Novel Silicon-Based Alternating Copolymers: Synthesis, Photophysical Properties, and Tunable EL Colors

Hwan Kyu Kim, Kyung Lim Paik, Nam Seob Baek, Youngil Lee*[†],
Katsumi Yoshino[‡]

National Creative Initiative Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejon 306-791, Korea; Email: hwankkim@mail.hannam.ac.kr
[†]Dongbu Research Council, Daejon 103-2, Korea
[‡] Department of Electronic Engineering, Osaka University, Osaka 565-0871, Japan

Summary: We synthesized novel silicon-based alternating copolymers for tunable electroluminescent (EL) colors by Heck synthetic method. Their thermal, photophysical and electroluminescent properties were studied. Most of them exhibited a blue-green EL color at the operating voltage of lower than 12 V. Unusually, we observed the white EL color from a EL device based on SiPhPVK. From photophysical studies and the time-resolved PL spectroscopies, it might be attributed to the formation of stabilized excited state in SiPhPVK. Furthermore, in order to reduce the operating voltage of their LED with increasing the electron affinity of the main chain in silicon-based alternating copolymers, we synthesized the silicon-based copolymers containing electron transporting oxadiazole units in main chain. We also studied their photophysical and electroluminescent properties.

Introduction

Since electroluminescence from π-conjugated polymer was discovered,[1] the polymeric light-emitting diodes (PLEDs) have attracted much attention because of academic interests and potential utility of this technology in a wide variety of applications such as flat panal displays and light-emitting diodes.[2,3] EL polymeric materials offer a number of advantages, such as low operating voltages, three primary R/G/B colors with the control of π-π* 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] However, the realization of potential uses is limited by their low quantum efficiency and EL efficiency. The EL efficiency of

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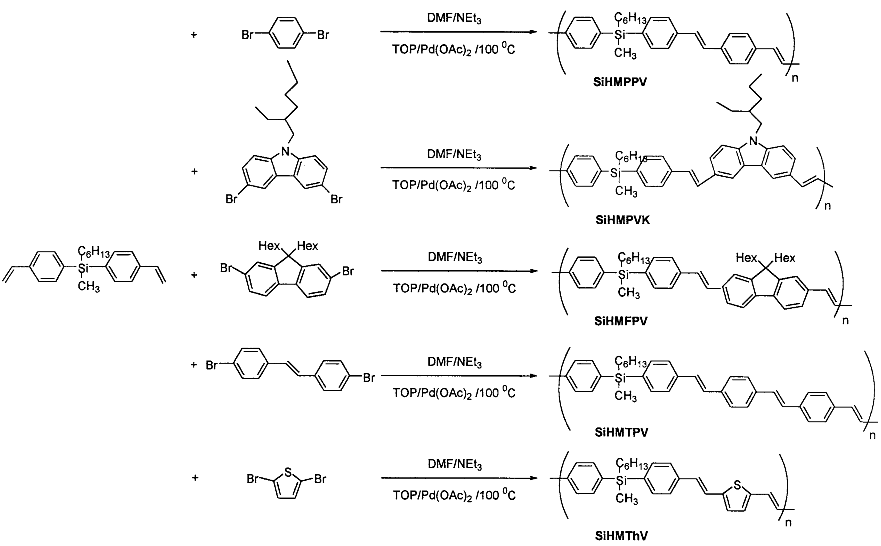
devices can be affected by the homogeneity of film quality, the injection efficiency of carriers from electrodes to organic materials, and the material's EL efficiency. The two former can be solved by thin film fabricating processes, but the latter can be only achieved by developing materials with high EL efficiency.

