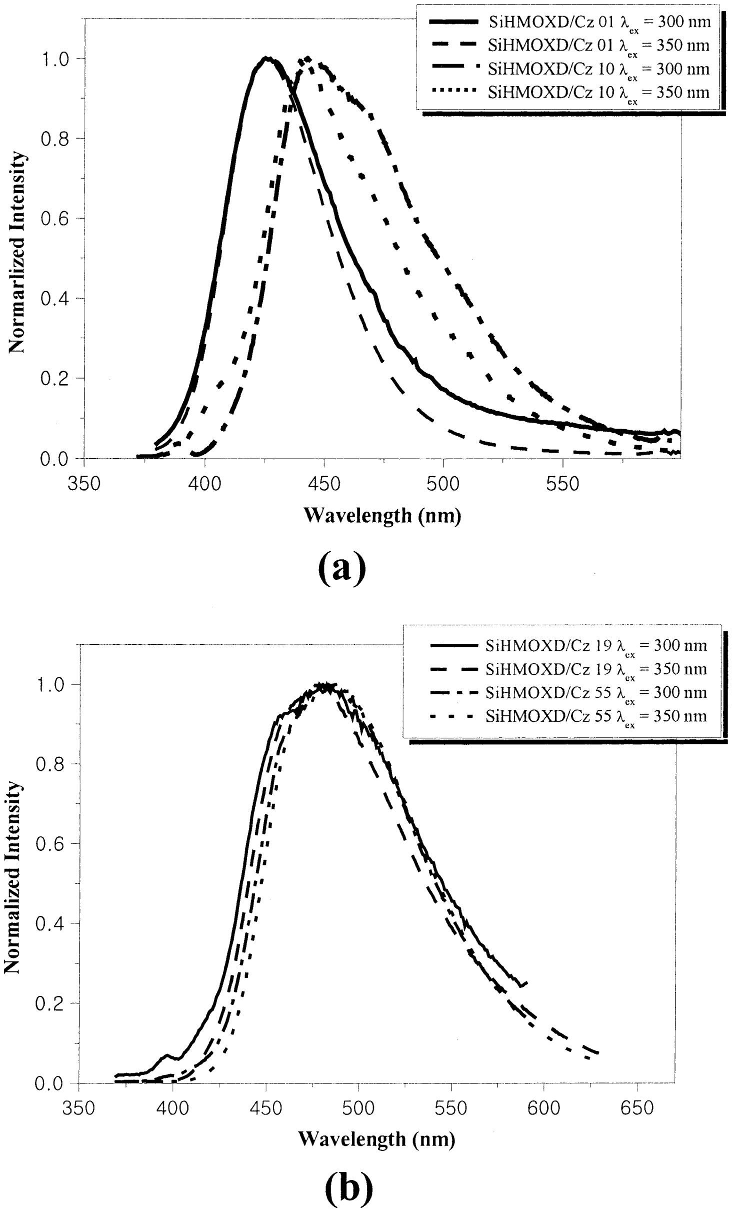


Figure 6. Emission spectra: (a) SiHMOXD/Cz 10 and SiHMOXD/Cz 01 and (b) SiHMOXD/Cz 55 and SiHMOXD/Cz 19 with two photoexcitation wavelengths at 300 and 350 nm.

segments with the carbazole unit (D_{π}). As seen from Scheme 3, a specific stabilized charge complex, more like an electroplex, formed from intramolecular interactions between the negative and positive polarons close to the silicon atoms, emits the longer emissive bands, which corresponds to the red EL color in EL spectra. In 1996, this kind of charge complex for the photoinduced charge separation occurring with donor–acceptor substituted silanes (A_{π}–SiMe$_2$–D_{π}) was reported.[27] However, some of a specific charge complex of the positive polaron in the carbazole units (D_{Cz}) as well as the π-conjugated segments with the carbazole unit (D_{π}) emits a blue EL color. Therefore, two broad EL bands combine to produce the white emissive color.

Conclusions

Silicon-based alternating copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties in the main chain (SiHMOXD/Cz 10–01) were synthesized by means of the Heck coupling reaction. The resulting polymers exhibit a strong UV–visible absorption band in the range 345–356 nm in chloroform solution and in the film state. Upon photoexcitation around the absorption maximum wavelength, their PL spectra show a maximum band around 435–485 nm in the blue region. The light-emitting diodes of Al (200 nm)/Ca (50 nm)/EL polymer (80 nm)/PEDOT (50 nm)/ITO were successfully fabricated. And, J–V curves show a turn-on voltage of 6–7 V. Their EL properties depend strongly on both the applied voltage and the loading amount of hole-transport carbazole moieties in the present copolymers. The EL spectra obtained from a device based on a copolymer containing hole-transport carbazole moieties (SiHMOXD/Cz 01) exhibit a broad band around 460 nm in the blue region at the operating voltage of higher than 12.5 V. The EL spectra obtained from the device based on the copolymers containing electron-transport oxadiazole moieties in the main chain (SiHMOXD/Cz 10) exhibit a strong band around 460 nm in the blue region and a very broad, weak band in the red region, at an operating voltage of lower than 12.5 V. With the applied voltage, these emissive EL bands were red-shifted from blue region to red region, exhibiting a very broad, weak band in the blue region and a very strong band in the red region. The EL spectra from the devices based on SiHMOXD/Cz 91−19 have a similar EL spectral feature with the applied voltage. Also, the intensity of a blue EL band at the relatively high operating voltages increases with the loading amount of carbazole units. Eventually, the LED device from the copolymer containing the mole ratio of electron-transport oxadiazole moiety to hole-transport carbazole moiety = 1/9 exhibits the almost same intensity of two emissive bands, like two crests, giving a strong white color. The maximum luminance of the white emissive color was 6.04 cd/m^2 at the applied voltage of 17 V. Two obvious crests in the blue region and the new red peak at about 650 nm can be assigned to emissions from the individual lumophore and a specific charge complex like electroplex, respectively: The blue EL color comes from the carbazole units in these silicon-based copolymers. The latter red EL color comes from a specific charge complex with oxadiazole (and carbazole moieties). The new red band is exhibited only in EL but not in PL spectra. The EL device based on SiHMOXD/Cz 19 has a luminescence efficiency of 0.052 lm/W and a power efficiency of 0.13 cd/A at an applied voltage of 9 V. In this paper, from the photophysical studies, a specific stabilized, intramolecular charge complex was proposed.

