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Hui Wang [a], Jeong-Tak Ryu [a], Yoon Soo Han [b], Youngjune Hur [c], Lee Soon Park [c], Minhyeon Song [d] & Younghwan Kwon [d]

[a] College of Information and Communication Engineering, Daegu University, Gyeongsan, Gyeongbuk, Korea

[b] Department of Display & Nano Materials, Daegu Gyeongbuk Institute of Science & Technology, Daegu, Korea

[c] ADMRC, Department of Polymer Science, Kyungpook National University, Daegu, Korea

[d] ADMRC, Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk, Korea

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Synthesis and Optical Properties of Copolymers Containing Electron Transporting 1,3,4-Oxadiazole Pendant Groups

Hui Wang
Jeong-Tak Ryu
College of Information and Communication Engineering, Daegu University, Gyeongsan, Gyeongbuk, Korea

Yoon Soo Han
Department of Display & Nano Materials, Daegu Gyeongbuk Institute of Science & Technology, Daegu, Korea

Youngjune Hur
Lee Soon Park
ADMRC, Department of Polymer Science, Kyungpook National University, Daegu, Korea

Minhyeon Song
Younghwan Kwon
ADMRC, Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk, Korea

Well-defined copolymer, P(3,6-EHCZ-alt-MPAOXD), containing a triarylamine and N-alkylcarbazole groups (as hole transport moieties with blue emission) in the main chain and a 1,3,4-oxadiazole pendant group (as an electron transporting moiety) was synthesized by Pd-catalyzed polycondensation of N-(2-ethylhexyl)-3,6-dibromo carbazole with 2-methylphenyl-5-(4-aminophenyl)-1,3,4-oxadiazole. For comparison, P(3,6-EHCZ-alt-AL) containing a triarylamine and a carbazole groups in the main chain was also prepared. P(3,6-EHCZ-alt-AL) exhibited $\lambda_{max,UV}$ *at 309 nm and* $\lambda_{max,PL}$ *in the range of blue emission at 452 nm. However, P(3,6-EHCZ-alt-MPAOXD) exhibited* $\lambda_{max,UV}$ *at 283 nm with a new peak at 359 nm, and red-shifted PL emission at 506 nm, possibly attributed to the extended conjugation by 1,3,4-oxadiazole pendant group. The electrochemical results revealed that incorporation of 1,3,4-oxadiazole group in the polymer side chain*

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Address correspondence to Younghwan Kwon, ADMRC, Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk, 712-714, Korea. E-mail: y_kwon@daegu.au.kr

provided a closely matched HOMO energy levels with hole-injecting PEDOT layer, and reduced the band gap energy level.

Keywords: hole transport; *N*-alkylcarbazole; 1,3,4-oxadiazole; triarylamine

INTRODUCTION

Polymer light emitting diodes (PLEDs) have been attracted attention because of their potential to use in display, which are based on conjugated polymers [1,2]. As for the simple sandwiched diode, holes injecting from the anode into the π orbital, while the electrons injecting from the cathode into the π^* orbital of the polymer, to form exitons and give light. To achieve high luminescence efficiency, it is very important to keep the balance of hole and electron current [3–5]. Many research groups have studied carbazole derivatives as hole-transporting materials and small molecular oxadiazoles as electron-transporting materials [6,7].

There are mainly two approaches to increase the efficiency of the diodes. One is to blend the charge injection/transport molecules into a polymer matrix and keep the single-layer structure by spinning coating. An available example showed that devices fabricated by blending 2-(4-biphenyl)-5-(4-*tert*-butylhpenyl)-1,3,4-oxadiazole (PBD) into poly(*N*-vinylcarbazole) (PVK) gave high efficiency and wide color tuning [6–9]. In these systems, however, the crystallization and phase separation are likely to form, which can make the defects and cause devices failure. Another approach is covalently attaching the hole and electron transporting moieties to the same polymer. Polymers containing carbazole and oxadiazole units in either the main chain or side group have been synthesized. Kido and his coworkers [10] synthesized well-defined copolymers with triarylamine (hole-transporting) and oxadiazole moieties in the backbone. Jiang *et al.* [11] incorporated carbazole and oxadiazole groups through free radical copolymerization of *N*-vinylcarbazole with two oxadiazole-bearing monomers. A series of polymers with poly(*p*-phenylene vinylene), PPV, and oxadiazole have been also synthesized. It demonstrated that no matter placing oxadiazole group in main chains or side chains, the polymers both showed great efficiencies [12–14].

