



Journal of Nanoscience and Nanotechnology Vol. 17, 5530–5538, 2017 www.aspbs.com/jnn

Synthesis and Characterization of Quinoxaline Derivative as Organic Semiconductors for Organic Thin-Film Transistors

Hyekyoung Kim^{1,†}, M. Rajeshkumar Reddy^{2,†}, Seong-Soo Hong³, Choongik Kim^{1,*}, and SungYong Seo^{2,*}

¹ Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 04107, Korea ² Department of Chemistry, Pukyong National University, Busan 48513, Korea ³ Department of Chemical Engineering, Pukyong National University, Busan, 48513, Korea

Three new quinoxaline-based derivatives, end-functionalized with 2,3,5,8-tetraphenyl (3), 2,3diphenyl-5,8-di(thiophen-2-yl) (4), and 2,3-diphenyl-5,8-bis(5-phenylthiophen-2-yl) (5) were synthesized, characterized, and incorporated as organic semiconductors in top-contact/bottom-gate organic thin-film transistors (OTFTs). Thermal, optical, and electrochemical properties of the newly developed compounds were fully investigated. For the fabrication of thin films of all three compounds, solution-shearing (SS) and vacuum deposition method were employed. Thin films of compound **5** showed *p*-channel characteristics with hole mobilities as high as 2.6×10^{-5} cm²/Vs and current on/off ratio of 1.8×10^{5} via solution process and 1.9×10^{-4} cm²/Vs and current on/off ratio of 3.5×10^{6} via vacuum deposition.¹¹

Keywords: Organic Thin-Film Transistors, Quinoxaline, Self-Assembled Monolayer.

1. INTRODUCTION

Small molecular organic semiconductors have been widely studied as active layers of organic thin-film transistors (OTFTs) to realize inexpensive, large-area, flexible, and solution-processable organic electronic devices such as flexible displays, sensors, and electronic papers.^{1,2} Among organic semiconductors which have been studied widely over the last few decades, representative examples include pentacene,³ oligothiophene,⁴ and thiazole⁵ derivatives. To realize various commercial products based on organic electronic devices, development of new organic semiconductors with high electrical performance is required. Until today, several quinoxaline based semiconductors have been designed and synthesized, and demonstrated their electrical device performance.⁶ Quinoxaline moiety has been attracted as an acceptor due to its high electron affinity which generated from the two symmetric nitrogen atoms in its pyrazine ring.⁷ For example, Dutta et al. reported three new solution-processable quinoxaline molecules and

5530 J. Nanosci. Nanotechnol. 2017, Vol. 17, No. 8

reported *p*-channel device characteristics with hole mobilities 9.7×10^{-4} cm²/Vs.⁸ More recently, Shi et al. synthesized two new quinoxaline derivatives and showed their applications in memory devices.⁹ Previous studies clearly showed the strong electron-withdrawing capability of quinoxaline moiety and its potential for optoelectronic applications. Therefore, it is desirable to investigate new organic semiconductors based on quinoxalines with high electrical performances.

To this end, we have synthesized three novel quinoxaline derivatives and these molecules were tested as potential organic semiconductors in OTFTs (Fig. 1). All new compounds were characterized for their thermal, optical, and electrochemical properties via thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-vis spectroscopy, and cyclic voltammetry (CV). Theoretical molecular calculation for the new compounds was performed via density functional theory (DFT) calculations to obtain molecular structure and HOMO/LUMO energy level of the compounds. Furthermore, fabrication of thin-films with functional materials and device application has become important in recent nanotechnology.¹⁰ In this

^{*}Authors to whom correspondence should be addressed. [†]These two authors contributed equally to this work.



Figure 1. Chemical structure of compounds 3, 4, and 5.

study, new compounds were employed as organic semiconductor films via solution process (solution-shearing) and vacuum-deposition method in a top-contact/bottom-gate OTFTs. Finally, the resulting devices were characterized with carrier mobility as high as 1.9×10^{-4} cm²/Vs and current on/off ratio of 3.5×10^{6} for thin films of compound **5**.

2. EXPERIMENT DETAILS

2.1. General Methods

Air and/or moisture sensitive reactions were carried out under an N₂ atmosphere in oven-dried glassware and with anhydrous solvents. All chemicals were purchased from commercial sources unless otherwise noted and used without further purification. Solvents were freshly distilled or dried by passing through an alumina column. Thin layer chromatography was carried out on glass plates coated with silica gel SiO₂ 60 F254 from Merck; visualization with a UV lamp (254 nm) or by staining with a *p*-anisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO₂ 60 (0.040–0.063 µm, 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Proton $(^1\mathrm{H})$ and carbon (¹³C) nuclear magnetic resonance (NMR) spectroscopy was performed on a JEOL ECP-400 spectrometer at 400 MHz (¹H) and 100 MHz (¹³C) at 294 K. Chemical shifts are reported in ppm relative to the residual non-deuterated solvent (CDCl₃: $\delta H = 7.26$ ppm, $\delta C =$ 77.16 ppm). All ¹³C NMR spectra are proton decoupled. The resonance multiplicity is described as s (singlet), d(doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), *m* (multiplet), and *br* (broad). High-resolution mass spectrometry (HRMS) was measured on a JEOL JMS-700 spectrometer. Mass peaks are reported in m/z units.

