

Synthesis and Characterization of Perylene-based Pyrrolopyrone Derivative for Organic Thin Film Transistor

Hyung-Sun Kim^{**a}, Sung-Ouk Jung^{**a}, Yun-Hi Kim^a, Lee-Mi Do^{*b}, and Soon-Ki Kwon^a

Abstract

Perylene-based pyrrolopyrone derivative (PPD) was synthesized via condensation reaction with perylenetetracarboxylic dianhydride and 1,2-phenylenediamine as n-type channel material. The structure of PPD was characterized by spectroscopic methods such as FT-IR and ¹H-NMR. PPD exhibited high thermal stability ($T_{d5wt\%}$: 560 °C) and was found to be soluble only in protonic solvents with high acidity such as methane sulfonic acid and trifluoroacetic acid. The PPD solution showed maximum absorption and emission at 601 and 628 nm, respectively. Thin film transistors were fabricated by vacuum deposition and solution casting method. The electron mobilities of the devices were achieved as high as $0.17 \times 10^{-6} \text{ cm}^2/\text{Vs}$ for vacuum deposited device and $0.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$ for spin coated device, respectively.

Keywords : perylenepyrrolopyrone, OTFT, mobility

1. Introduction

Organic field-effect transistors (OTFTs) based on molecular and polymeric organic semiconductors have recently received considerable attention because of their fundamental optoelectronic properties and their potential applications for organic integrated circuit sensors [1], low-cost memories, smart cards, and driving circuits for large-area display device applications such as active-matrix flat-panel liquid-crystal displays (AMFPDs), organic light-emitting diodes, and electronic paper displays [2,3].

Many of the organic semiconductors used for the fabrication of the p-channel in OTFTs have been derived from thiophene-based π -conjugated systems, oligothiophene, acenes, phthalocyanines, and regioregular poly-3-hexylthiophene [4]. α,ω -Dialkylsubstituted oligothiophenes,

with pentacene are, the most promising p-type materials, due to their capacity to self-assemble into close-packed structures. It has been reported by different groups that when oligothiophene is synthesized and purified according to optimized procedures, it can reach field-effect mobilities of up to $0.1 \text{ cm}^2/\text{Vs}$ for vacuum-evaporated 2,5''''-dihexylsexithiophene [5].

Although high-mobility TFTs based on n-type materials are crucial for fabrication of complementary circuits, to date few n-type candidates have been discovered, and the FET performances are not satisfactory. Semiconductors based on perfluoro-phthalocyanine, naphthalene and perylene skeletons is known to be the most promising n-type materials [6]. For perylene tetracarboxylic dianhydride derivatives, the majority charge carriers are electrons in the conduction band, and these materials are thus classified as n-type semiconductors [7]. For example N,N'-dialkyl-3,4,9,10-perylene tetracarboxylic dimides have resulted in good TFT performance by Malenfant [8] *et al.*

In this study, we will discuss perylene-based pyrrolopyrone derivative (PPD) that can be used as an n-type channel material. PPD containing 1,2-phenylene was synthesized and characterized. Strong electron withdrawing

Manuscript received November 2, 2005; accepted for publication December 9, 2005.

This research was supported by a grant (F0004021) from Information Display R&D Center, one of the 21st Century Frontier R&D Program funded by the Ministry of Commerce, Industry and Energy of Korean government.

* Member, KIDS; ** Student Member, KIDS.

Corresponding Author : Soon-Ki Kwon

^aDepartment of Polymer Science and Engineering and Engineering Research Institute, Gyeongsang National University, Jinju, 660-701, Korea

^bBasic Research Laboratory, ETRI, Taejeon, 305-350, Korea

E-mail : skwon@gsnu.ac.kr Tel : +055 751-5296 Fax : +055 753-6311

group and planar structure of the PPD will affect its polarity and electron affinity, and thin film morphology. The present paper mainly discusses the synthesis, characterization and electron mobility characteristics of PPD as active layer.