Recently, we have studied the development of novel silicon-based copolymers exhibiting blue-white emissive colors. The synthesis of silicon-based alternating copolymers was carried out using well-known Heck reaction.[6-8] Instead of the Wittig method used in the early stage of this research [6, 9], the Heck synthetic routes to the preparation of silicon-based 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 arising from the unreacted or remained aldehyde functional groups in the copolymers obtained from the Wittig reaction. (2) To obtain quantitatively trans-double bond from cis-double bond, the Wittig reaction requires a further post-reaction of isomerization step, achieved by heating the crude polymers with a trace of iodine in toluene. However, the Heck reaction directly produces the desired polymers with trans configuration, which is important to optimize the luminescence efficiency and the emissive wavelength. According to our results, the introduction of organosilicon units into π-conjugated systems also improves their processability and limits the π-conjugation length, resulting blue light emission. And, silicon-based copolymers exhibit the blue LEDs operated at the low voltages, due to the lowering of the LUMO levels and d-orbital participation of silicon atoms.[10] In this paper, we describe the Pd-catalyzed direct synthesis, photophysical, and EL properties of the silicon-based copolymers.

Results and Discussion

We have synthesized the silicon-based alternating copolymers by the Heck reaction of alkyl/aryl-substituted distyrylsilanes with various aromatic or heteroaromatic dibromides, as shown in Scheme 1 and 2. The polymerization results, thermal and photophysical properties of silicon-based copolymers are summarized in Table 1. All the copolymers have the glass transition temperature (T_g) in the range of 94 to 126 °C. They did not show any definite melting points, implying that the silicon-based copolymers could be amorphous. All of the polymers showed good thermal stability up to 300 °C, since a small amount (or less than 5 %) of weight loss began to occur at 300 °C in a nitrogen atmosphere. The maximum absorption wavelengths (λ_{max}) of SiHMPPV and SiPhPPV exhibit at 322 and 365 nm. The absorption spectra of SiHMPVK and SiPhPVK show two peaks around 322 and 356 nm, which are attributed to π-π* transition of the carbazole segments and the π-conjugated segment (see Figure 1). Also the absorption spectra of SiHMFPV and SiPhFPV show the UV absorption bands around 380 nm. The maximum absorption wavelength (λ_{max}) of SiHMThV, SiPhThV and SiPhThThV appears at the longer wavelength of 400, 407, and 416 nm, due to the strong delocalization of the π-conjugated thiophene units, respectively.

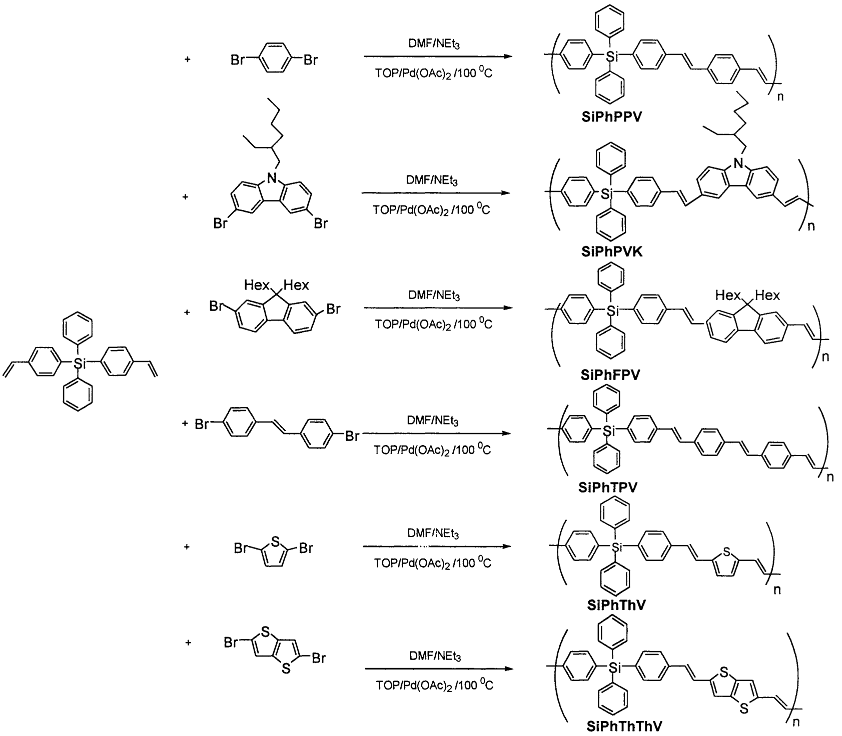


Scheme 1. Synthesis of silicon-based copolymers using alkyl substituted distyrylsilane monomer.