2.2. Synthesis

2.2.1. Synthesis of 5,8-dibromo-2, 3-diphenylquinoxaline (1)

5,8-Dibromo-2,3-diphenylquinoxaline was synthesized by modifying previous literature. 4,7-Dibromobenzo[c] [1,2,5]thiadiazole (1.0 g, 3.4 mmol), CoCl₂·6H₂O (10 mg, 0.07 mmol), sodium borohydride (686.2 mg, 18.13 mmol) was dissolved in ethanol (10 mL) and tetrahydrofuran

J. Nanosci. Nanotechnol. 17, 5530-5538, 2017

(30 mL), and the reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was washed with water and diethyl ether. The organic layer was collected and concentrated in vacuo to get crude product. To the crude product, benzil (630 mg, 3 mmol) was added in toluene (10 mL) and acetic acid (10 mL) and the reaction mixture was heated up to 100 °C and stirred for another 12 h. After the reaction was completed, the mixture was washed with water, brine solution and dichloromethane. The organic layer was concentrated in vacuo. Finally, the crude product was recrystallized from ethanol to afford 5,8-dibromo-2,3-diphenylquinoxaline as white solid (846.4 mg, 56.6%).^{11,12} ¹H NMR (400 MHz, CDCl₃) δ 7.90 (*s*, 2H), 7.65–7.62 (*m*, 4H), 7.39–7.34 (*m*, 6H).

versity of New York at Binghamton

2.2.2. Synthesis of (5-phenylthiophen-2yl)boronic Scientific acid (2)

(5-Phenylthiophen-2-yl)boronic acid was synthesized according to the literature with slight modification. 2-Bromothiophene (1.0 g, 6.13 mmol), Pd(PPh₃)₄ (354 mg, 0.30 mmol), phenylboronic acid (853.3 mg, 6.99 mmol), and 2M Na₂CO₃ (10 mL, 20 mmol) was dissolved in dimethoxy ethane (20 mL) at room temperature, stirred for 10 min, and then refluxed for 2 h under N₂ atmosphere. After cooling down the reaction mixture to room temperature, the mixture was washed with water and ethyl acetate. The organic layer was collected and concentrated in vacuo. The crude product was purified by column chromatography using hexane as eluent to give 2-phenylthiophene as colorless solid (948.3 mg, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.61–7.57 (*m*, 2H), 7.38–7.34 (*m*, 2H), 7.30–7.25 (*m*, 2H), 7.06 (*q*, 3.3 Hz, 1H).

2-Phenylthiophene (1.0 g, 6.24 mmol) was dissolved in THF (20 mL) and this reaction mixture was cooled to -78 °C under N₂ atmosphere. Then n-BuLi (1.6M, 3.9 mL, 6.42 mmol) was added over 15 min to the solution and stirred for 1 h at the same temperature. Triisopropyl borate (1.44 mL, 6.24 mmol) was added dropwise at -78 °C to the cooled solution for the duration of 10 min, and the resulting mixture was allowed to warm up to room temperature for overnight. The reaction mixture was acidified with 10% HCl, and stirred for 1 h. The aqueous mixture was extracted with diethyl ether for three times (50 mL) and the organic layer was washed with water. The resulting solution was concentrated under reduced pressure. The crude product was recrystallized from ethanol:water (1:20) to afford compound **2** as light blue solid (810 mg, 63.6%).¹³ ¹H NMR (400 MHz, DMSO- d_6) δ 8.25 (*s*, 2H), 7.68–7.64 (*m*, 3H), 7.52 (*d*, 3.7 Hz, 1H), 7.41 (*t*, 8.1 Hz, 2H), 7.32 (*t*, 7.3 Hz, 1H).

2.2.3. Synthesis of 2,3,5,8-tetraphenylquinoxaline (3)

Compound 1 (100 mg, 0.22 mmol), phenyl boronic acid (66 mg, 0.54 mmol), Pd(PPh₃)₄ (26.2 mg, 0.022 mmol), 2M Na₂CO₃ (2 mL, 4 mmol), and aliquot (100 μ L) was dissolved in toluene (10 mL) and refluxed for 12 h under N₂ atmosphere under vigorous stirring. After cooling to room temperature, the mixture was extracted with dichloromethane and dried over anhydrous MgSO4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane: ethyl acetate (10:1) as eluent to give compound **3** as pale yellow solid (55 mg, 55.7%).¹⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 2H), 7.86–7.84 (m, 4H), 7.58–7.56 (m, 4H), 7.54–7.50 (m, 4H), 7.44–7.40 (*m*, 2H), 7.30–7.25 (*m*, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 139.4, 139.0, 138.5, 138.2, 130.9, 130.0, 129.8, 128.7, 128.1, 127.9, 127.5. HRMS-EI(m/z): [M+Na⁺] calcd. for C₃₂H₂₂N₂Na⁺, 457.1675; found, 457.1680.