2. Experiments

Materials. 1, 2-phenylenediamine perylene-3, 4, 9, 10-tetracarboxylic dianhydride and benzoic acid were purchased from Aldrich. Isoquinoline was purchased from Fluka. All reagents purchased commercially were used as received and without any further purification process. m-Cresol was dried over CaCl_2 and distilled under reduced pressure, and stored under nitrogen in the dark.

Measurements. A Genesis II FT-IR spectrometer was used to record IR spectra. ^1H -NMR and ^{13}C -NMR spectra were recorded by using Avance 300 and DRX 500 MHz NMR Bruker spectrometers, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA instrument 2050 thermogravimetric analyzer. The sample was heated using a $10\text{ }^\circ\text{C}/\text{min}$ heating rate from $50\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 differential scanning calorimeter. The sample was heated with the $10\text{ }^\circ\text{C}/\text{min}$ from $30\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. Mass spectrum was measured by Jeol JMS-700 mass spectrometer. UV-vis absorption spectra and photoluminescence (PL) spectra were measured by Perkin Elmer LAMBDA-900 UV/VIS/NIR spectrophotometer and LS-50B luminescence spectrophotometer, respectively. Cyclic voltammograms of the oligomers were recorded on an epsilon E3 at a room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile under nitrogen gas protection at a scan rate of 50 mV/s . A Pt wire was used as the counter electrode and an Ag/AgNO_3 electrode as the reference electrode.

Device fabrication. The thin film field-effect transistors were fabricated by using bottom contact geometry. A highly conductive Si wafer was used as substrate and gate electrode. The gate dielectrics for all devices were thermally grown to 300 nm thick SiO_2 layer. Ti (10 nm)/Au (80 nm) source and drain contacts were photo-lithographically defined on the SiO_2 such that the

channel width W is $25\text{ }\mu\text{m}$ and the channel length L is $5\text{ }\mu\text{m}$. Active layer with sublimed PPD was fabricated under vacuum of less than 2×10^{-6} Torr directly on the TFT substrate above $630\text{ }^\circ\text{C}$. The spin coated PPD as active layer was obtained from a ca. $0.1\text{ wt.}\%$ solution in methanesulfonic acid (MSA). The resulting spin coated PPD thin film was then immersed in deionized water to remove any remaining MSA solvent. Transistor I-V characteristics were measured using a Hewlett Packard 4145B at room temperature.

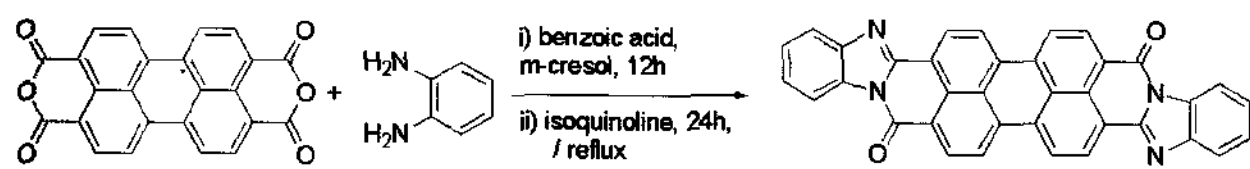
Synthesis

Perylene-based pyrrolopyrone derivative (PPD)

