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Synthesis and Properties of Random Carbazole/1,3,4-Oxadiazole/Aniline Copolymers for Organic Light-Emitting Devices

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Random copolymers, poly[($\mathbf{M_1}$-$\mathbf{M_2}$*)*-ran-*(*$\mathbf{M_1}$-$\mathbf{M_3}$*)], have been synthesized by* N-*(3,6-dibromo)carbazole (*$\mathbf{M_1}$*), aniline (*$\mathbf{M_2}$*) and 2-*p-*methylphenyl-5-(4-aminophenyl)-1,3,4-oxadiazole (*$\mathbf{M_3}$*). The random copolymers were obtained with high solubility and good film forming properties. Optical properties of these copolymers were investigated. As increasing the content of* $\mathbf{M_3}$*, the maximum absorption peaks (*$\lambda_{max,UV}$*) of copolymers at 360 nm increased gradually, which was the typical* $\lambda_{max,UV}$ *of poly(*$\mathbf{M_1}$-alt-$\mathbf{M_3}$*). Compared with maximum photoluminescence emission peak (*$\lambda_{max,PL}$*) at 452 nm of poly(*$\mathbf{M_1}$-alt-$\mathbf{M_2}$*), all the random copolymers displayed* $\lambda_{max,PL}$ *at about 519 nm, similar with that of poly(*$\mathbf{M_1}$-alt-$\mathbf{M_3}$*). It was notable that* $\lambda_{max,PL}$ *of the random copolymers shifted to that of poly(*$\mathbf{M_1}$-alt-$\mathbf{M_3}$*) with the addition of* $\mathbf{M_3}$ *in the copolymers, and then remained almost unchanged irrespective of further increasing the content of* $\mathbf{M_3}$*, implying the emission from the lower band gap segment of poly(*$\mathbf{M_1}$-alt-$\mathbf{M_3}$*). The band gap energy of the copolymers was measured in the range of 2.82 ~ 2.91 eV, and HOMO energy in the range of −4.95 ~ −5.11 eV. Hole transporting properties of the synthesized copolymers in OLEDs were measured with the configuration of ITO/copolymer/Alq*$_3$*/LiF/Al, where Alq*$_3$ *was used as an emitting layer. It appeared that the random copolymers (***P4** ~ **P5***) with the compositions of* $\mathbf{M_1}$:$\mathbf{M_2}$:$\mathbf{M_3}$ *(10:4:6~10:6:4 mole ratio) showed better hole-transporting property.*

Keywords: 1,3,4-oxadiazole; aniline; carbazole; copolymer; hole transport

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INTRODUCTION

It is well known that the charge injection and transport can be facilitated by sandwiching the emitting layer between a hole-injection/transporting layer (HIL/HTL) above the anode and an electron-injection/transporting layer (EIL/ETL) under the cathode. The use of multilayer structure with appropriate HTL and ETL can not only lower the driving voltage but also balance the charge transporting, and improve the performance of the devices with long lifetime and high quantum efficiency [1,2]. It has been revealed [3,4] that carbazole and its derivates are well known as good hole-transporters, while oxadiazole and its derivates as electron-transporters. Polymers containing carbazole and oxadiazole units in either the main chain or side group also have been synthesized. For example, copolymers with 9-octylcarbazole and 9,9-diocylfluorene showed improved hole-transporting property [5]. Jin *et al.* reported increased electron transporting property of a series of PPV-based copolymers containing oxadiazole group [6]. Jiang *et al.* incorporated carbazole and oxadiazole groups through free radical copolymerization of *N*-vinylcarbazole with two different oxadiazole-bearing monomers [7]. Varying the chemical structure of polymers can influence the hole- or electron transporting capabilities of the polymers in organic light emitting diodes (OLEDs). It was also found that the polymers with oxadiazole group in the side chain could make the holes transport through a hopping mechanism, which could increase the hole-transporting property of the polymers [8]. The relevant experimental results were observed in a series of copolymers of poly(*N*-(2-ethylhexyl)-3,6-carbazole-*co*-2-(*p*-aryl)-5-(4-aminophenyl)-1,3,4-oxadiazole) (aryl = phenyl, methylphenyl and methyloxylphenyl) in our previous work [9]. The synthesized copolymers could work as hole-transporting materials in OLEDs.