2.2.4. Synthesis of

2,3-diphenyl-5,8-di(thiophen-2-yl)quinoxaline (4)

Compound 1 (100 mg, 0.22 mmol), 2-thiophene boronic acid (70 mg, 0.54 mmol), Pd(PPh₃)₄ (26.2 mg, 0.022 mmol), 2M Na₂CO₃ (2 mL, 4 mmol), and aliquot (100 μ L) was dissolved in toluene (10 mL) and refluxed for 12 h under N₂ atmosphere under vigorous stirring. After cooling to room temperature, the mixture was extracted with dichloromethane and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane:ethyl acetate (10:1) as eluent to give compound 4 as yellowish orange solid (42.5 mg, 42.7%).¹¹ ¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 2H), 7.87 (dd, 1.1 Hz, 3.7 Hz, 2H), 7.74-7.71 (m, 4H), 7.51 (dd, 0.7 Hz, 5.1 Hz, 2H), 7.38–7.36 (m, 6H), 7.17 (q, 3.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 138.6, 138.6, 137.1, 131.2, 130.4, 128.9, 128.8, 128.1, 127.0, 126.5, 126.3. HRMS-EI(m/z): [M+Na⁺] calcd. for $C_{28}H_{18}N_2S_2Na^+$, 469.0804; found, 469.0808.

2.2.5. Synthesis of 2,3-diphenyl-5,8-bis(5phenylthiophen-2-yl)quinoxaline (5)

Compound 1 (100 mg, 0.22 mmol), compound 2 (111.3 mg, 0.54 mmol), Pd(PPh₃)₄ (26.2 mg, 0.022 mmol), 2M Na₂CO₃ (2 mL, 4 mmol), and aliquot (100 μ L) was dissolved in toluene (10 mL) and refluxed for 12 h

under N₂ atmosphere under vigorous stirring. After cooling to room temperature, the mixture was extracted with dichloromethane and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using hexane:ethyl acetate (10:1) as eluent to give compound **5** as dark red solid (120.8 mg, 88.8%).¹⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.15 (*s*, 2H), 7.88 (*d*, 4.0 Hz, 2H), 7.78 (*dd*, 2.6 Hz, 7.7 Hz, 4H), 7.70 (*d*, 7.3 Hz, 4H), 7.40–7.38 (*m*, 12H), 7.29 (*t*, 7.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 152.4,147.0, 138.6, 138.1, 137.1, 134.7, 131.0, 130.5, 129.0, 128.9, 128.2, 127.5, 127.4, 126.5, 125.7, 122.9. HRMS-EI(m/z): [M+Na⁺] calcd. for C₄₀H₂₆N₂S2Na⁺, 621.1430; found, 621.1432.

2.3. Theoretical Calculation

Density functional theory (DFT) calculations on the present semiconductor were performed using the B3LYP (Becke's 3 parameters employing the Lee-Yang-Parr) functional and the 6-31G(d) basis set as implemented in Gaussian 03W program.

2.4. Device Fabrication

Top-contact/bottom-gate organic thin-film transistors (OTFTs) were fabricated on a highly n-doped (100) silicon wafer with a thermally grown 300 nm silicon dioxide as dielectric layer. The Si/SiO₂ substrates were cleaned via sonication in acetone for 10 min, dried with N_2 , and cleaned by air plasma for 5 min (Harrick Plasma, 18W). The general recipes were employed for the treatment of gate dielectric layers including PS-brush layer,¹⁶ PS (polystyrene) polymer layer¹⁷ and selfassembled monolayers (octadecyltrimethoxysilane; OTMS and hexamethyldisilane; HMDS)¹⁸ on the Si/SiO₂ substrates. Hydroxyl end-functionalized polystyrene ($M_n = 10$ kg/mol, Polymer Source) and polystyrene ($M_n = 20$ kg/mol, Sigma Aldrich) was employed for the formation of PS-brush layer and PS layer, respectively. Two methods including solution-shearing (SS)¹⁹ and vacuum deposition were employed for the formation of semiconducting layers. For the optimization of solution-shearing process, various solvents including toluene, chlorobenzene, and 1,2,4-trichlorobenzene were employed. The solution-sheared substrates were placed in a vacuum oven at 80 °C overnight to remove the residual solvent. Vacuum deposition was performed on various substrates (bare SiO₂, PS, HMDS and OTMS) at two different substrate temperatures (20 °C and 50 °C). The deposition rate was 0.2–0.3 Å/s under 5×10^{-6} torr. Film thicknesses were characterized by profilometer (DEKTAK-XT, Brucker) as 55-60 nm (for solution-sheared films) and 40-60 nm (for vacuum-deposited films). Gold source and drain electrodes (40 nm) were thermally evaporated through a shadow mask with various channel lengths and widths (L; 50–100 μm, W; 1000–2000 μm).