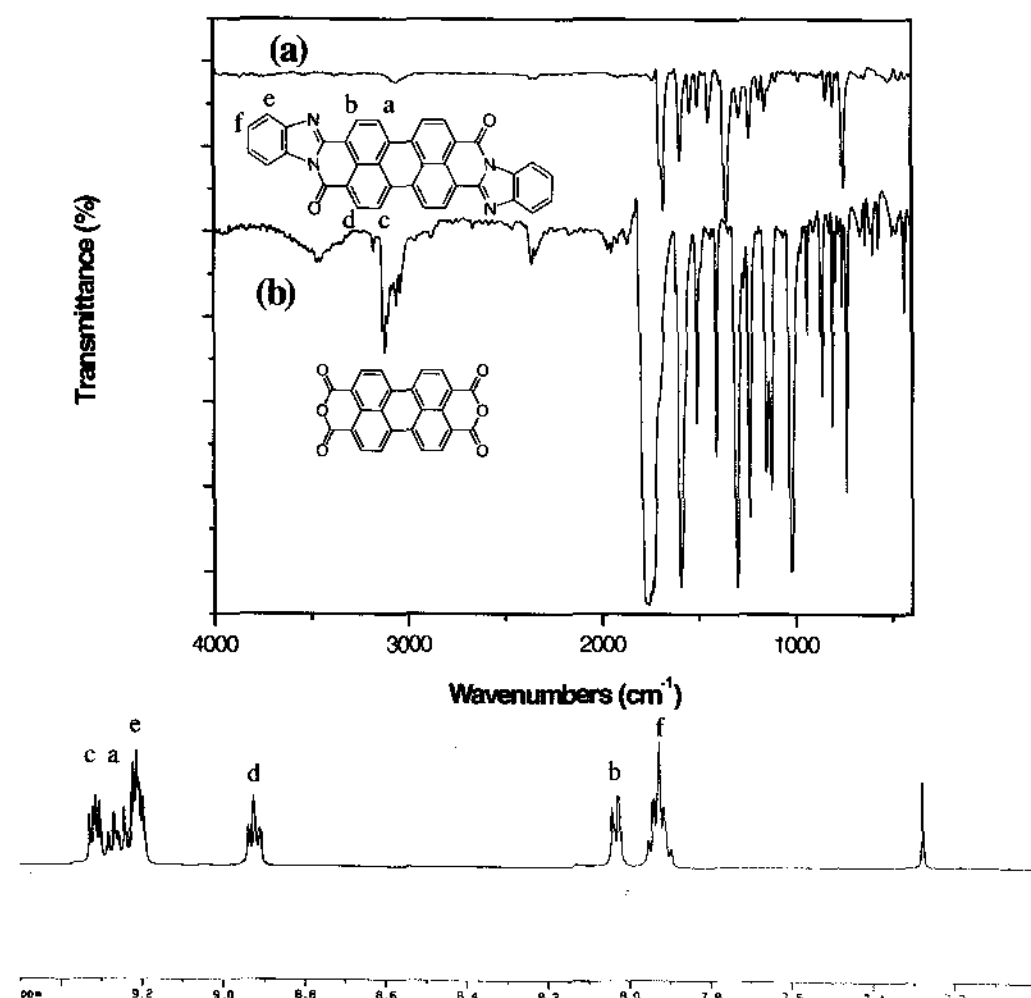
Perylene tetracarboxylic dianhydride (2 g , 5.1 mmol), 1,2-diaminobenzene (1.65 g , 15.3 mmol), benzoic acid (1.25 g , 10.2 mmol) and m-cresol (20 mL) were placed in a 100 mL three-necked round bottomed flask equipped with a mechanical stirrer, a Dean-stark trap, nitrogen inlet and outlet. The reaction mixture was heated at $200\text{ }^\circ\text{C}$ under nitrogen for 12 h . Then isoquinoline (1.32 g , 10.2 mmol) was added and the heating was continued for another 24 h . The reaction mixture was poured into methanol. The precipitate was filtered off and washed with NaOH-solution, water, and methanol several times. The product was dried in vacuum oven. Yield; 1.9 g (70%), $\text{mp} > 300\text{ }^\circ\text{C}$. ^1H -NMR (500 MHz , $\text{CF}_3\text{COOD}/\text{CDCl}_3$, ppm): $9.3\text{--}9.2$ (m, 4H), 8.92 (t, 1H), 8.04 (d, 1H), 7.3 (m, 2H).

