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Synthesis and Optical Properties of Heteroaromatic Ring Compounds Containing EDOT

Sun Woo Hwang, Eun Rang Park, Yeon Joon Chung, Young Ju Bae, and In Tae Kim*

*Department of Chemistry, Kwangwoon University, Seoul 139-701, Korea. *E-mail: itkim@kw.ac.kr*
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Thiophene-based conjugated polymers and oligomers have been widely used as active materials for the fabrication of optoelectronic devices such as field-effect transistors, light-emitting devices and photovoltaic cells.[1]

The optical and electronic properties of the active material depend on the energy levels of the HOMO and LUMO. In order to control the levels, extensive studies aiming at the modification of the oligothiophene backbone have been carried out.[2]

As an electronic material, 3,4-ethylenedioxythiophene (EDOT) is an important versatile building block for the molecular engineering of functional π-conjugated systems with electronic and optical properties specifically tailored for applications in light-emitting devices, chromophores for non-linear optics, low energy gap systems or more recently organic semi-conductors.

Various oligo-EDOTs have been synthesized and the analysis of their structure and electronic properties has shown that a judicious use of EDOT as building block allows a fine tunning of the electronic properties of π-conjugated systems.[3]

This increasing attention for EDOT-based systems has in turn generated a strong interest in the chemistry of the EDOT molecule itself and/or in the modification of its structure.

Introduction of electron-withdrawing groups to EDOT represents the most immediate way to tune the HOMO and LUMO energy levels of a conjugated system. As shown in previous work, introduction of acceptor groups such as nitro, carboxyl or cyano at the 3-position of the thiophene unit induces a large increase in the oxidation potential.[4,5] The cyclovoltammetry (CV) curve of EDOT shows oxidation at 1.3 eV and broad reduction waves, which is located between 0.30 eV and −0.60 eV.[6] In addition, the EDOT trimer was first synthesized by Reynolds and coworkers as a precursor for electropolymerization.[7] They demonstrated that the EDOT trimer had oxidation potential at 0.2 eV, while they did not mentioned reduction potential of EDOT trimer.

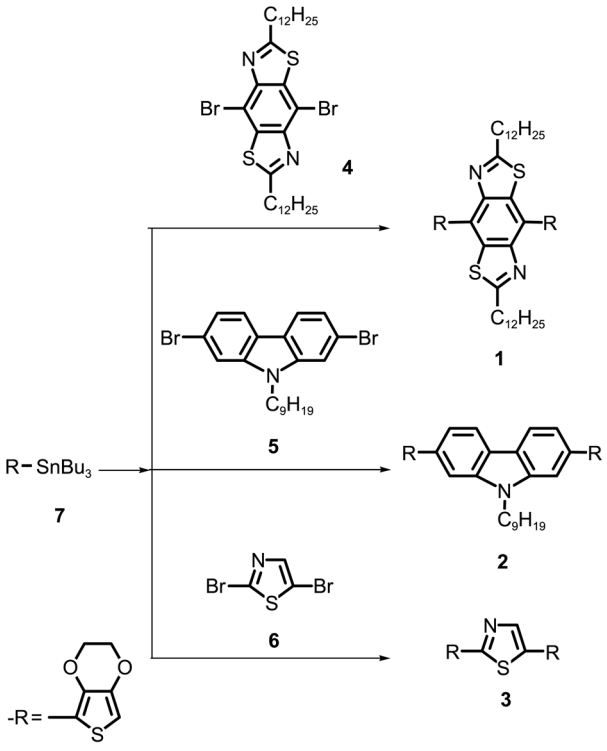
Here in, we introduced the various aromatic system in EDOT unit in order to control the HOMO and LUMO levels, and the new compounds are expectant of active materials for fabrication of the various optoelectronic devices.

Results and Discussion

Three new compounds are synthesized as shown in Scheme 1. Tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)stannane (**7**) was synthesized according to a method reported in the literature.[8] 4,8-dibromo-2,6-didodecyl-benzo[1,2-*d*;4,5-*d*′]bisthiazole (**4**) have been reported by our previous work.[9] 9-Nonyl-9*H*-carbazole was prepared as described in the literature.[6] 9-Nonyl-9*H*-carbazole was substituted on the nitrogen atom with a linear alkyl chain using literature procedure to provide compound (**5**) in a yield of 91%.[10] 2,5-Dibromothiazole (**6**) was purchased from Aldrich and used without purification. The compounds **1**, **2** and **3** were prepared by Stille reaction at 110 °C for 1 day in 80-90% yield range.

The reaction of Scheme 1 offers a convenient route to make aromatic heterocyclic oligomers with EDOT moiety.

The new compounds **1**, **2** and **3** were characterized using ^{1}H-NMR, ^{13}C-NMR, FT-IR and elemental analysis. We measured UV-vis absorption spectra of the compounds **1**, **2** and **3** in chloroform solution. The values of the absorption



Scheme 1. Synthesis of new heteroaromatic ring compounds containing EDOT by stille reaction.