J. Nanosci. Nanotechnol. 17, 5530-5538, 2017

Kim et al. Synthesis and Characterization of Quinoxaline Derivative as Organic Semiconductors for Organic Thin-Film Transistors

2.5. Characterization

Thermogravimetric analyses (TGA, TA Instrument Q50-1555) were performed on each sample in a platinum crucible heating from 40 to 700 °C (heating rate of 20 °C min⁻¹ under N₂ atmosphere). Differential scanning calorimetry (DSC) analyses (TA instrument Q20-2487) were performed from 40 to 350 °C (heating rate of 20 °C min⁻¹). UV-visible spectra of the compound in dilute chloroform (conc. 1×10^{-5} M) were obtained using JASCO V-530 spectrometer with quartz cuvette over the spectral range of 200-800 nm. Cyclic voltammetry (CV) experiments were performed with a conventional three-electrode configuration (glassy carbon working electrode, platinumwire counter electrode, and Ag/AgCl reference electrode) with supporting electrolyte of tetrabutylammonium tetrafluoroborate in dry dichlorobenzene on AUT302N Electrochemical Analyzer (Autolab). All electrochemical potentials were referenced to an Fc⁺/Fc internal standard. The current-voltage characteristics of fabricated OTFT devices were measured at room temperature under vacuum and in ambient using a Keithley 4200 SCS. Carrier mobilities (μ) were calculated in the saturation regime by the standard relationship, $\mu_{sat} = (2I_{DS}L)/[WC_i(V_G - V_T)^2]$, where I_{DS} is the source-drain current, L is the channel length, W is the channel width, C_i is the areal capacitance of the gate dielectric ($C_i = 11.4 \text{ nF cm}^{-2}$), V_G is the gate voltage, and V_T is the threshold voltage. The surface morphology and film microstructure of the semiconducting films were investigated by atomic force microscope (AFM, NX10, Park Systems) and X-ray diffraction (XRD, Miniflex, Rigaku), respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis

Both 5,8-dibromo-2,3-diphenylquinoxaline $(1)^{8,9}$ and (5-phenylthiophen-2yl)boronic acid $(2)^3$ were prepared in two steps as shown in Scheme 1 and Scheme 2. 2,3,5,8-Tetraphenylquinoxaline (3), 2,3-diphenyl-5,8-di(thiophen-2-yl)quinoxaline (4), and 2,3-diphenyl-5,

Table I. Physical and electrochemical properties of the compounds 3,4, and 5.

_	DSC T _m (°C)	TGA (°; 5%)	UV-Vis $\lambda_{\max} \ (nm)^a$	$E_{ m red}^{ m peak}$ $({ m V})^b$	LUMO (eV) ^b	E_{ox}^{peak} (V) ^b	HOMO (eV) ^b	$E_{\rm gap}$ (eV) ^b
3 4	266 221	313 174	264, 356 312, 384, 434	-0.95 -0.86	-3.19 -3.28	1.29 1.15	-5.43 -5.29	2.24 2.01
5	265	131	344, 476	-0.83	-3.31	1.14	-5.28	1.97

Notes: ^{*a*} measured by UV-vis spectroscopy. ^{*b*} measured by cyclic voltammetry in $o-C_6H_4Cl_2$ at 25 °C (using ferrocene/ferrocenium as intermal standard at +0.66 V for all compounds).

8-bis(5-phenylthiophen-2-yl)quinoxaline (5) were synthesized in one step following Scheme 3.^{11,12} The compounds **3–5** were synthesized using Suzuki coupling of 5,8-dibromo-2,3-diphenylquinoxaline (1) with phenylboronic acid, 2-thiopheneboronic acid, and (5-phenylthiophen-2yl)boronic acid (2), respectively.

3.2. Theoretical Calculation

Theoretical calculation was performed to determine the molecular structure and HOMO/LUMO energy distribution of quinoxaline derivatives by Gaussian 03W program (B3LYP with 6-31G(d) basis sets). For all compounds, HOMOs of all compounds were rather distributed on the main backbone moieties, while LUMOs were localized on the quinoxaline moiety. The theoretical HOMO/LUMO energy levels were calculated as -5.69/-2.21 eV for compound 3, -5.20/-1.97 eV for compound 4, and -4.96/-2.30 eV for compound 5, respectively (Fig. 2). Consequently, theoretically calculated HOMO-LUMO energy bandgap were 3.48 eV for compound 3, 3.23 eV for compound 4, and 2.66 eV for compound 5, respectively. Lower HOMO-LUMO bandgaps in the following order of compound 3, 4 and 5 indicate the increasing electron-donating character of the substituents.