In this work, we extended our previous study of alternating copolymers, poly($\boldsymbol{M_1}$-alt-$\boldsymbol{M_2}$) and poly($\boldsymbol{M_1}$-alt-$\boldsymbol{M_3}$) [9,10], to new random copolymers of poly[($\boldsymbol{M_1}$-$\boldsymbol{M_2}$)-*ran*-($\boldsymbol{M_1}$-$\boldsymbol{M_3}$)]. The purpose of this study was to investigate effect of the composition of $\boldsymbol{M_2}$ and $\boldsymbol{M_3}$ in the random copolymers on the properties such as UV-Visible absorption, photoluminescence emission, electrochemical property and their preliminary application in OLEDs.

EXPERIMENTAL

Materials

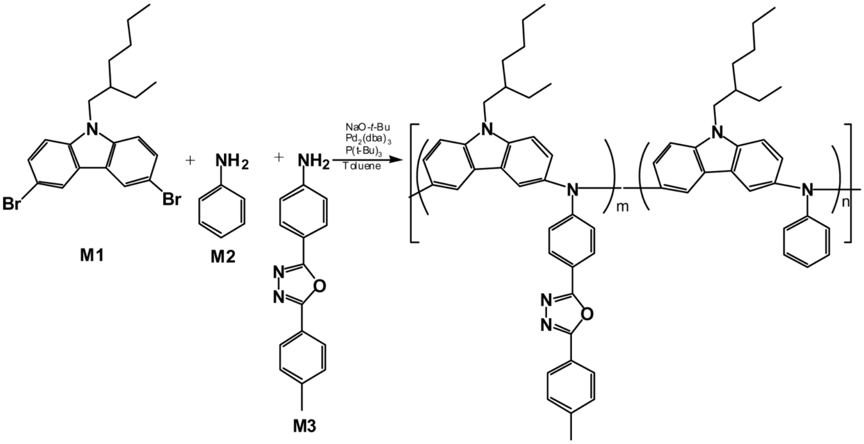
2-*p*-methylphenyl-5-(4-aminophenyl)-1,3,4-oxadiazole ($\boldsymbol{M_3}$) and *N*-(3,6-dibromo)-carbazole ($\boldsymbol{M_1}$) were prepared and characterized according to the procedure reported previously [9–10]. Anlinie (***M_2***), sodium-*tert*-butoxide (NaO-*t*-Bu), tris(dibenzylidene-acetone)dipalladium(0) ($Pd_2(dba)_3$), and tri-*tert*-butylphosphine ($P(t\text{-}Bu)_3$) were purchased from Aldrich Chemical Co. Tri(8-hydroxyquinolate)- aluminum (Alq_3) and lithium fluoride (LiF) were obtained from Tokyo Kasei Co. Aluminum was purchased from CERAC, USA. Indium-tin oxide (ITO) coated glass with a sheet resistance of $50\,\Omega/\square$ was obtained from Sin'an SNP Co.

Synthesis of Polymers

Random polymers were prepared by using Pd-catalyst polycondensation as presented in Scheme 1. A mixture of ***M_1***, ***M_2*** and ***M_3*** were dissolved in toluene. NaO-*t*-Bu, $Pd_2(dba)_3$ and $P(t\text{-}Bu)_3$ were added to the solution at room temperature. The reaction mixture was stirred at 100°C for 48 h. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia and the product was extracted with $CHCl_3$. The organic fraction was concentrated and reprecipitated from $CHCl_3$/methonal several times. Then, the products were filtered, dried in vacuum and obtained as yellow powder.