3. Results and Discussion

Scheme 1 illustrates the synthetic route of perylene-based pyrrolopyrone derivative. PPD was obtained by benzoic acid and isoquinoline catalyzed condensation reaction of perylene tetracarboxylic dianhydride and 1, 2-diaminobenzene. The obtained material was confirmed by FT-IR and ^1H -NMR spectrometric analysis and the results were consistent with the predicted chemical structures. Fig. 1 shows the typical FT-IR spectra of perylene tetracarboxylic dianhydride (PTCDA) and PPD. PTCDA showed major absorption peak at 1768 cm^{-1} as a result of the carbonyl group. However, in case of PPD, the characteristic absorption of carbonyl group of amidine is narrowed and shifted to 1681 cm^{-1} . From this figure, C-N peak can be seen to be 1355 cm^{-1} . The characteristic proton peaks of PPD were assigned in the ^1H -NMR spectrum. (Fig. 1)



Scheme 1. Synthetic route to PPD.

Fig. 1. FT-IR spectra of PPD (a) and PTCDA (b) and ^1H -NMR spectrum of PPD. (solution in $\text{CF}_3\text{COOD}/\text{CDCl}_3$)

The obtained PPD was soluble only in protonic solvent with high acidity such as methane sulfonic acid and trifluoroacetic acid at room temperature. Therefore, PPD was able to manufacture a TFT device by solution process due to good solubility in protonic solvent with high acidity, in spite of its highly rigid structure. The thermal properties of PPD were evaluated based on TGA and DSC curves. The weight loss of PPD was less than 5% up to a heating temperature of 560 °C in nitrogen atmosphere. Glass transition temperature was not detected until the temperature reached 300 °C. These results show that, PPD demonstrates good thermal stability. It is assumed that the thermal stability was increased due to the introduction of pyrrolopyrone unit into a rigid perylene center.

Fig. 2 shows the optical absorption and photoluminescence spectra of a dilute solution of PPD in trifluoroacetic acid. The absorption spectrum of the dilute solution of PPD showed three relatively narrow absorption peaks at 518, 556, and 601 nm. The PL spectrum of the dilute solution of PPD has a maximum peak at 628 nm, which corresponds to red emission. It is suggested that the extension of the π -system and the increase of intermolecular stacking due to the introduction of pyrrolopyrone induced a dramatic bathochromic shift as compared to