Their photoluminescence (PL) spectra similarly shifts to those observed in the absorption spectra. With an excitation wavelength of 365 nm, the SiHMPPV, SiPhPPV, SiHMFPV and SiPhFPV spectra show a peak around 470 nm, indicating a blue emission. And, the PL spectra of both SiHMPVK and SiPhPVK give a peak in the blue emission region at 440 nm. With an excitation wavelength of 410 nm, the PL spectra of SiHMThV, SiPhThV and SiPhThThV exhibit a peak at 520, 526, and 512 nm in the green region, respectively.

The single-layered light-emitting diode of an Al/SiPhPPV or SiHMPPV/ITO glass was fabricated. The threshold voltage is in the range of 10 to 12 V from the I-V curve. The EL spectrum showed a peak at 450 nm, when the operating voltage of 12 V was applied. Furthermore, the multi-layered light-emitting diodes of an Al/LiAl/SiPhPVK or SiHMPVK/

PANI/ITO glass were fabricated. The threshold voltage is in the range of 6 ~ 12 V. The EL spectrum of SiHMPVK exhibits a broad band around 460 nm in the blue region at the operating voltage of higher than 12 V. However, the EL property of SiPhPVK depends strongly on the applied voltage. Unusually, we observed the white EL color from a EL device based on SiPhPVK at the applied voltage of higher than 11V (see Figure 2). The EL spectrum gives a peak at 467 nm, when the operating voltage of 7 V was applied. When the operating voltage of 11 V was applied, however, the EL spectrum gives a peak at 467 nm and an additional strong EL emissive band in the red region. Therefore, two EL peaks may combine to produce a white EL color at the operating voltage of higher than 11 V. Also, we observed that the intensity of two EL peaks increases with the applied voltage.



Scheme 2. Synthesis of silicon-based copolymers using aryl substituted distyrylsilane monomer.

In order to understand the origin of an additionally new red EL band, we measured the emission and the excitation spectroscopies of SiPhPVK. [7, 9] Figure 3 (a) shows the PL spectra of SiPhPVK with photoexcitation at two different wavelengths. These two excitation wavelengths at 300 and 400 nm were chosen for selective photoexcitation of carbazole and SiPh segments in SiPhPVK, respectively. The PL spectra exhibit the emission maximum band around 440 nm, in addition to the emission band at 520 nm. Upon photoexcitation of carbazole unit at 300 nm, the intensity ratio between these two bands is different from that

Table 1. Summary of polymerization results, thermal and photophysical properties of silicon-based alternating copolymers.

Polymers	Yield (%)	$M_w \times 10^{-3}$	T_{ID} (^oC)	T_g (^oC)	UV(λ_{max}) (nm)	PL(λ_{max}) (nm)	PL efficiency	EL(λ_{max}) (nm)
SiHMPPV[a)]	52	8.5	180	94	356&365	470	-	450
SiHMPVK[a)]	51	2.3	175	106	322&356	440	-	460
SiHMFPV	70	9.8	185	96	378	470	12.7	-
SiHMTPV	66	2.7	200	112	386	470	-	-
SiHMThV	50	10.3	150	94	400	520	-	-
SiPhPPV[a)]	48	6.3	250	127	355&365	470	26.4	450
SiPhPVK[b)]	43	3.7	253	102	325&356	440	-	467& 620
SiPhFPV	77	12.7	250	109	380	476	11.6	-
SiPhTPV	45	4.5	253	110	374&388	463	-	-
SiPhThV	55	13.3	225	112	407	526	5.3	-
SiPhThThV	50	18.6	200	116	416	512	-	-

a) EL data from single-layered LED of Al/SiPHPPV or SiHMPPV/ITO
b) EL data from multi-layered LED of Al/LiAl/SiPHPVK/PANI/ITO