In this paper, we present the synthesis of new copolymer, P(3,6-EHCZ-*alt*-MPAOXD), consisting of a triarylamine and a carbazole groups (hole transporting ability with blue emission) in the main chain as well as the electron transporting 1,3,4-oxadiazole pendant moiety through palladium-catalyzed polycondensation. In addition, P(3,6-EHCZ-*alt*-AL)

with a triarylamine and a carbazole groups in the main chain was also synthesized. Structural effect of the polymers on the optical and electrochemical properties was investigated.

EXPERIMENTAL

Materials

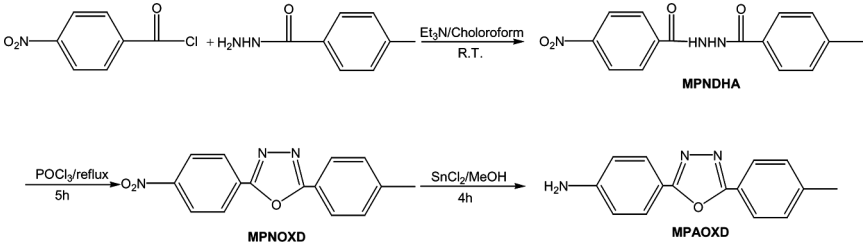
2-Ethylhexylbromide (97%), 3,6-dibromocarbazole (97%), *p*-toluic hydrazide (99%), phosphorus oxychloride ($POCl_3$, 99%), tin(II) chloride ($SnCl_2$, 98%), sodium *tert*-butoxide (NaO-*t*-Bu, 97%), tri(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), tri-*tert*-butylphosphine (P(*t*-Bu)$_3$, 90%) and aniline (99%) were purchased from Aldrich Chemical Co. Reagent grades of potassium carbonate anhydrous (K_2CO_3) and 4-nitrobenzoyl chloride were obtained from Tokyo Kasei Co. and used as received. Solvents were reagent grades and purified prior to use.

Synthesis of Monomers

N-(2-Ethyhexyl)-3,6-dibromocarbazole (3,6-DBEHCZ) was synthesized according to the reference [15].

2-Methylphenyl-5-(4-aminophenyl)-1, 3, 4-Oxadiazole (MPAOXD)

The synthetic scheme for MPAOXD is shown in Scheme 1. In the first step, 4-nitrobenzoyl chloride (0.1 mol) was added dropwise to a solution of *p*-toluic hydrazide (0.1 mol), triethylamine (0.1 mol), and chloroform (150 ml) at room temperature. The resulting mixture was stirred for 2 h and then filtered. The solid collected was washed with water and methanol to give the product, 2-methylphenyl-5-(4-nitrophenyl)-dihydrazide (MPNDHA), with the yield of 98%. ^{1}H NMR (300 MHz in $CDCl_3$): δ 10.88 (1H, $-$N***H***$-$), 10.62 (1H, $-$N***H***$-$), 8.45 (2H, Ar$-$***H***), 8.21 (2H, Ar$-$***H***), 7.88 (2H, Ar$-$***H***), 7.40 (2H, Ar$-$***H***), 2.36 (3H, Ar$-$C***H***$_3$); ^{13}C NMR (300 MHz in $CDCl_3$): δ 166.5, 165.2, 150.3, 142.9, 139.1, 130.4, 129.9, 129.8, 128.4, 124.7, 21.9. GC-MS $m/z = 299$ (m+).



SCHEME 1 Synthetic route to MPAOXD.

In the second step, a mixture of MPNDHA (0.1 mol) and $POCl_3$ (50 ml) was refluxed for 6 h. The excess $POCl_3$ was evaporated out and the residue was poured into water. The crude solid product was collected by filtration, and purified by recrystallization from chloroform/methanol to give the product, 2-methylphenyl-5-(4-nitrophenyl)-1,3,4-oxadiazole (MPNOXD), with the yield of 90%. ^{1}H NMR (300 MHz in $CDCl_3$): δ 8.41 (2H, Ar–***H***), 8.32 (2H, Ar–***H***), 8.05 (2H, Ar–***H***), 7.35 (2H, Ar–***H***), 2.46 (3H, Ar–C$\boldsymbol{H}_3$); ^{13}C NMR (300 MHz in $CDCl_3$): δ 166.1, 163.0, 149.9, 143.4, 130.3, 129.9, 128.1, 127.5, 124.8, 120.9, 22.1. GC-MS $m/z = 281$ (m+).