Characterization

Number and weight average molecular weights of the polymers were measured by using Waters gel permeation chromatograph (GPC) equipped with Styragel HR 5E column by using THF as an eluent



SCHEME 1 Synthetic route to random copolymers.

against polystyrene standards at room temperature. UV-Visible absorption spectra were taken by Shimadzu UV-2100. Photoluminescence (PL) emission spectra were made by Shimadzu RF-5301PC fluorometer utilizing a He-Cd laser at 325 nm. The ionization potential was measured by a photoelectron spectroscopy (Riken Keiki AC-2). The EL spectra were measured on Spectroscan PR 650 analyzer. The current-voltage (*I-V*) characteristics and luminescence-voltage (*J-V*) were measured by using a dc power supply connected with Model 8092A Digital Multimeter and luminance meter (Minolta LS-100), respectively.

Fabrication of OLEDS

ITO coated glass was cut into 5.0 cm × 5.0 cm, and electrode area was prepared by photo-etching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water solution. For the device with the configuration of ITO/polymers/Alq_3 (60 nm)/LiF (1 nm)/Al (100 nm), first a polymer film was spin-coated on ITO glass from polymer solution (1 wt% in 1,1,2,2-tetrachloroethane) at a speed of 2,000 rpm, and then baked on hot plate at 80°C for 10 min. Subsequently, an emissive Alq_3 layer was deposited onto the surface of polymer film. Finally, LiF and Al were successively deposited under pressure $<10^{-6}$ torr.

RESULTS AND DISCUSSION

As depicted in Scheme 1, the random copolymers of poly[($\boldsymbol{M_1}$-$\boldsymbol{M_2}$)-*ran*-($\boldsymbol{M_1}$-$\boldsymbol{M_3}$)] possess triarylamine units in the backbone and oxadiazole groups in the side chain. It has been known that the triarylamine unit can impart the polymers with property of hole-transporting, while oxadiazole pendants may make the holes transport through a hopping mechanism to increase the hole-transporting property of the polymers.

The random copolymers were readily soluble in common organic solvents such as chloroform, benzene, toluene and THF, and showed good quality of film forming. Molecular weights and molecular weight distributions of the random copolymers were summarized in Table 1. It showed that molecular weights (Mw) of the random copolymers were in the range of 7,230–9,690 g/mol with narrow polydispersity indices of 1.01–1.07. For comparison, alternating copolymers, poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_2}$) and poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_3}$), were also synthesized and characterized.

UV-Visible absorption spectra of random copolymers measured in the dilute chloroform solution are presented in Figure 1, and the results are also summarized in Table 1. **P1** with the composition of

TABLE 1 Physical, Optical and Electrochemical Properties of the Random Copolymers, poly[(M_1-M_2)-*ran*-(M_1-M_3)]

Copolymers	M_1:M_2:M_3 (mole ratio)	M_w (g/mol)	PDI	$\lambda_{max,UV}$ (nm)	$\lambda_{max,PL}$ (nm)	Band gap (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]
Poly(M_1-*alt*-M_2)	10:10:0	7,800	1.30	309	452	2.91	−5.19	−2.28
P1	10:8:2	7,760	1.01	304	517	2.91	−5.06	−2.15
P2	10:7:3	8,900	1.05	361	519	2.87	−5.06	−2.19
P3	10:6:4	9,610	1.07	363	520	2.83	−5.07	−2.24
P4	10:5:5	9,690	1.07	363	519	2.83	−4.95	−2.12
P5	10:4:6	9,440	1.06	361	519	2.82	−4.97	−2.15
P6	10:3:7	7,230	1.01	360	519	2.83	−5.10	−2.27
P7	10:2:8	7,720	1.01	360	517	2.84	−5.11	−2.27
Poly(M_1-*alt*-M_3)	10:0:10	3,800	1.27	357	517	2.88	−5.13	−2.25

[a] Calculated from the crosspoint of UV-visible and PL spectrum.
[b] Measured by a RIKENKeiki AC-2.
[c] Estimated from the HOMO and band gap.