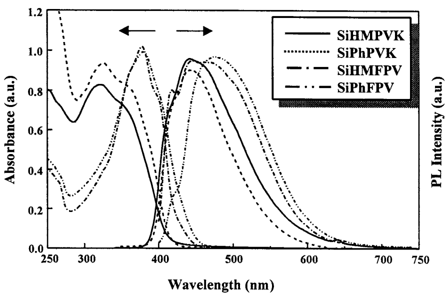


Figure 1. UV-visible and PL spectra of SiHMPVK, SiPhPVK, SiHMFPV and SiPhFPV in $CHCl_3$.

obtained with photoexcitation of SiPh segment at 400 nm. From this result, we can suggest that the origin of these two emission bands is different. Thus, we measured the excitation spectra in the wavelength range from 280 to 420 nm at the emission wavelengths of 440 and 520 nm. We could observe two excitation spectra were obviously different (see Figure 3 (b)). Considering the above results, it is reasonable to suppose that the shorter wavelength emission band results from the carbazole segments. Meanwhile, it is not straightforward to assign the origin of the emission band at low energy side to the conjugated SiPh segments in SiPhPVK, because no such emission band is found in either PL or EL spectra from a SiPhPPV thin film. Therefore, it may be considered that the longer wavelength emission band in SiPhPVK could result from the formation of either the exciplex between excited state carbazole and PPV segment or the excimer between a ground state and an excited state of carbazole segments. In fact, it is well known that a carbazole unit with small substituent group in the polymer could easily form an excimer between ground and excited states of carbazole units. In our system, however, the longer wavelength emission is mainly due to the optical transition of SiPh main chain because the carbazole unit in our system has a branched and bulky alkyl chain which should hinder the excimer formation between carbazole units. The other probable explanation can be drawn from the stabilized excited state arising from the intramolecular interaction. Since the carbazole unit in SiPhPVK has a high hole affinity, the SiPh unit may possess the electron affinity with respect to the carbazole unit. Thus, we can suggest that the long wavelength emission in SiPhPVK originates from other stabilized excited state, e.g. CT state.

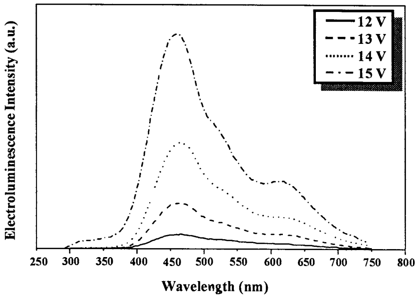


Figure 2. Electroluminescence spectra of SiPhPVK as a function of applied voltages.

In order to gain further insight into the nature of the long wavelength emission, we measured the PL decay profiles of SiPhPVK with photoexcitations at 300 and 400 nm. Figure 4 shows the PL decay profiles of SiPhPVK monitored at 430, 480 and 550 nm. The long wavelength PL lifetime of SiPhPVK, which is believed to be due to the charge transfer process, is approximately 1.5 ns. However, the PL lifetime at 550 nm seems to be too long to be explained in terms of the energy migration process. The long emission lifetime is characteristic feature of the charge transfer formation along with a long tail emission. Thus, we can suggest that the charge transfer process between carbazole and SiPh units in the same chain induces the long wavelength emission of SiPhPVK. It is generally accepted that upon photoexcitation with high energy the PL decay in polymers becomes fast as compared to the photoexcitation with lower energy because of defect sites. However, upon photoexcitation with high energy (300 nm), the PL decay time of SiPhPVK is longer than that obtained by photoexcitation at lower energy (400 nm). Therefore, we can suggest that the charge transfer process is facile upon photoexcitation of a carbazole unit in SiPhPVK as compared with the photoexcitation of SiPh unit.