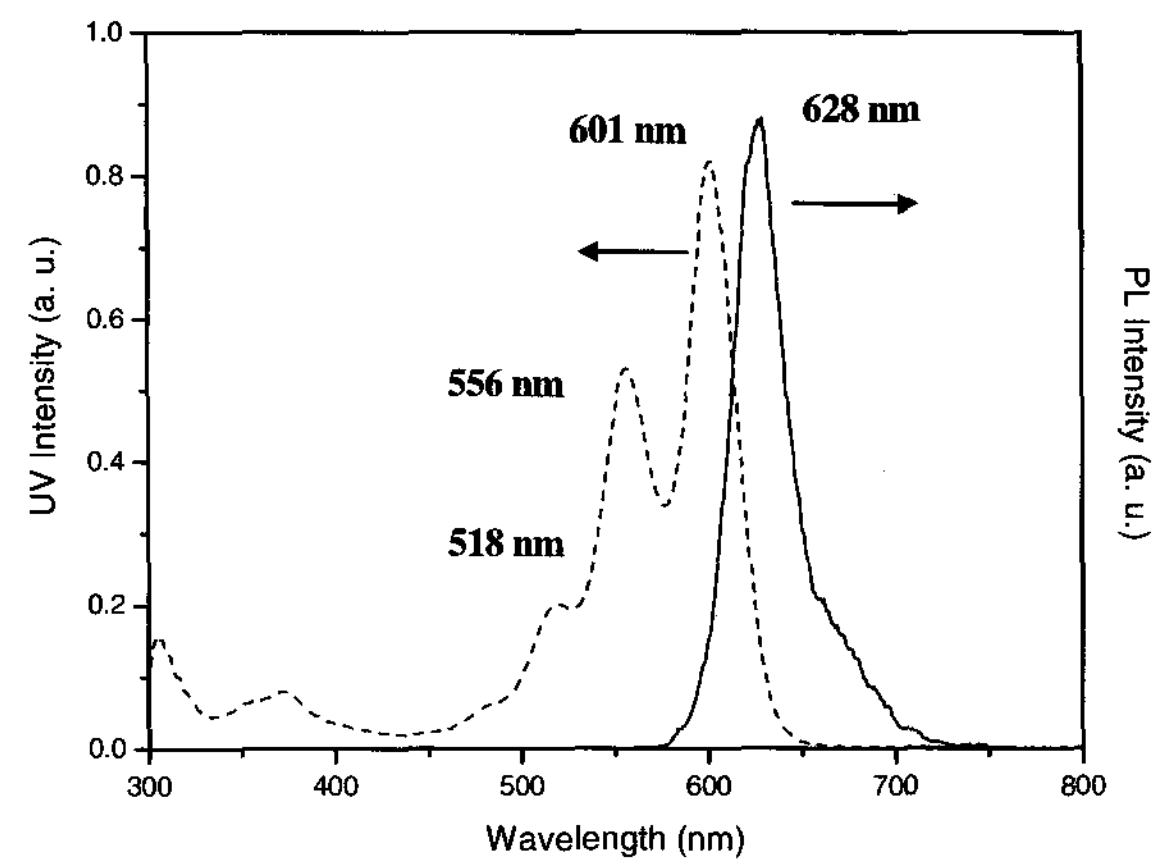


Fig. 2. UV-visible and PL spectra of PPD in trifluoroacetic acid.

perylene diimide derivatives [9]. In solid state, the photoluminescence spectrum could not be measured or showed very low intensity. The reason may be that the quenching was caused by enhanced intermolecular interaction.

To understand the charge transport properties and the electrochemical stability of the materials, electrochemistry measurement of the thin film was carried out. All the electrochemical data of PPD, which was obtained from the film, were prepared by dip-coating the PPD solutions onto the Pt wire. All measurements were calibrated using ferrocene value of -4.4 eV [12]. The onsets of oxidation and reduction potentials of PPD were at 1.40 V and -0.80 V, respectively. HOMO and LUMO levels of PPD were 5.8 and 3.6 eV, respectively and bandgap was 2.2 eV. The clear reductive waves and the good reversibility not only prove that the PPD is a good potential candidate as an active channel material to be applied to organic TFT but also allow us to study the electronic properties of the PPD. Moreover, it is proved that the low LUMO energy level of PPD is suitable as n-type semiconductor because of allowing more favorable electron injection.

Fig. 3 shows the typical FET characteristic of a TFT made of PPD deposited at room temperature. All electrical measurements were performed in ambient air. The device did not show p-channel characteristics. Instead, typical n-channel FET output characteristic was observed as exemplified in Fig. 3. We calculated the field-effect mobility of electrons by using the saturation region transistor equation (1):