3.3. Thermal, Optical, and Electrochemical Properties

Thermal properties of new compounds were characterized by thermogravimetric analysis (TGA) and differential



Scheme 1. Synthetic scheme of compound 1.



Scheme 2. Synthetic scheme of compound 2.

J. Nanosci. Nanotechnol. 17, 5530-5538, 2017



Scheme 3. Synthetic scheme of compounds 3, 4 and 5.



Figure 2. Molecular orbital surfaces of HOMO and LUMO by DFT calculation of compounds 3,4, and 5.

J. Nanosci. Nanotechnol. 17, 5530–5538, 2017



Figure 3. (a) Thermogravimetric analysis and (b) differential scanning calorimetry graphs of the new compounds 3–5.

scanning calorimetry (DSC) (Fig. 3). For new compounds **3–5**, weight loss (~5%) temperatures were observed above 313 °C, 174 °C, and 131 °C, respectively. Compound **5** showed much larger thermal degradation compared to compounds **3** and **4**. Furthermore, sharp endotherms for the quinoxaline derivatives exhibited above 221 °C (Table I). It indicates the possible temperature for thermal treatment of each compounds in this study.

The optical absorption spectra of the compounds 3 (λ_{max} = 264, 356 nm), 4 (λ_{max} = 312, 384, 434 nm) and 5 (λ_{max} = 344, 476 nm) in dilute chloroform solution are shown in Figure 4. It exhibited slightly red-shifts in the following order of compound 3, 4 and 5. Increasing the extent of conjugation leads to red-shifts of the absorption spectra and decreases HOMO-LUMO bandgap.²⁰ The HOMO-LUMO energy gaps calculated from the onset of the experimental optical absorption were 3.06 (3), 2.47 (4), and 2.23 eV (5), respectively. Compound 5 with largest conjugation among all compounds in this study showed smallest energy gap compared to other compounds.

Cyclic voltammetry (CV) measurements of the new compounds were performed in $o-C_6H_4Cl_2$ at room

J. Nanosci. Nanotechnol. 17, 5530–5538, 2017



Figure 4. Optical UV-vis spectra of the new compounds 3–5 in chloroform solution.

temperature. The compounds **3**, **4**, and **5** exhibited oxidation peaks at +1.29 V, +1.15 V, and +1.14 V and reduction peaks at -0.95 V, -0.86 V, and -0.83 V, respectively, using ferrocene/ferrocenium as internal standard at +0.66 V. Hence, HOMO energy level calculated by the conversion of oxidation potential using ferrocene as the standard was -5.43 eV, -5.29 eV, and -5.28 eV, respectively. In the same way, LUMO energy was obtained as -3.19 eV, -3.28 eV, and -3.31 eV, respectively (Fig. 5). The HOMO-LUMO energy gaps of the compounds **3**, **4**, and **5** were calculated as 2.24 eV, 2.01 eV, and 1.97 eV, respectively, showing same trend as the values determined optically (Table I).



Figure 5. Cyclic voltammograms of the new compounds 3–5 in o-C₆H₄Cl₂.

Material	Method	Substrate	$\mu(\mu_{\rm avg})~({\rm cm}^2/{\rm Vs})$	$I_{\rm on}/I_{\rm off}$	$V_T(V)$				
3			Not active						
4		Not active							
5	SS	PS-brush	$2.6 \times 10^{-5} (2.0 \times 10^{-5})$	1.8×10^{5}	-16				
	Vacuum deposition $(T_D = 50 \text{ °C})$	Bare	$3.2 \times 10^{-5} (3.2 \times 10^{-5})$	2.4×10^{5}	-49				
		PS	$9.6 \times 10^{-5} (5.4 \times 10^{-5})$	1.1×10^{5}	-29				
		OTMS	$6.7 \times 10^{-5} (5.3 \times 10^{-5})$	8.3×10^{5}	-52				
		HMDS	$3.9 \times 10^{-5} (1.7 \times 10^{-5})$	8.3×10^{5}	-51				
	Vacuum deposition $(T_D = 50 \text{ °C})$	Bare	$4.6 \times 10^{-5} (4.5 \times 10^{-5})$	1.3×10^{5}	-34				
		PS	$1.9 \times 10^{-4} (1.7 \times 10^{-4})$	3.5×10^{6}	-31				
		OTMS	$5.7 \times 10^{-5} (4.2 \times 10^{-5})$	8.6×10^{5}	-22				
		HMDS	$2.8 \times 10^{-5} \ (2.7 \times 10^{-5})$	1.6×10^{5}	-27				

Table II. TFT device performance parameters based on thin films of compounds **3**, **4**, and **5** employed in this study (μ : maximum carrier mobility, μ_{ave} : average carrier mobility, I_{on}/I_{off} : current on/off ratio, V_T : threshold voltage).^{*a*}

Notes: a Devices were measured under vacuum. The average carrier mobilities are averaged values of three devices made under identical conditions.