Table 1. The λ_{max} value and optically measured bandgap of compounds **1**, **2** and **3**

Compound	UV λ_{max} (nm)[a]	PL λ_{max} (nm)[a]	ΔE^{op} (eV)
1	360	427	3.1
2	379	418	3.1
3	354	446	2.9

[a]in $CHCl_3$ solution.

Table 2. The peak value of oxidation and reduction potential and electrochemically measured bandgap of compounds (**1-3)**

Compound	E_{ox} (eV)	E_{re} (eV)	ΔE_{el} (eV)
1	1.6	−1.4	3.0
2	0.4	−2.6	3.0
3	0.5	−2.3	2.9

spectra of these compounds are summarized in Table 1. The UV-vis spectra of the compounds **1**, **2** and **3** showed λ_{max} (in $CHCl_3$ solution) at 360, 379 and 354 nm with band edge at 400 (3.1 eV), 401 (3.1 eV) and 421 nm (2.9 eV), respectively. Compounds **1**, **2** and **3** were also characterized by photoluminescence spectroscopy. The results on λ_{max} of the compounds **1**, **2** and **3** are 427, 418 and 446 nm, respectively.

Oxidation and reduction potential for the compound **1**, **2**, and **3** were obtained using cyclic voltammetry (CV). The electrochemical data of cyclovoltammograms of the compound **1**, **2**, and **3** are summarized in Table 2. Compound **1**, **2**, and **3** exhibit oxidation peak potentials of 1.6, 0.4, and 0.5 eV, respectively (*vs* $AgNO_3$). Reduction peak potentials of these compounds are exhibited at −1.4, −2.6, and −2.3 eV, respectively (*vs* $AgNO_3$).

The oxidation potential of these new compound **1**, and **3** shows higher than that of EDOT trimer. This is mainly attributed to electron-acceptor moieties in compound **1**, **2** and **3**. Also, the compound **2** with carbazole moiety shows slightly higher oxidation potential than that of EDOT. We fabricated organic light-emitting diodes (OLEDs) using compound **1** as emitting material. For the experiments, glass substrate (0.7 mm) coated with ITO (80 nm, 10-20 Ω/sq sheet resistance) was used to fabricate device. After routine cleaning procedures with ultraviolet-ozone treatment of the substrate, a blended solution of organic materials was spin coated (900 rpm) on top of ITO, precoated with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer. The blended solution consisted of compound **1**, 1,3-bis[(*p-tert*-butyl)phenyl-1,3,4-oxadiazoyl]benzene (OXD-7), and polyvinyl carbazole (PVK) at an appropriate concentration into mixed solvents of 1,2-dichloroethane and chloroform having different volatilities. OXD-7 and PVK were purchased from Sigma Aldrich Co. and compound **1** was synthesized as described herein. The organic salt, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), was also dissolved into the organic solution. Then, a cathode layer of

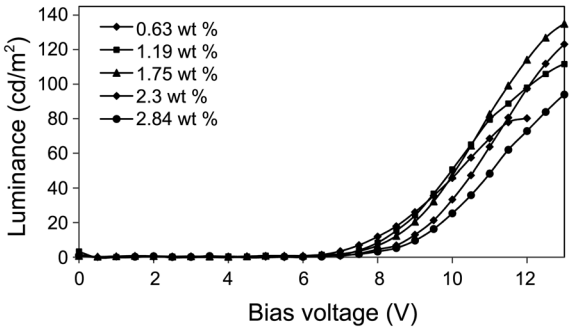


Figure 1. The current density-applied voltage curves for the device ITO/PEDOT/**1**/Al.

CsF (1 nm)/Al (100 nm) was formed on top of the organic layer via thermal deposition.

We observed the characteristics luminance-voltage (L-V) performance of the fabricated device as shown in Figure 1. Compound **1** was used blending with OXD-7 and PVK for fabricating device by spin coating. We blended 0.05 g of OXD-7 dissolved in 5 mL of CH_2Cl_2 and 0.15 g of PVK dissolved in 5 mL of $CHCl_3$. We fabricated devices with 10 mL solution of various compound **1** concentration for optimizing L-V performance. Figure 1 shows that optimized concentration of compound **1** with the fixed rate of OXD-7 to PVK is 0.63 wt %. A primary L-V curves demonstrate that the maximum luminescence of the device reaches 140 cd/m^2 at the driving voltage of 13.5 V.

In summary, we have accomplished the synthesis of new heteroaromatic ring compounds, of which are highly soluble in organic solvent such as CH_2Cl_2, $CHCl_3$, and THF and studied on their optical properties. Future work of the new compounds **1**, **2** and **3** will focus on the fine tuning of emitting properties through measurement of their electrophysical characteristics.