A mixture of MPNOXD (10 mmol), $SnCl_2$ (60.7 mmol) and ethanol (30 ml) was heated at 70°C for 4 h. After the mixture was cooled to room temperature, 1 M of NaOH solution was added until the mixture became alkaline. After extraction with ethyl acetate, the combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated. The residue was recrystallized from ethanol and final compound, 2-methylphenyl-5-(4-aminophenyl)-1,3,4-oxadiazole (MPAOXD), was obtained with the yield of 90%. ^{1}H NMR (300 MHz in $CDCl_3$): δ 7.98 (2H, Ar–***H***), 7.77 (2H, Ar–***H***), 7.32 (2H, Ar–***H***), 6.74 (2H, Ar–***H***), 4.50 (2H, –N$\boldsymbol{H}_2$), 2.46 (3H, Ar–C$\boldsymbol{H}_3$); ^{13}C NMR (300 MHz in $CDCl_3$): δ 164.7, 163.9, 149.6, 141.8, 129.7, 128.6, 126.7, 121.5, 114.7, 113.8, 21.6. GC-MS $m/z = 251$ (m+).

Polymerization

A mixture of 3,6-EHDBCZ (1.30 mmol) (or MPAOXD) and aniline was dissolved in toluene (15 ml). NaO-*t*-Bu (3.9 mmol), $Pd_2(dba)_3$ (0.033 mmol) and P(*t*-Bu)$_3$ (0.2 mmol) 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 (25 ml) 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 and dried in vacuum.

Characterization

NMR spectra were recorded on a Varian Unity Plus 300 with $CDCl_3$ solvent. GC Mass (GC-MS) spectra were recorded on a QP 5050 mass spectrometer. Molecular weights and molecular weight distributions were measured by Waters gel permeation chromatograph (GPC) equipped with Styragel HR 5E column using THF as an eluent against polystyrene standards at room temperature. Thermal analysis was

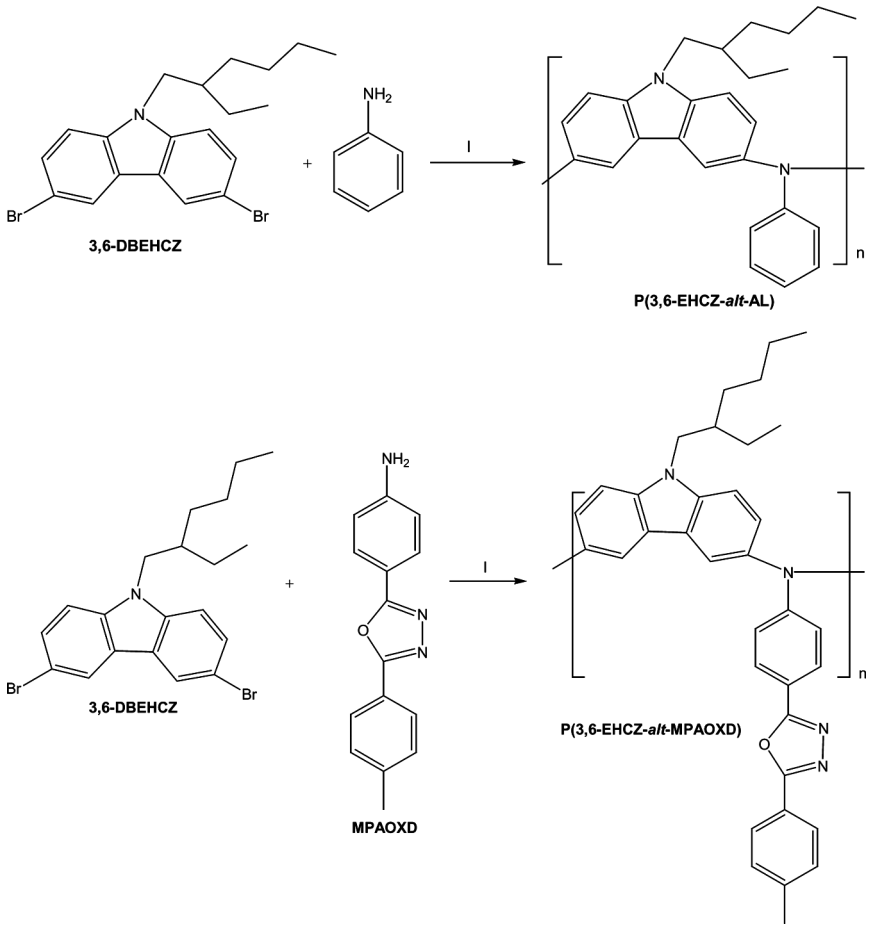
performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating of 20°C/min for thermogravimetric analyzer (TGA) and at a heating of 10°C/min for differential scanning calorimetry (DSC). UV-Visible absorption spectra were taken by Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). The ionization potential (IP) was measured by a photoelectron spectroscopy (Riken Keiki AC-2).