3.4. Thin-Film Transistor Characterization

To test the new quinoxaline derivatives as organic semiconductors, top-contact/bottom-gate OTFT devices were fabricated via two different methods: solution-shearing and vacuum deposition. The OTFT data are summarized in Table II and representative transfer and output plots are shown in Figure 6. Overall, only thin films of compound 5 exhibited *p*-channel activity with carrier mobilities of 10⁻⁴-10⁻⁵ cm²/Vs and a current on/off ratio of 10⁵-10⁶. Vacuum-deposited thin films showed slightly higher device performance than those formed via solutionshearing. Among vacuum-deposited films, films on PS or OTMS substrates showed better device performance than others, exhibiting highest carrier mobility of $1.9 \times$ 10^{-4} cm²/Vs and a current on/off ratio of 3.5×10^{6} on PScoated substrate at $T_D = 50$ °C. Furthermore, all devices based on thin films of compound 5 were measured in ambient and showed slightly lower device performance (<50%) than those measured under vacuum.

3.5. Thin-Film Microstructure and Morphology

Thin-film microstructure and morphology of solutionsheared and vacuum-deposited films were characterized by AFM and wide-angle θ -2 θ XRD to evaluate device performance. Surface morphologies based on compound 5 were characterized by AFM, as shown in Figure 7. As shown, different film-forming methodologies afforded different film morphologies, Solution-sheared organic semiconductor thin films based on compound 5 exhibited skein-like morphology with a surface roughness of ~ 40.9 nm (Fig. 7(a)), while vacuum-deposited films at deposition temperatures $(T_D s)$ of 20 and 50 °C showed small grains with a surface roughness of ~ 21.9 nm and 54.5 nm, respectively (Figs. 7(b and c)). Higher deposition temperature affored larger grain sizes for thin films of 5 on PS-coated substrates. Furthermore, conventional θ -2 θ XRD scans of thin films were characterized to analyze microstructural order in semiconductor films. All of the films did not exhibit any significant Bragg reflections, indicating poor film texture (not shown).



Figure 6. Representative (a) transfer and (b) output characteristics of the OTFT device based on thin films of compound 5.

J. Nanosci. Nanotechnol. 17, 5530-5538, 2017

Kim et al. Synthesis and Characterization of Quinoxaline Derivative as Organic Semiconductors for Organic Thin-Film Transistors



Figure 7. AFM topographic image of thin films of compound 5 via solution-shearing (a) and vacuum-deposition on PS substrates (b) at $T_D = 20$ °C; (c) at $T_D = 50$ °C), respectively. (Inset: $\theta - 2\theta$ XRD scans of the corresponding thin films). Scale bar denotes 1 μ m.

4. CONCLUSION

In this study, newly developed quinoxaline derivatives were synthesized and characterized for organic thin-film transistors. Devices were fabricated via solution process and vacuum deposition process and exhibited *p*-channel device characteristics with carrier mobility as high as $1.9 \times$ 10^{-4} cm²/Vs. The magnitudes of the device performance were relatively low due to the poor film microstructure. We expect that our study would contribute to studies of new

J. Nanosci. Nanotechnol. 17, 5530–5538, 2017

quinoxaline-based organic semiconductors for the realization of applications in organic electronics.

Acknowledgments: This study was supported by a Research Grant of Pukyong National University (2016).

References and Notes

- 1. (a) H. Sirringhaus, Adv. Mater. 26, 1319 (2014); (b) S. Vegiraju, C.-M. Hsieh, D.-Y. Huang, Y.-C. Chen, P. Priyanka, J.-S. Ni, F. A. Esya, C. Kim, S. L. Yau, C.-P. Chen, C.-L. Liu, and M.-C. Chen, Dves Pigm. 133, 280 (2016); (c) J. Yang, D. Yan, and T. S. Jones, Chem. Rev. 115, 5570 (2015); (d) M. Ozdemir, D. Choi, G. Kwon, Y. Zorlu, B. Cosut, H. Kim, A. Facchetti, C. Kim, and H. Usta, ACS Appl. Mater. Inter. 8, 14077 (2016); (e) Y. B. Yuan, G. Giri, A. L. Ayzner, A. P. Zoombelt, S. C. B. Mannsfeld, J. H. Chen, D. Nordlund, M. F. Toney, J. S. Huang, and Z. Bao, Nat. Commun. 5, 3005 (2014); (f) M. Ozdemir, D. Choi, G. Kwon, Y. Zorlu, H. Kim, M.-G. Kim, S. Seo, U. Sen, M. Citir, C. Kim, and H. Usta, RSC Adv. 6, 212 (2016); (g) X. Guo, A. Facchettim, and T. J. Marks, Chem. Rev. 114, 8943 (2014); (h) J. Mei, Y. Diao, A. L. Appleton, L. Fang, and Z. Bao, J. Am. Chem. Soc. 135, 6724 (2013); (i) J.-M. Yun, D.-Y. Kim, and Y.-Y. Noh, Sci. Adv. Mater. 8, 450 (2016); (j) J.-M. Yun, D.-Y. Kim, and Y.-Y. Noh, Sci. Adv. Mater. 8, 450 (2016); (k) H.-C. Yu, G. Kwon, S. Vegiraju, C.-W. Chao, L.-H. Li, J.-S. Ni, P.-Y. Huang, S. L. Yau, Y.-C. Chao, C. Kim, and M.-C. Chen, Dyes Pigm. 126, 261 (2016)
- (a) X. Wang, B. Liu, Q. Lu, L. Meng, C. Li, W. Duan, and A. Tang, Sci. Adv. Mater. 7, 2436 (2015); (b) J. Youn, S. Vegiraju, J. D. Emery, B. J. Leever, S. Kewalramani, S. J. Lou, S. Zhang, K. Prabakaran, Y. Ezhumalai, C. Kim, P.-Y. Huang, C. Stern, W.-C. Chang, M. J.