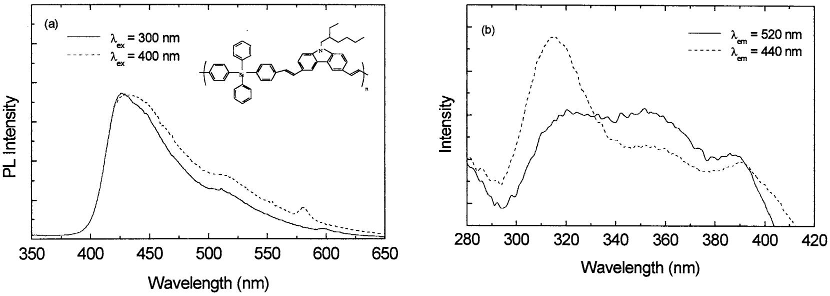


Figure 3. (a) The PL spectra of SiPhPVK with two photoexcitation wavelengths at 300 and 400 nm and (b) the PL excitation spectra for SiPhPVK at two probes of 440 and 520 nm.

From time-resolved PL measurement and photophysical studies, we proposed that the additional new PL band, unlikey SiHMPVK, might be attributed to the formation of a certain charge transfer complex, as shown in Scheme 3. [11] The stable resonance structure in the excited state was formed through stabilizing it with phenyl side groups in the SiPh unit of SiPhPVK. Phenyl side groups in the SiPh unit of SiPhPVK behave like electron-withdrawing group.

Similarly, to increase the electron-withdrawing property of the main chain in silicon-based alternating copolymers, we synthesized the silicon-based copolymers containing oxadiazole units (SiHMOXD/Cz 10) to balance the hole-electron charges injected and to see the structure-property relations (see Scheme 4).[12] In the UV-visible spectrum, the absorption maximum wavelength (λ_{max}) of SiHMOXD/Cz 10 appears at 355 and 357 nm in chloroform solution and thin film, respectively.

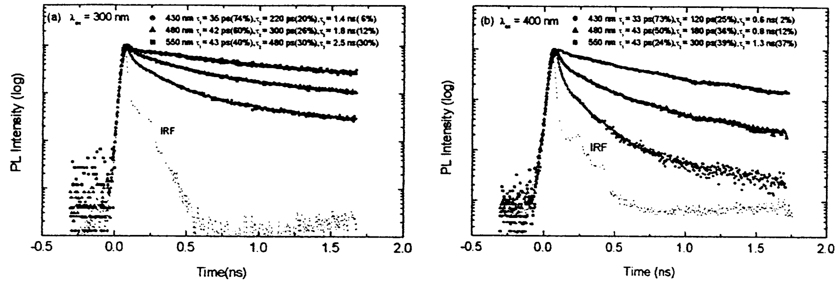
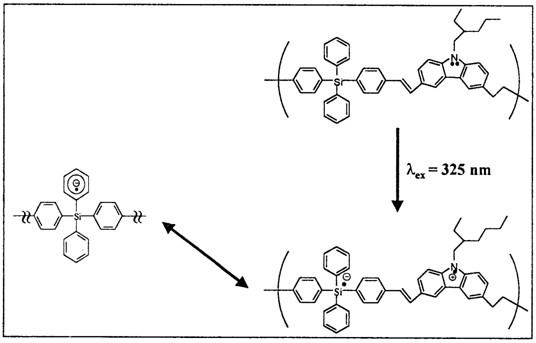
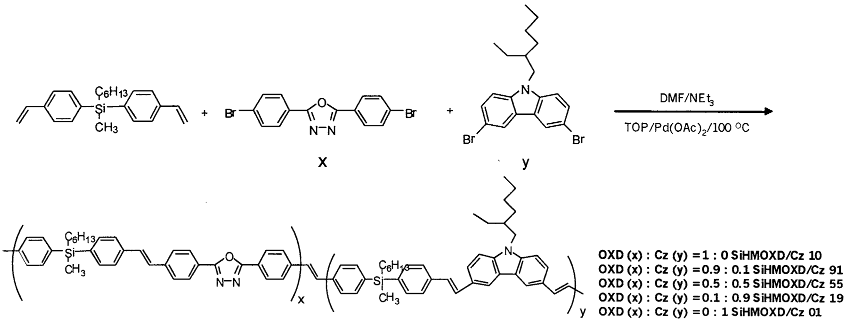


Figure 4. Transient PL decay profiles for SiPhPVK monitored at 430, 480 and 550 nm with two photoexcitation wavelengths of (a) 300 nm and (b) 400 nm.