RESULTS AND DISCUSSION

Conjugated copolymers such as P(3,6-EHCZ-*alt*-AL) and P(3,6-EHCZ-*alt*-MPAOXD) were prepared by Pd-catalyzed polycondensation, as depicted in Scheme 2. P(3,6-EHCZ-*alt*-AL) was designed to have a triarylamine and a carbazole groups (hole transporting ability with blue emission) in the main chain. In addition to these functional groups of P(3,6-EHCZ-*alt*-AL), the electron transporting 1,3,4-oxadiazole moiety was incorporated into the side chain of P(3,6-EHCZ-*alt*-MPAOXD).

The molecular weights and molecular weight distributions were measured by using GPC, and summarized in Table 1. It appeared that the molecular weight of P(3,6-EHCZ-*alt*-MPAOXD) was lower than that of P(3,6-EHCZ-*alt*-AL), which was likely to be explained by the poor solubility of P(3,6-EHCZ-*alt*-MPAOXD). Though the solubility of P(3, 6-EHCZ-*alt*-MPAOXD) is not favorable, it is still readily soluble in chloroform, DMF and THF. Figure 1 represents thermal stability of the polymers measured by TGA. Based on the decomposition temperature (T_d) at 5 wt% loss of the initial weight, two polymers exhibited relatively high T_d around 440°C. The weight loss at 800°C was measured to be around 37% and 46% for P(3,6-EHCZ-*alt*-AL) and P(3,6-EHCZ-*alt*-MPAOXD), respectively. More weight loss of P(3,6-EHCZ-*alt*-MPAOXD) could be possibly assigned to the decomposition of 1,3,4-oxadiazole pendant groups. While DSC curves of two polymers showed neither glass transition temperature nor melting peak.

UV-Vis absorption and PL emission spectra of P(3,6-EHCZ-*alt*-AL) and P(3,6-EHCZ-*alt*-MPAOXD) are presented in Figures 2 and 3, respectively. In Figure 2, maximum absorption of P(3,6-EHCZ-*alt*-AL) was observed at 309 nm, however, P(3,6-EHCZ-*alt*-MPAOXD) exhibited $\lambda_{max,UV}$ at 359 nm, attributed to the π-π^* electronic transitions of *N*-alkylcarbazole and 1,3,4-oxadiazole moieties [16]. PL emission spectra were obtained after excitation at their $\lambda_{max,UV}$ of two copolymers. As can be seen in Figure 3, PL emission of P(3,6-EHCZ-*alt*-AL) was in the blue range at 452 nm, while P(3,6-EHCZ-*alt*-MPAOXD) exhibited $\lambda_{max,PL}$ at 506 nm. These optical properties such as red-shifted UV-Vis absorption



SCHEME 2 Polymerizations via palladium catalyzed polycondensation; Reaction condition (I): Toluene, NaO-*t*-Bu, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, 100°C.

TABLE 1 Physical Properties of Polymers

Copolymers	M_n (g/mol)	M_w/M_n	T_d (°C)[a]
P(3,6-EHCZ-*alt*-AL)	7,300	1.3	442
P(3,6-EHCZ-*alt*-MPAOXD)	3,400	1.2	443

[a]Temperature measured at 5% weight loss based on initial weight.

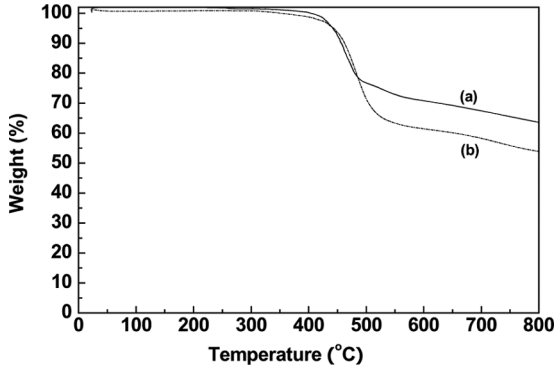


FIGURE 1 TGA curves of the polymers; (a) P(3,6-EHCZ-alt-AL) and (b) P(3,6-EHCZ-*alt*-MPAOXD).

and PL emission of P(3,6-EHCZ-*alt*-MPAOXD) might be originated from the extended conjugation by the presence of 1,3,4-oxadiazole group in the polymer side chain.