Bedzyk, L. X. Chen, M.-C. Chen, A. Facchetti, and T. J. Marks, Adv. Electron. Mater. 1, 1500098 (2015): (c) W.-C. Chen, O.-X. Tong, and

- Electron. Mater. 1, 1500098 (2015); (c) W.-C. Chen, Q.-X. Tong, and C.-S. Lee, Sci. Adv. Mater. 7, 2193 (2015); (d) M. Kang, K. Chung, K.-J. Baeg, D. H. Kim, and C. Kim, Appl. Phys. Lett. 106, 043302 (2015); (e) S. K. Gupta, P. Jha, A. Singh, M. M. Chehimi, and D. K. Aswal, J. Mater. Chem. C 3, 8468 (2015); (f) Y. Zang, F. Zhang, D. Huang, X. Gao, C.-A. Di, and D. Zhu, Nat. Commun. 6, 6269 (2015); (g) X. Wang, B. Liu, Q. Lu, L. Meng, C. Li, W. Duan, and A. Tang, Sci. Adv. Mater. 7, 2436 (2015); (h) J. S. Kim, D. I. Kim, B. U. Hwang, Y. G. Seol, T. U. Kim, and N.-E. Lee, Sci. Adv. Mater. 7, 1469 (2015); (i) M. A. M. Sarjidan, N. Jubri, S. H. Basri, N. K. Zaaba, M. S. Zaini, S. N. Zaini, and W. H. A. Majid, Nanosci. Nanotechnol. Lett. 6, 1035 (2014).
- (a) Y. Diao, B. C.-K. Tee, G. Giri, J. Xu, D. H. Kim, H. A. Becerril, R. M. Stoltenberg, T. H. Lee, G. Xue, S. C. B. Mannsfeld, and Z. Bao, *Nat. Mater.* 12, 665 (2013); (b) J. S. Kim and C. K. Song, *Thin Solid Films* 589, 620 (2015); (c) V. Raghuwanshi, D. Bharti, and S. P. Tiwari, *Org. Electron.* 31, 177 (2016); (d) V. Raghuwanshi, D. Bharti, and S. P. Tiwari, *Org. Electron.* 31, 177 (2016); (e) D.-K. Kim, J.-D. Oh, J.-W. Kim, H.-Y. Lee, and J.-H. Choi, *J. Phys. Chem. C* 120, 13716 (2016).
- (a) M. C. Chen, S. Vegiraju, C. M. Huang, P. Y. Huang, K. Prabakara, S. L. Yau, W. C. Chen, W. T. Peng, I. Chao, C. Kim, and Y. T. Tao, *J. Mater. Chem. C* 2, 8892 (2014); (b) J. C. Ribierre, L. Zhao, S. Furukawa, T. Kikitsu, D. Inoue, A. Muranaka, K. Takaishi, T. Muto, S. Matsumoto, D. Hashizume, M. Uchiyama, P. Andre, C. Adachi, and T. Aoyama, *Chem. Commun.* 51, 5836 (2015).
- (a) Y. Lin, H. Fan, Y. Li, and X. Zhan, *Adv. Mater.* 24, 3087 (2012);
 (b) G. Reginato, A. Mordini, L. Zani, M. Calamante, and A. Dessi, *Eur. J. Org. Chem.* 2016, 233 (2016);
 (c) B. Fu, C.-Y. Wang, B. D. Rose, Y. Jiang, M. Chang, P.-H. Chu, Z. Yuan, C. F. Hernandez, B. Kippelen, J.-L. Bredas, D. M. Collard, and E. Reichmanis, *Chem. Mater.* 27, 2928 (2015).