M_1:M_2:M_3 (10:8:2 mole ratio) presented $\lambda_{max,UV}$ at around 304 nm, similar with 309 nm of poly(M_1-*alt*-M_2). With increasing the content of M_3 in the copolymers, $\lambda_{max,UV}$ values of **P2** ~ **P7** were measured at around 360 nm. It can be obviously seen that $\lambda_{max,UV}$ peaks of random copolymers at 360 nm increased gradually with increasing the content of M_3, which was the typical UV-Visible absorption peak of poly(M_1-*alt*-M_3).

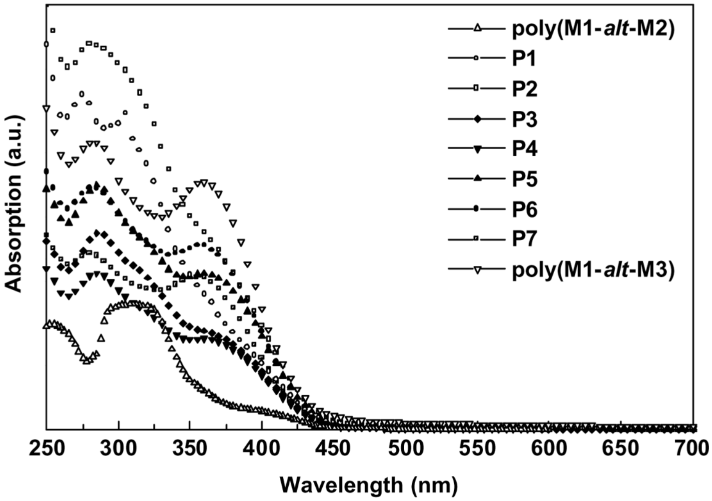


FIGURE 1 UV-Visible absorption spectra of random copolymers.

With the excitation at their $\lambda_{\max,\mathrm{UV}}$, PL emission peaks of the copolymers are shown in Figure 2. Poly(***M₁***-*alt*-***M₂***) showed blue emission with $\lambda_{\max,\mathrm{PL}}$ at 452 nm, which could be attributed to the emission from carbazole chromophore. Regardless of the compositions of the random copolymers, however, the emission peaks of all random copolymers, poly[(M_1-M_2)-*ran*-(M_1-M_3)], were shifted in the range of green emission at around 519 nm. Interestingly, all $\lambda_{\max,\mathrm{PL}}$ values of the random copolymers were similar to that of poly(M_1-*alt*-M_3). Similar phenomenon was reported in random copolymers with fluorene and carbazole groups [5]. This feature was attributed to poly(M_1-*alt*-M_3) segment, which had the lower band gap energy than poly(M_1-*alt*-M_2). In the process of emission, therefore, poly(M_1-*alt*-M_3) segments might effectively collect the exitons from other parts of the polymer backbone and give light [5,11].

Electrochemical behaviors of the copolymers were investigated. The band gap energies of the copolymers were estimated from UV-visible absorption and PL emission spectra, and the electrochemical properties of polymers were also listed in Table 1. Similar band gap energies around 2.82 ~ 2.91 eV were measured in the random copolymers. HOMO energy levels from ionization potential values were measured by a RIKEN Keiki AC-2 instrument. The random copolymers showed similar HOMO energy levels of −4.95 ~ −5.11 eV as well, and such kind of energy levels might provide a closer match to the work function of ITO (work function = − 4.8 eV) when they were used as hole-transporting materials.

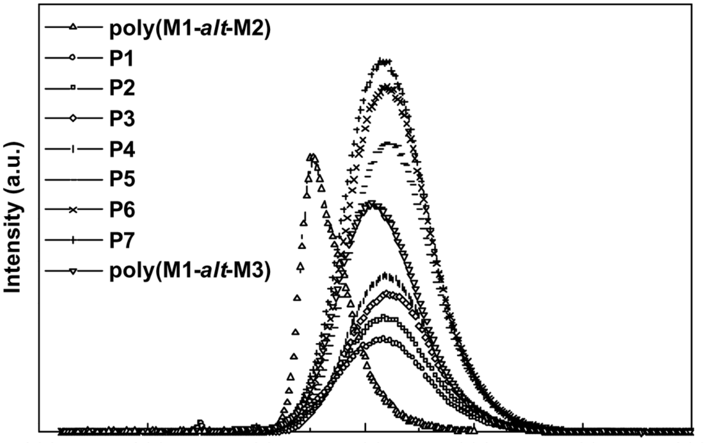


FIGURE 2 PL emission spectra of copolymers.