The electrochemical properties of the copolymers are summarized in Table 2. The copolymers showed HOMO energy levels of −5.19 eV for P(3,6-EHCZ-*alt*-AL) and −5.16 eV for P(3,6-EHCZ-*alt*-MPAOXD), respectively. LUMO energy levels of the copolymers were also calculated from HOMO energy and band gap energy levels to be −2.28 eV for P(3,6-EHCZ-*alt*-AL) and −2.30 eV for P(3,6-EHCZ-*alt*-MPAOXD). Based on the above information, schematic fabrication of a device is shown in Figure 4. These results revealed that such HOMO energy

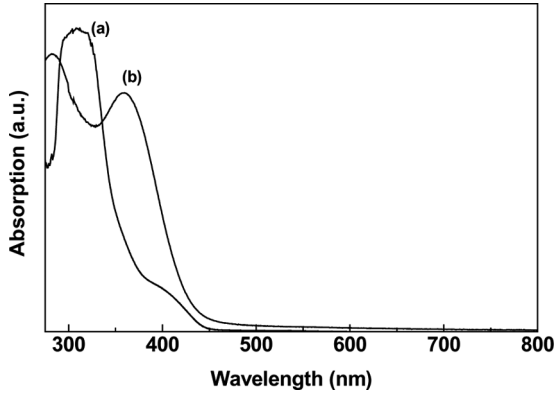


FIGURE 2 UV-Vis absorption spectra of the polymers; (a) P(3,6-EHCZ-alt-AL) and (b) P(3,6-EHCZ-*alt*-MPAOXD).

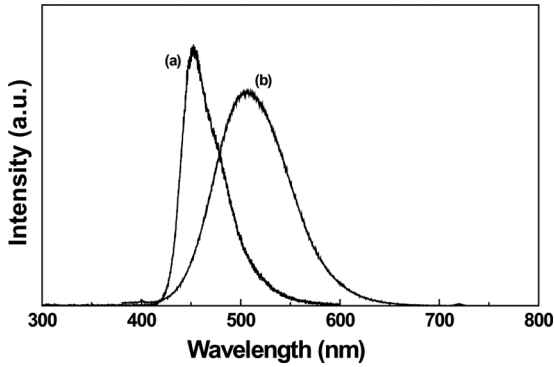


FIGURE 3 Photoluminescence spectra of the polymers; (a) P(3,6-EHCZ-alt-AL) and (b) P(3,6-EHCZ-*alt*-MPAOXD).

TABLE 2 Electronic Properties of Polymers

Copolymers	$\lambda_{max,UV}$ (nm)	$\lambda_{max,\ PL}$ (nm)	Band gap (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]
P(3,6-EHCZ-*alt*-AL)	309	452	2.91	–5.19	–2.28
P(3,6-EHCZ-*alt*-MPAOXD)	359	506	2.86	–5.16	–2.30

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

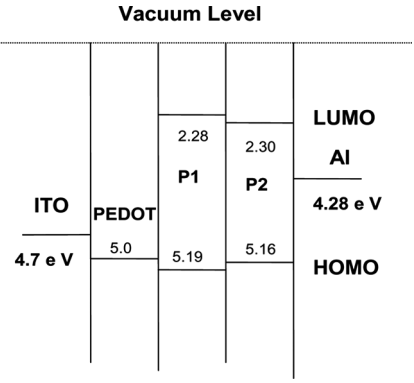


FIGURE 4 Schematic view of energy levels of the polymers; P1: P(3,6-EHCZ-alt-AL) and P2: P(3,6-EHCZ-*alt*-MPAOXD).

levels of the copolymers might provide a close match to the function of hole-injecting PEDOT layer, especially when they were used as hole-transporting materials in the PLEDs. It was also found that the incorporation of the 1,3,4-oxadiazole group in the polymer side chain reduced the electronic band gap energy level of the copolymer, which might be explained by more conjugation formed in the molecular chain by introducing 1,3,4-oxadiazole pendant groups in the side chain.

CONCLUSIONS

Conjugated copolymer, P(3,6-EHCZ-*alt*-MPAOXD), consisting of a triarylamine and a carbazole groups (hole transporting ability with blue emission) in the main chain as well as the electron transporting 1,3,4-oxadiazole pendant moiety was synthesized through palladium-catalyzed polycondensation. For comparison, P(3,6-EHCZ-*alt*-AL) with a triarylamine and a carbazole groups in the main chain was also synthesized and characterized. The optical and electrochemical results revealed that the incorporation of the 1,3,4-oxadiazole group in the polymer side chain reduced the electronic band gap energy level of the copolymer. It was also found that the copolymers could be used as hole-transporting materials in the PLEDs, due to closely matched HOMO energy levels between the copolymers and hole-injecting PEDOT layer.

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