Scheme 3. Proposed scheme for the formation of a charge complex in SiPhPVK.

And, the PL spectra show a strong band around 435 and 451 nm in chloroform and thin film, respectively. The multi-layered light emitting diode of Al (200nm)/Ca (50 nm)/ SiHMOXD/Cz 10 (80nm)/PEDOT (50nm)/ITO glass was fabricated. The I-V curve shows the turn-on voltage of 7 V (see Figure 5). This value is a little lower than any other silicon-based copolymers developed by our research group, due to the more electron affinity of the oxadiazole units. Its EL spectrum, as shown in Figure 6, exhibits a broad band around 460 nm in the blue region and a very broad, weak band in the red 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 new red EL peak is generated only by electric field, since this new red band is exhibited only in EL, but not in PL spectra (see Figure 7). In other word, a certain charge complex, more like electroplex, is formed under a strong electric field inside the device and cannot be produced by photoexcitation. A similar phenomenon has been reported in an oxadiazole-containing conjugated polymer.[13] Therefore, two broad emissive bands combine to produce the white emissive color above 13 V. And, the maximum luminance of the white emissive color was 3.71 cd/m^2 at the applied voltage of 12 V.



Scheme 4. Synthetic routes of silicon-based copolymers containing oxadiazole units.

And, to overcome the poor solubility of the resulting polymer containing only an oxadiazole unit and to improve the quantum efficiency and luminescent properties, we introduced 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 (SiHMOXD/Cz xy) (see Scheme 4). [14] The maximum absorption wavelength (λ_{max}) of SiHMOXD/Cz 91, 55, and 19 appears at the wavelength of 357, 360, and 349 nm in film state, respectively. The PL spectra of these polymers exhibit a strong band around 455, 483, and 475 nm in the blue region, respectively. The multi-layered light-emitting diodes with the same device structure of SiHMOXD/Cz xy were fabricated. Their EL properties depend strongly on both the applied voltage and the loading amount of hole-transport carbazole moieties in the present copolymers. The turn-on voltage is in the range of 6 ~ 7 V (see Figure 5). The EL spectra from the device based on the copolymers containing only 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 the 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.

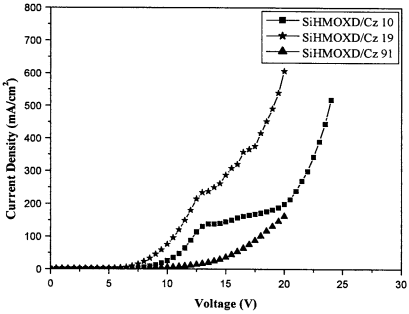
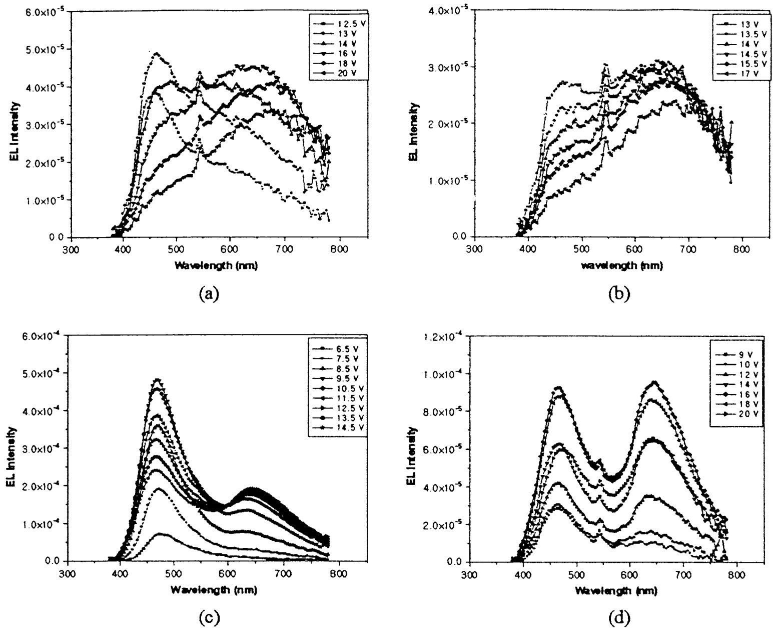


Figure 5. I-V curves of SiHMOXD/Cz 10, SiHMOXD/Cz 91, and SiHMOXD/Cz 19.