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References and Notes

(1) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (b) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941. (c) Gustafasson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature (London)* **1992**, *357*, 477. (d) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

(2) (a) Berggrenm, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature (London)* **1994**, *372*, 444. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402. (c) Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog. Polym. Sci.* **2000**, *25*, 1089.

(3) See http://www.kodak.com/go/oled.

(4) (a) Zhang, C.; Seggern, H. von; Parbaz, K.; Kraabel, B.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35. (b) Fisher, T. A.; Lidzey, D. G.; Pate, M. A.; Weaver, M. S.; Whittaker, D. M.; Skolnick, M. S.; Bradley, D. D. C. *Appl. Phys. Lett.* **1995**, *67*, 1355. (c) Zhang, X.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069.

(5) (a) Chang, S. C.; Bharathan, J.; Yang, Y.; Helgeson, R.; Wudl, F.; Ramey, M. B.; Reynolds, J. R. *Appl. Phys. Lett.* **1998**, *73*, 2561. (b) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bassler, H. *Adv. Mater.* **2001**, 258.

(6) Hide, F.; Diazgarcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430.

(7) Rothberg, L. J.; Lovinger, A. J. *J. Mater. Res.* **1996**, *11*, 3174.

(8) Son, S.; Lovinger, A. J.; Galvin, M. E. *Polym. Mater. Sci. Eng.* **1995**, *72*, 567.

(9) (a) Peng, Z.; Bao, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086. (b) Peng, Z.; Bao, Z.; Galvin, M. E. *Adv. Mater.* **1998**, *10*, 680.

(10) Peng, Z.; Zhang, J. *Chem. Mater.* **1999**, *11*, 1138.

(11) (a) Kim, H. K.; Ryu, M.-K.; Lee, S.-M. *Macromolecules* **1997**, *30*, 1236.; (b) Kim, H. K.; Ryu, M. K.; Kim, K. D.; Lee, S. M.; Cho, S. W.; Park, J. W.; *Macromolecules* **1998**, *31*, 1114. (c) Kim, K. D.; Park, J. S.; Kim, H. K.; Lee, T. B.; No, K. T. *Macromolecules* **1998**, *31*, 7267.

(12) (a). Jung, S. H.; Kim, H. K.; Kim, S. H.; Jeoung, S. C.; Kim, Y. H.; Kim, D.; *Macromolecules* **2000**, *33*, 9277. (b) Baek, N. S.; Jung, S. H.; Oh, D. J.; Kim, H. K.; Hwang, G. T.; Kim, B. H. *Synth. Met.* **2001**, *121*, 1743.

(13) Yoshida, Y.; Nichihara, Y.; Ootake, R.; Fujii, A.; Ozaki, M.; Yoshuno, K.; Kim, H. K.; Baek, N. S.; Choi, S. K. *J. Appl. Phys.* **2001**, *90*, 6061.

(14) Paik, K. L.; Baek, N. S.; Kim, H. K.; Lee, J. H.; Lee, Y. *Opt. Mater.*, in press.

(15) (a) Zugang, L.; Nazare, H. *Synth. Met.* **2000**, *111*−*112*, 47; (b) Kido, J.; Hongawa, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815.

(16) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281.

(17) Tasch, S.; List, E. J. W.; Ekstrom, O.; Graupner, W.; Leising, G.; Schlichting, P.; Rohr, U.; Geerts, Y.; Scherf, U.; Mullen, K. *Appl. Phys. Lett.* **1997**, *71*, 2883.

(18) Chao, C.-I.; Chen, S.-A. *Appl. Phys. Lett.* **1998**, *73*, 426.

(19) Dodabalapur, A.; Rothberg, L. H.; Miller, T. M. *Appl. Phys. Lett.* **1994**, *65*, 2308.

(20) (a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815. (a) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281.

(21) Jordan, R. H.; Dodabalapur, A.; Strukelj, M.; Miller, T. M. *Appl. Phys. Lett.* **1996**, *68*, 1192.

(22) Kalinowski, J.; DiMarco, P.; Cocchi, M.; Fattori, V.; Camaioni, N.; Duff, J. *Appl. Phys. Lett.* **1996**, *68*, 2317.

(23) Kido, J.; Kimum, M.; Nagai, K. *Science* **1995**, *267*, 1332.

(24) (a) Stolle, J. *J. Prakt. Chem.* **1904**, *69*, 480. (b) Chen, Z.-K; Meng, H.; Lai, Y.-H.; Huang, W. *Macromolecules* **1999**, *33*, 9277. (c) Meng, H.; Huang, W. *J. Org. Chem.* **2000**, *65*, 3894.

(25) Lee, Y.-Z.; Chen, X.; Chen, M.-C.; Chen, S.-A. *Appl. Phys. Lett.* **2001**, *79*, 308.

(26) Lee, S. N.; Baek, N. S.; Kim, H. K.; Shim, S. D.; Joo, T. *Mol. Cryst. Liq. Cryst.* 2002, *377*, 121.

(27) Walree, C. A. V.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.

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