$$I_d = (W/2L)\mu_e C_o (V_g - V_t)^2 \quad (1)$$

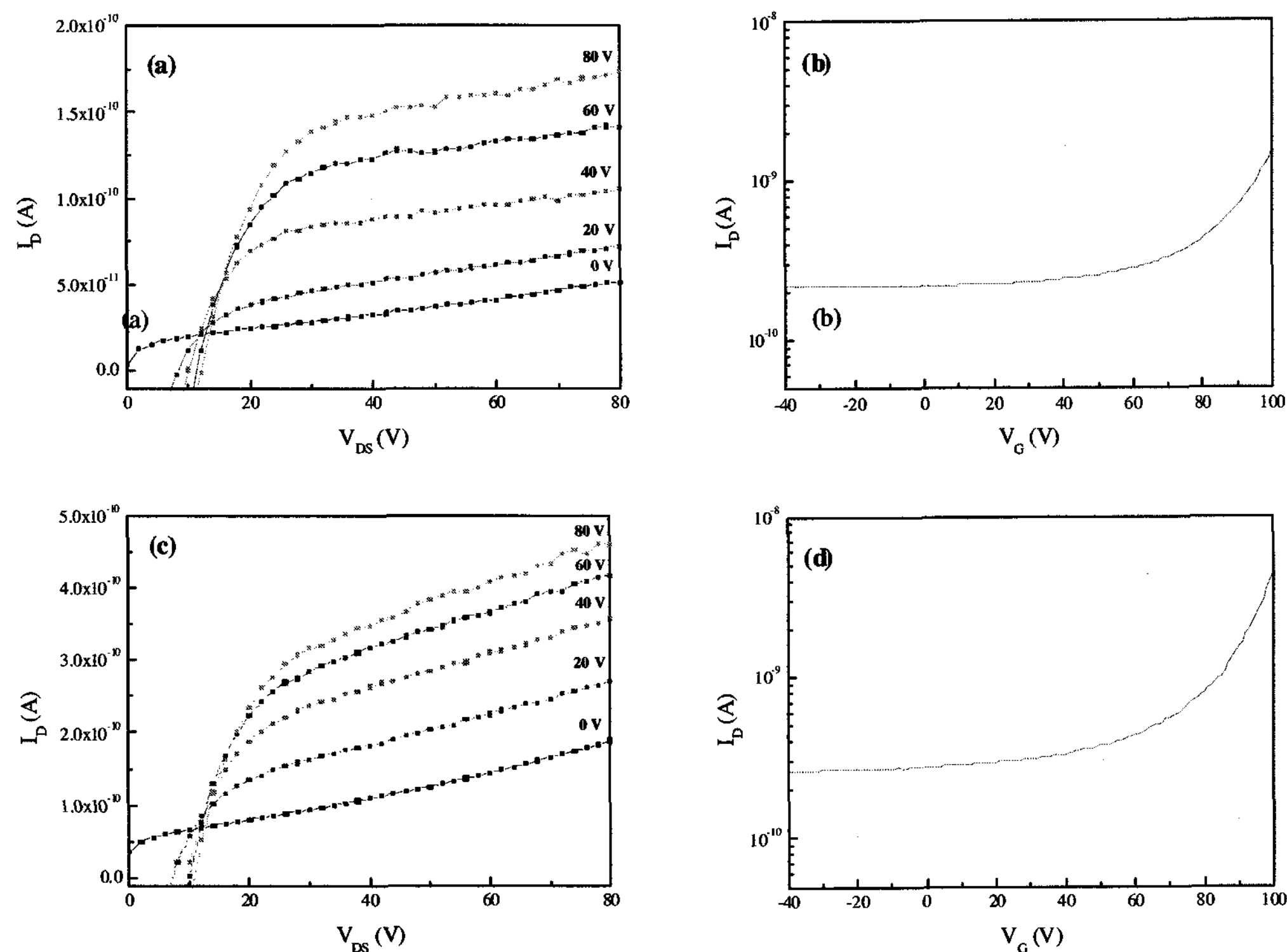


Fig. 3. (a) Electrical output characteristics and (b) transfer characteristics of PPD TFT prepared vacuum deposition at room temperature. (c) electrical output characteristics and (d) transfer characteristics of PPD TFT prepared spin coating at room temperature.

Here, I_d is the source-drain current, V_g is the gate voltage, C_o is the capacitance per unit area of the dielectric layer, and V_t is the threshold voltage. Vacuum deposited device and spin coated device at room temperature gave a maximum electron mobility value of $0.17 \times 10^{-6} \text{ cm}^2/\text{Vs}$, $0.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$, respectively, and on/off ratio was below 10^1 (V_t : 73 V and 71 V, for vacuum deposited and spin coated device, respectively).