Also, the EL spectra from the devices based on SiHMOXD/Cz 91 – 19 have a similar EL spectral feature with the applied voltage. 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 bands. Surprisingly, the intensity of two emissive EL bands increases concomitantly with the applied voltage, showing two strong emissive bands, like two crests. They combine together and emit a strong white color. And, 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 certain charge complex like excimer, exciplex, or electroplex, respectively.

Also, in order to gain further insight into the nature of the certain charge complex, we fabricated two LED devices from the blend systems of SiHMOXD/Cz 19 with polystyrene (PS). Even with the device from the blend system of SiHMOXD/Cz 19 with the large amount of PS (80%), in which intermolecular interaction between the polymer chains can be avoid, we still obtained two crests similar to that of SiHMOXD/Cz 19. It indicates that these unusual EL properties, originating from the formation of a certain charge complex, do not exclude intra-chain interaction.



(a) (b) (c) (d)

Figure 6. EL spectra of SiHMOXD/Cz 10 (a), SiHMOXD/Cz 91 (b), SiHMOXD/Cz 55 (c), and SiHMOXD/Cz 19 (d).

Then, we measured the emission and the excitation spectroscopies for SiHMOXD/Cz 01, SiHMOXD/Cz 10, SiHMOXD/Cz 55, and SiHMOXD 19 at the various wavelengths (see Figure 7). 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 segments with the carbazole unit (D_{π}) or the oxadiazole unit (A_{π}). The PL spectra of the SiHMOXD/Cz 01 and the SiHMOXD/Cz 10 show the same emission maximum band around 430 nm and 455 nm, which are attributed to photoexcitation of the carbazole unit and the oxadiazole unit, respectively. However, these PL spectral features behave quite differently from SiPhPVK (see Figure 3 (a) and Scheme 3), while the stable resonance structure in the excited state was formed through stabilizing it with phenyl side groups in the SiPh unit of SiPhPVK.

From these different results, we suggest 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

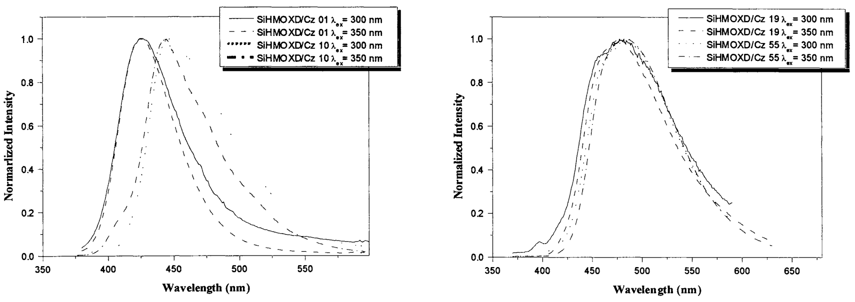
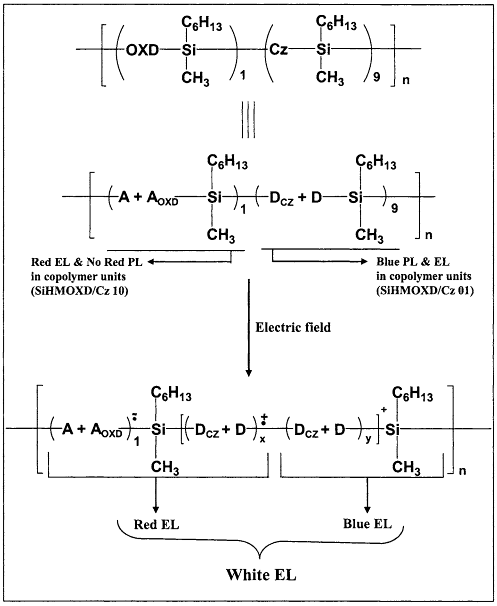