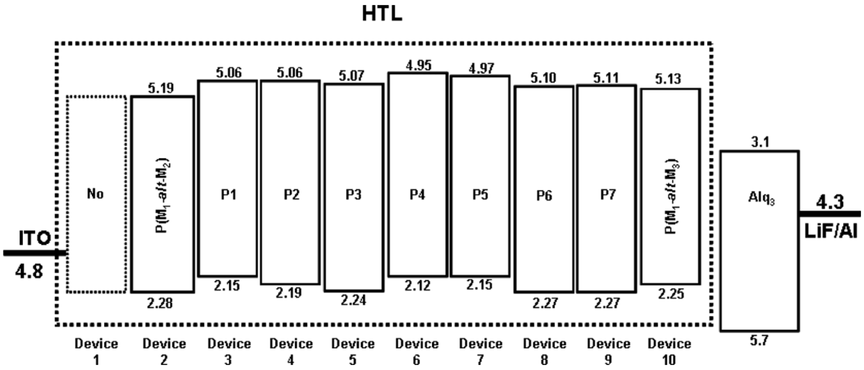


FIGURE 3 Schematic diagrams of devices with copolymers as HTL.

OLEDs (Device 3 ~ Device 9) with the configuration of ITO/poly[($\boldsymbol{M_1}$-$\boldsymbol{M_2}$)-*ran*-($\boldsymbol{M_1}$-$\boldsymbol{M_3}$)]/Alq$_3$ (60 nm)/LiF (1 nm)/Al (100 nm) were fabricated to study the hole affinity of the random copolymers, where Alq$_3$ worked as the emitting material. Poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_2}$) and poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_3}$) were also used to fabricate Device 2 and Device 10, respectively. Device 1 without HTL was used as a reference. The schematic diagrams of devices were shown in Figure 3. When voltages were applied on the electrodes, devices emitted bright green lights at around 530 nm, as shown in Figure 4, indicating the emission from the Alq$_3$ layer. Compared with Device 1, however, the emission peaks of other devices had a slight red-shift, which might be caused by the interface between each layer or the degradation of the polymers