Generally, field-effect mobilities of vacuum deposited devices are higher than those of solution processed devices. However, in the case of a PPD FET device, the field-effect mobility of spin-coated device is higher than that of vacuum deposited device. This may be due to that PPD was carbonized during vacuum evaporation process because of high evaporation temperature (630 – 830 °C). The on/off ratio characteristics were very low. It seems that PPD has some impurities due to simple filtering and washing used in the purification process, where in fact the purity of organic semiconductor materials are crucial to good device performance. Many materials were purified by Soxhlet or sublimation method for the improvement of device performance. In case of PPD, device performance could be

improved by further purification such as Soxhlet and sublimation.

This first attempt to fabricate TFTs with this new material produced promising results. Further improvements can be achieved through systematic optimization of the film deposition parameters and spin coating condition, and the further purification such as Soxhlet and sublimation.

4. Conclusions

In this study, the perylene-based pyrrolopyrone derivative, PPD was synthesized and characterized. It was found that PDD is soluble only in protonic solvents with high acidity such as methane sulfonic acid and trifluoroacetic acid. PPD had good thermal stability, and UV-vis. and PL maximum spectra were 601 nm, 628 nm, respectively. Electron mobilities of the vacuum evaporated and spin coated devices were $0.17 \times 10^{-6} \text{ cm}^2/\text{Vs}$, and $0.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$, respectively. The reason why the lower mobility of vacuum evaporated device seems carbonized during vacuum evaporation process is because of high

evaporation temperature (630 – 830 °C). These are the results of preliminary test. It may be possible to align this oligomer from molecular orientation by their substrate temperature variation, which may lead to further improvement in the performance of mobility and on/off ratio in thin film electronic device.

References

- [1] B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H. E. Katz, A. J. Lovinger, and Z. Bao, *Appl. Phys. Lett.*, **78**, 2229 (2001).
- [2] R. Wisnieff, *Nature* **394**, 225 (1998).
- [3] S. W. Pyo, J. H. Shin, and Y. K. Kim, *J. Inform. Dis.* **4**, 1 (2003).
- [4] C. D. Dimitrakopoulos, S. Purushothaman, J. Kyminsis, A. Callegari, and J. M. Shaw, *Science* **283**, 822 (1999).
- [5] H. Akimichi, K. Waragai, S. Hotta, H. Kano, and H. Sakaki, *Appl. Phys. Lett.* **58**, 1500 (1991).
- [6] Z. Bao, A. J. Lovinger, and J. Brown, *J. Am. Chem. Soc.* **120**, 207 (1998).
- [7] G. Horowitz, F. Kouki, P. Spearman, D. Fichou, C. Nogues, X. Pan, and F. Garnier, *Adv. Mater.* **8**, 242 (1996).
- [8] P. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, and T. O. Graham, *Appl. Phys. Lett.* **80**, 2517 (2002).
- [9] S. G. Liu, G. Sui, R. A. Cormier, R. M. Leblanc, and B. A. Gregg, *J. Phys. Chem. B* **206**, 1307 (2002).
- [10] C. Videlot, J. Ackermann, P. Blanchard, J. M. Raimundo, P. Frère, M. Allain, R. de Bettignies, E. Levillain, and J. Roncali, *Adv. Mater.* **15**, 306 (2003).
- [11] H. E. Katz, J. Johnson, A. J. Lovinger, and W. Li, *J. Am. Chem. Soc.* **122**, 7787 (2000).
- [12] D. C. Shin, Y. H. Kim, H. You, and S. K. Kwon, *Macromolecules* **36**, 3222 (2003).
- [13] C. D. Dimitrakopoulos, and P. Malenfant, *Adv. Mater.* **14**, 99 (2002).