Figure 7. Emission spectra of SiHMOXD/Cz 10 and SiHMOXD/Cz 01 (a), SiHMOXD/Cz 55 and SiHMOXD/Cz 19 with two photoexcitation wavelengths at 300 & 350 nm.

indirectly to silicon atoms via styryl groups, unlike SiPhPVK (see Scheme 3). Their PL spectra of SiHMOXD/Cz 55 and SiHMOXD/Cz 19 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 segments with the oxadiazole unit (A_π). Even though the carbazole units (D_{Cz}) as well as the π -conjugated segments 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 due to the energy transfer of the excited state of carbazole moieties to the ground state of the oxadiazole units. From these emission studies, we could not observe the red PL spectra, ascribed to the formation of a certain intramolecular charge complex. Therefore, we could propose the formation of a certain intramolecular charge complex for the silicon-based copolymers containing both electron-transport oxadiazole and hole-transport carbazole moieties, corresponding to a red color, as shown in Scheme 5. The proposed scheme can be deduced as follows: In the LED device of SiHMOXD/Cz 10, this new red band is exhibited only in EL, but not in PL spectra. And, in the LED device of SiHMOXD/Cz 01, 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 certain charge complex, more like excimer, exciplex, or electroplex, is formed under a strong electric field inside the device and cannot be produced by photoexcitation. From the blending study, the charge complex can be formed intramolecularly between the oxadiazole units and the carbazole units. When the voltage was applied, the electrons can inject into the oxadiazole units (A_{OXD}) and π-conjugated segments with the oxadiazole unit (A_π), yielding a certain charge complex of the negative polarons in the oxadiazole units (A_{OXD}) and π-conjugated segments with the oxadiazole unit (A_π).



Scheme 5. Proposed scheme for the formation of charge complex in SiHMOXD/Cz 19.

Alternatively, the holes can inject into the carbazole units (D_{Cz}) as well as the π-conjugated segments with the carbazole unit (D_π), forming a certain 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). As seen from Scheme 5, a certain charge complex emits the longer emissive bands, which corresponds to the red EL color in EL spectra. In 1996, this kind of the charge complexes from the photoinduced charge separation occurring donor-acceptor substituted silanes (A_π-$SiMe_2$-D_π) was reported.[15] Also, some of a certain charge complex of the positive polaron in the 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

We successfully synthesized novel silicon-based alternating copolymers for tunable electroluminescent (EL) colors using Heck synthetic method. Their thermal, photophysical and electroluminescent properties were reported. Most of them exhibited a blue-green EL color at the operating voltage of lower than 12 V. Unusually, we observed the white EL color from a EL device based on SiPhPVK. From photophysical studies and the time-resolved PL spectroscopies, it might be attributed to the formation of stabilized excited state in SiPhPVK. Also, the silicon-based copolymers containing electron transporting oxadiazole and hole-transport carbazole units in main chain were successfully synthesized using Heck synthetic method. We studied their photophysical and electroluminescent properties. The resulting polymers exhibit a strong UV-visible absorption band in the range of 345 ~ 356 nm in chloroform solution and in film state. Upon a 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 (200nm)/Ca (50nm)/EL polymer (80nm)/PEDOT (50 nm)/ITO were successfully fabricated. And, I-V curves show the turn on voltage of 6 ~ 7V. 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 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 13 V. The EL spectra 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 the 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. Two EL bands combine to exhibit a moderate white color. 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 bands, like two crests, giving a strong white color. And, its 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 certain charge complex like excimer, exciplex, or electroplex, respectively: The blue EL color comes from the carbazole segments in these silicon-based copolymers. The latter red EL color comes from a certain charge complex arising from oxadiazole (and carbazole) segments. The new red band is exhibited only in EL, but not in PL spectra. From the photophysical studies, a certain intramolecular charge complex was proposed.

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