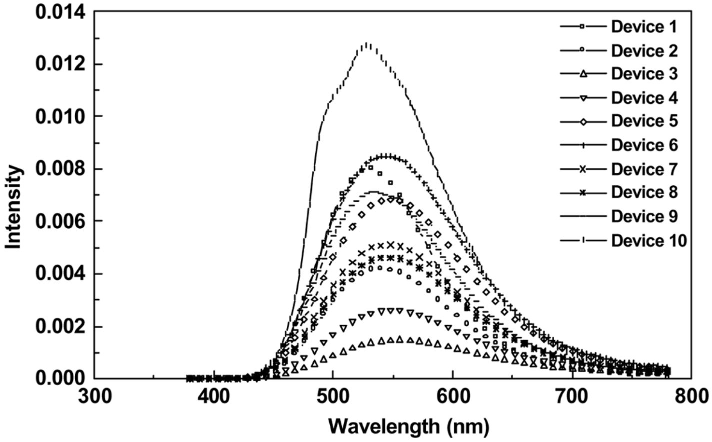
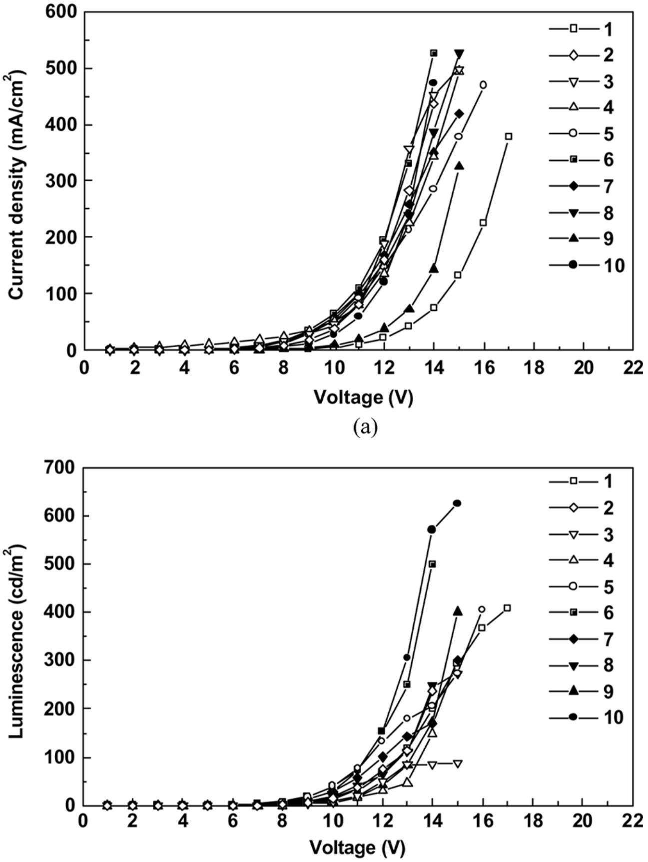


FIGURE 4 EL spectra of devices with copolymers as HTL.

during operating [12,13]. Turn-on voltage of OLEDs was measured as the voltage at which the emission appeared from the device. Compared to Device 1 showing the turn-on voltage at 8 V, Device 2 and 10 with alternating copolymers as HTL decreased the turn-on voltage to 7 V. With random copolymers as HTL, Device 3, 4, 8 and 9 displayed turn-on voltage at 8 V, while Device 5, 6 and 7 presented turn-on voltage at 7 V. *J-V* and *L-V* plots of the OLEDs were presented in Figures 5(a) and (b), respectively. Table 2 summarized the device data. It was clearly seen from Figure 5(a) that, at the same voltage, the devices with HTL showed higher current density. In Figure 5(b),



(a)

(b)

FIGURE 5 (a) Current-voltage and (b) luminescence-voltage plots of OLEDs with the configuration of ITO/Random Copolymer/Alq_3/LiF/Al.

TABLE 2 Summary of EL Properties of OLEDs

Devices	Polymers	Turn-on voltage (V)	Maximum luminescence (cd/m^2)	Maximum power efficiency (cd/A)
1	No HTL	8.0	406.9	0.30
2	poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_2}$)	7.0	237.9	0.05
3	P1	8.0	88.0	0.02
4	P2	8.0	154.8	0.03
5	P3	7.0	404.2	0.09
6	P4	7.0	500.0	0.10
7	P5	7.0	300.2	0.07
8	P6	8.0	273.0	0.06
9	P7	8.0	400.8	0.05
10	poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_3}$)	7.0	625.0	0.15

Device 2 with poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_2}$) and Device 10 with poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_3}$) as HTL showed maximum luminescence of 237.9 cd/m^2 at 14 V and 625 cd/m^2 at 15 V with maximum luminescence of 0.05 cd/A and 0.15 cd/A, respectively. Similar EL properties of Device 3–9 with the random copolymers as HTL were observed, except Device 3 with lowest luminescence. Although this could not be explained by compositional dependency of copolymers used as HTL, it was worth noting that Device 5 ~ 7 utilizing the random copolymers with the compositions of $\boldsymbol{M_1}$:$\boldsymbol{M_2}$:$\boldsymbol{M_3}$ (10:4:6 ~ 10:6:4 mole ratio) exhibited higher luminescence at the same voltage and higher efficiency than any other devices, attributing the highly improved hole-transporting property of copolymers and stability in those compositions. This result indicated, therefore, that the random copolymers, poly[($\boldsymbol{M_1}$-$\boldsymbol{M_2}$)-*ran*-($\boldsymbol{M_1}$-$\boldsymbol{M_3}$)], with the compositions of $\boldsymbol{M_1}$:$\boldsymbol{M_2}$:$\boldsymbol{M_3}$ (10:4:6 ~ 10:6:4 mole ratio) showed better property as HTL for OLEDs fabricated in this study.