Synthesis and Characterization of Quinoxaline Derivative as Organic Semiconductors for Organic Thin-Film Transistors Kim et al.

- (a) D. W. Chang, S.-J. Ko, J. Y. Kim, L. Dai, and J.-B. Baek, Synth. Met. 162, 1169 (2012); (b) R. Singh, G. Pagona, V. G. Gregoriou, N. Tagmatarchis, D. Toliopoulos, Y. Han, Z. Fei, A. Katsouras, A. Avgeropoulos, T. D. Anthopoulos, M. Heeney, P. E. Keivanidis, and C. L. Chochos, Polym. Chem. 6, 3098 (2015); (c) L. Bai, X. Yang, C. Y. Ang, K. T. Nguyen, T. Ding, P. Bose, Q. Gao, A. K. Mandal, X. W. Sun, H. V. Demir, and Y. Zhao, Nanoscale 7, 11531 (2015); (d) S. Yang, D. Liu, X. Xu, and Q. Miao, Chem. Commun. 51, 4257 (2015); (e) C. An, S. Zhou, and M. Baumgarten, Cryst. Growth Des. 15, 1934 (2015); (f) M. L. Keshtov, A. R. Khokhlov, S. A. Kuklin, F. C. Chen, A. Y. Nikolaev, E. N. Koukaras, and G. D. Sharma, Polym. Chem. 7, 4025 (2016).
- (a) M.-F. Falzon, M. M. Wienk, and R. A. J. Janssen, J. Phys. Chem. C 115, 3178 (2011); (b) C. Liu, Y. Si, X. Pan, and G. Yang, RSC Adv. 5, 72907 (2015).
- 8. G. K. Dutta and S. Patil, Org. Electron. 13, 1266 (2012).
- E. Shi, H. Zhuang, Z. Liu, X. Cheng, H. Hu, N. Li, D. Chen, Q. Xu, J. He, H. Li, J. Lu, and J. Zheng, *Dyes Pigm.* 122, 66 (2015).
- (a) K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K. C.-W. Wu, and J. P. Hill, *Chem. Lett.* 43, 36 (2014); (b) T.-B. Song, Q. Chen, H. Zhou, C. Jiang, H.-H. Wang, Y. Yang, Y. Liu, J. You, and Y. Yang, *J. Mater. Chem. A* 3, 9032 (2015); (c) M.-K. Tsang, G. Bai, and J. Hao, *Chem. Soc. Rev.* 44, 1585 (2015).

- J.-H. Kim, C. E. Song, H. U. Kim, I.-N. Kang, W. S. Shin, M.-J. Park, and D.-H. Hwang, *Polym. Sci. B Polym. Phys.* 51, 4136 (2013).
 S. Jo, J. Kim, J. Noh, D. Kim, G. Jang, N. Lee, E. Lee, and T. S.
- Lee, ACS Appl. Mater. Interfaces 6, 22884 (2014). 13. S. Kuiper, W. F. Jager, T. J. Dingemans, and S. J. Picken, Liquid
- Crystals 36, 389 (2009).
 14. T. Hu, L. Han, M. Xiao, X. Bao, T. Wang, M. Sun, and R. Yang, J. Mater. Chem. C 2, 8047 (2014).
- X. Zhang, R. Yamaquchi, K. Moriyama, M. Kadowaki, T. Kobayashi, T. Ishi-i, T. Thiemann, and S. Mataka, *J. Mater. Chem.* 16, 736 (2006).
- 16. S. H. Park, H. S. Lee, J. D. Kim, D. W. Breiby, E. Kim, Y. D. Park, D. Y. Ryu, D. R. Lee, and J. H. Cho, *J. Mater. Chem.* 21, 15580 (2011).
- 17. C. Kim, A. Facchetti, and T. J. Marks, Science 318, 76 (2007).
- (a) Y. Ito, A. Virkar, J. Locklin, S. Mannsfeld, M. Toney, and Z. Bao, *Proc. of SPIE* 7417, 741718 (2009); (b) M.-H. Yoon, C. Kim, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* 128, 12851 (2006).
- 19. G. Giri, E. Verploegen, S. C. B. Mannsfeld, S. A. Evrenk, D. H. Kim, S. Y. Lee, H. A. Becerril, A. A. Guzik, M. F. Toney, and Z. Bao, *Nature* 480, 504 (2011).
- (a) G. L. Eakins, J. S. Alford, B. J. Tiegs, B. E. Breyfogle, and C. J. Stearman, *J. Phys. Org. Chem.* 24, 1119 (2011); (b) E. Kim, M. Koh, J. Ryu, and S. B. Park, *J. Am. Chem. Soc.* 130, 12206 (2008).

Received: 26 July 2016. Accepted: 23 August 2016.

Delivered by Ingenta to: State University of New York at Binghamton IP: 146.185.200.35 On: Fri, 09 Jun 2017 02:36:33 Copyright: American Scientific Publishers