Experimental Section

Tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)stannane (7). A solution of EDOT in 10 mL of anhydrous THF was purged with N_2 during 5 min. Then, stirring the solution of EDOT, cooling down under −78 °C, adds 6.32 mL of *n*-BuLi (2.2 M in Hexane). Warming at −20 °C until the mixture turned to milk-white and stirred for 1 hr. 3.76 g of trimethyltin chloride was slowly added to the stirred mixture at −78 °C under a nitrogen atmosphere, then white precipitate was formed. After the reaction mixture was stirred for 1 hr at room temperature, then the solution turned into orange color. Filter the reaction mixture solved in an excess dichloromethane, and the filtrate was evaporated to give the orange oil crude. The crude was purified by column chromatography to give the transparent oil in 85% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59-6.56 (t, 1H), 4.20-4.14 (m, 4H), 1.64-1.51 (m, 8H), 1.40-1.28 (m, 8H), 1.25-1.05 (m, 8H), 0.90-0.87 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 152.3, 97.4, 95.6, 65.0, 28.8, 27.3, 13.8, 11.0 ppm Found: C, 50.14; H, 7.50; S, 7.42. Calc. for $C_{12}H_{32}O_2SSn$: C, 50.14;

H, 7.48; S, 7.44.

2,7-Dibromo-9-nonylcarbazole (5). 9-Nonyl-9*H*-carbazole were prepared as described in the literature.[8] 9-Nonyl-9*H*-carbazole was substituted on the nitrogen atom with a linear alkyl chain using common procedure to provide compound **6** in 91% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H), 7.56-7.53 (q, 2H), 7.26 (d, 2H), 4.25-4.21 (t, 2H), 1.83-1.80 (m, 2H), 1.30-1.22 (m, 14H), 0.88-0.84 (t, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 154.7, 132.7, 130.3, 128.7, 122.1, 121.2, 56.2, 49.4, 41.9, 31.9, 29.7, 28.4, 27.4, 22.8, 14.1 ppm Found: C, 55.88; H, 5.59; N, 3.11. Calc. for $C_{21}H_{25}Br_2N$: C, 55.90; H, 5.58; N, 3.10.

General Procedure for Stille Reaction. All reactions were carried out in dry nitrogen. DMF was dried over CaH_2 and distilled just before use. A solution of starting material (**5** or **6** or **7**) (2.0 mmol) in dried DMF was purged by N_2 for 5 min and heated at 30-50 °C, then the solution came to be transparent. Compound **8** (4.5 mmol) and $Pd(PPh_3)_4$ (0.01 mmol) was added to the solution and the resulting mixture was stirred at room temperature for 5 min then heated quickly at 110-140 °C for 24-26 hrs. The progress of the reaction was observed by TLC check and color was changed during reaction. After the reaction, the mixture was cooled to room temperature and solvent was evaporated. The residue was dissolved in 100 mL of dichloromethane and washed with 100 mL of stilled water five times. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was subjected to chromatography on a neutral silica gel column eluting with dichloromethane/hexane or ethyl acetate/hexane to give compound **1**.

Compound 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.29 (m, 8H), 3.12-3.09 (t, 4H), 1.90-1.83 (m, 4H), 1.33-1.25 (m, 36H), 0.89-0.86 (t, 6H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 173.1, 149.0, 141.4, 139.0, 135.9, 119.1, 112.8, 101.1, 64.7, 34.7, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 22.7, 14.1 ppm. Found: C, 65.64; H, 7.81; N, 3.74; S, 16.17. Calc. for $C_{44}H_{60}N_2O_4S_4$: C, 65.31; H, 7.47; N, 3.46; S, 15.85.

Compound 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H), 7.79 (s, 2H), 7.58 (d, 2H), 6.33 (s, 2H), 4.38-4.25 (m, 10H), 1.41-1.18 (m, 14H), 0.88-0.82 (t, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 142.3, 141.3, 137.8, 130.5, 126.1, 121.5, 120.3, 117.7, 106.3, 97.3, 64.9, 64.5, 31.8, 29.5, 29.4, 29.3, 28.9, 27.2, 22.6, 14.1 ppm. Found: C, 69.41 ; H, 6.44; N, 2.75; S, 11.45. Calc. for $C_{33}H_{35}NO_4S_2$: C, 69.08; H, 6.15; N, 2.44; S, 11.18.

Compound 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 6.43 (s, 1H), 6.28 (s, 1H), 4.45-4.43 (m, 2H), 4.38-4.36 (m, 2H), 4.30-4.25 (m, 4H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.1, 152.4, 147.7, 143.0, 119.0, 114.3, 94.9, 65.3, 65.0 ppm. Found: C, 52.99; H, 3.65; S, 26.62. Calc for $C_{15}H_{11}NO_4S_3$: C, 52.73; H, 3.32; S, 26.39.

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