CONCLUSIONS

The random copolymers, poly[($\boldsymbol{M_1}$-$\boldsymbol{M_2}$)-*ran*-($\boldsymbol{M_1}$-$\boldsymbol{M_3}$)], were synthesized and characterized. It was found that UV-Visible absorption property of the random copolymers was affected by the composition of repeating units, increasing the peak intensity of UV-Visible absorption at 360 nm with increasing the content of $\boldsymbol{M_3}$ in the random copolymers. On the other hand, PL emission of the random copolymers was the same as that of poly($\boldsymbol{M_1}$-*alt*-$\boldsymbol{M_3}$) with the addition of $\boldsymbol{M_3}$ in the copolymers, and then remained almost unchanged irrespective of further increasing the content of $\boldsymbol{M_3}$. Similarly, electrochemical properties of the random copolymers were observed irrespective of composition.

Preliminary study on the hole transporting properties of the random copolymers in OLEDs (ITO/random copolymer/Alq_3/LiF/Al) revealed that the random copolymers (**P4** ~ **P6**) with the compositions of M_1:M_2:M_3 (10:4:6 ~ 10:6:4 mole ratio) showed better property as HTL.

REFERENCES

[1] Jiang, X. R., Register, A., Killeen, K. A., Thompson, M. E., Pschenitzka, F., & Sturm, M. E. (2000). *Chem. Mater.*, *12*, 2542.
[2] Pei, Q. & Yang, Y. (1995). *Chem. Mater.*, *7*, 1568.
[3] Kido, J., Hongawa, K., & Okuyama, K. (1993). *Appl. Phys. Lett.*, *63*, 2627.
[4] Jiang, X. Z., Liu, Y. Q., Song, X. Q., & Zhu, D. B. (1997). *Synth. Met.*, *87*, 175.
[5] Li, Y., Ding, J., Day, M., Tao, Y., Lu, J., & D'iorio, M. (2004). *Chem. Mater.*, *16*, 2165.
[6] (a) Jin, S. H., Kim, M. Y., Kim, J. Y., Lee, K., & Gal, Y. S. (2004). *J. Am. Chem. Soc.*, *126*, 2474; (b) Liang, F., Pu, Y., Kurata, T., Kido, J., & Nishide, H. (2005). *Polymer*, *46*, 3767.
[7] Jiang, X., Register, R. A., Killeen, K. A., Thompson, M. E., Pschenitzka, F., & Sturm, J. E. (2000). *Chem. Mater.*, *12*, 2542.
[8] Wang, H., Ryu, J. T., Han, Y. S., Hur, Y., Park, L. S., Song, M., & Kwon, Y. (2006). *Mol. Cryst. Liq. Cryst.*, *459*, 389.
[9] Wang, H., Ryu, J. T., Cao, C., Kown, Y., Park, L. S., & Kim., J. W. (2007). *J. Nanosci. Nanotechno.*, submitted.
[10] Wang, H., Ryu, J. T., Han, Y. S., Kim, D. H., Choi, B. D., Park, L. S., & Kwon, Y. (2006). *Mol. Cryst. Liq. Cryst.*, *459*, 365.
[11] Yamazaki, I., Tamai, N. T., & Amazaki, Y. (1990). *J. Phys. Chem.*, *94*, 516.
[12] Ke, L., Chua, S.-J., Zhang, K., & Yakovlev, N. (2002). *Appl. Phys. Lett.*, *80*, 2195.
[13] Giebeler, C., Antoniadis, H., Bradley, D. D. C., & Shirta, Y. (1999). *J. Appl. Phys.*, *85*, 608.