

# Synthesis and Properties of 6,13-Bis(4-propylphenyl)pentacene

E-Joon Choi<sup>\*a</sup>, Heung-Gyu Kim<sup>a</sup>, Jae-Hoon Park<sup>b</sup>, and Jae-Hoon Kim<sup>\*b</sup>

## Abstract

In this study, 6,13-Bis(4-propylphenyl)pentacene was synthesized and characterized. The structures of the products that were obtained during the reaction steps were identified via FT-IR and NMR spectroscopy and elemental analysis. The compound was found to be soluble in organic solvents like chloroform, dichloromethane, THF, and toluene. The charge transport mobility was  $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , and the on/off current ratio was  $10^2$ , while the compound was 2.5 times more stable under oxidation in a solution compared with pentacene.

**Keywords:** soluble pentacene, OTFT, organic semiconductor

## 1. Introduction

In the last decade, intensive research and development efforts were made on organic semiconducting materials and their new and diverse applications. Today, the impact of organic semiconductors is starting to be felt, and such semiconductors now offer potential applications in organic light-emitting diodes (OLED), organic photovoltaic cells (OPVCs), chemical sensors, and organic thin-film transistors (OTFTs). Due to their easier fabrication processes, organic semiconductors have attracted much more attention than silicon technologies have as the latter require high-temperature and high-vacuum-deposition processes in thin-film transistors (TFTs). Moreover, organic semiconductors can be fabricated through solution processes like spin-coating, inkjet printing, and screen printing. Therefore, organic semiconductors can be considered the most suitable candidate for use in the application of fabrication processes in OTFTs because it is expected

that the key factors in the future display industry will be simplicity, durability, and flexibility.

Many conjugated materials for semiconductors have been studied, but pentacene derivatives attract continuous attention and have been most widely studied. Pentacene, which consists of five fused benzene rings, has emerged as a viable candidate for the charge transport layer in OTFTs, which are being developed for potential applications in active-matrix displays as a switching device. The interest in pentacene, which exhibits p-type transport, stems primarily from its relatively high charge transport mobility and high on/off current ratio in OTFTs. The practical uses of pentacene, however, are still limited by its high sensitivity to oxygen and its low solubility in organic solvents [1-4]. To improve the oxidative stability and solubility of pentacene, many research groups are attempting to design and synthesize new pentacene derivatives [5, 6].

In this study, a pentacene derivative with a lateral propylphenyl substituent was synthesized and characterized, and its oxidative stability and solubility in common organic solvents were described.

## 2. Experiment

### 2.1 Chemicals and Instruments

All the reagent-grade starting materials that were used in this study were purchased from Aldrich and TCI. Commercially available reagents were used without further purification, and silica gel (0.063 ~ 0.200 mm) was purchased from Merck for column chromatography. The structure of the

Manuscript Received September 04, 2009; Revised September 22, 2009; Accepted for publication September 25, 2009.

These authors gratefully acknowledge the funding that they obtained for this research from the New University for Regional Innovation, which is receiving support from the Ministry of Education, Science, and Technology of the Republic of Korea. This work was accomplished with partial support from the Korea Science and Engineering Foundation grant funded by the Korean government (no. R01-2008-000-11521-0).

<sup>\*</sup> Member, KIDS

Corresponding author: E-Joon Choi

<sup>a</sup> Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Yangho-dong, Gumi, Gyungbuk 730-701, Korea

<sup>b</sup> Department of Electronics and Communications Engineering, Department of Information Display Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

**E-mail:** ejchoi@kumoh.ac.kr **Tel:** +82-54-478-7684 **Fax:** +82-54-478-7710

compounds was characterized via FT-IR spectroscopy (Jasco, FT/IR-300E in KBr pellet form) and  $^1\text{H}$  NMR spectroscopy (Bruker, DPX 200MHz). The  $^1\text{H}$  chemical shifts were given in the  $\delta$  (ppm) unit relative to tetramethylsilane (TMS), where  $\delta$  (TMS)=0, and were referenced to the peaks of the residual solvent. The oxidative stability of the pentacene derivative was measured using a UV-visible spectrophotometer (Mecasys, UV-3220). The charge transport mobility and on/off current ratio were obtained at room temperature under a dark state, using a semiconductor parameter analyzer (ELECS, EL421C).

## 2.2 Synthesis

**Pentacenequinone (1):** 1,4-cyclohexanedione (3.86 g, 33.0 mmol) and potassium hydroxide (7.50 g, 132 mmol) were dissolved in ethanol (100 ml), and the solution was cooled down to  $0^\circ\text{C}$ . Then o-phthalaldehyde (9.00 g, 66.0 mmol) was added to the solution. The reaction mixture was stirred for 1 h at  $0^\circ\text{C}$ , and for an additional 1 h at  $60^\circ\text{C}$ . After the reaction, the product was collected via filtration and then thoroughly washed with water and ethanol [7]. Yield: 76%; IR (KBr pellet,  $\text{cm}^{-1}$ ): 3054 ( $\text{sp}^2$  =C-H stretch), 1671 (C=O stretch), and 1608-1392 (C=C stretch);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 9.10 (s, 4H, Ar-H), 8.20 (t, 4H, Ar-H), and 7.76 (t, 4H, Ar-H).

**6,13-Bis(4-propylphenyl)-6,13-dihydropentacene-6,13-diol (2):** A 2.0M solution of n-BuLi in hexane (2.0 mL, 4.0 mmol) was added dropwise to a solution of 1-bromo-4-propylbenzene (0.40 g, 3.9 mmol) in dry THF (20 mL) at  $-78^\circ\text{C}$ , under a nitrogen atmosphere. The solution was stirred for 40 min. After the addition of 6,13-pentacenequinone (0.30 g, 1.0 mmol) to the solution, the obtained mixture was stirred for 1 h at  $-78^\circ\text{C}$ , and for an additional 7 h at room temperature. After the reaction, the mixture was poured into water (200 mL), and then dichloromethane (200 mL) was added to it. After the resultant organic layer was separated and then washed with water (200 mL $\times$ 2), the solvent was removed via evaporation under reduced pressure. Yield: 64%; IR (KBr pellet,  $\text{cm}^{-1}$ ): 3401 (O-H stretch), 3050 ( $\text{sp}^2$  =C-H stretch), 2958, 2865 ( $\text{sp}^3$  C-H stretch), and 1508, 1454 (C=C stretch);  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ,  $\delta$  in ppm): 8.55 (m, 4H, Ar-H), 8.05 (s, 4H, Ar-H), 7.55 (m, 4H, Ar-H), 7.15 (d, 4H, Ar-H), 6.95 (d, 4H, Ar-H), 2.23 (t, 4H, Ar- $\text{CH}_2$ - $\text{CH}_2$ ), 1.52 (m, 4H, Ar- $\text{CH}_2$ - $\text{CH}_2$ ), and 1.14 (t, 6H,  $\text{CH}_3$ ).

**6,13-Bis(4-propylphenyl)pentacene (3):** Tin(II) chloride dihydrate (2.4 g, 10.0 mmol) and 50% acetic acid (2.0

mL) were added to a solution of 6,13-bis(4-propylphenyl)-6,13-dihydropentacene-6,13-diol (0.50 g, 0.9 mmol) in 1,4-dioxane (80 mL), under a nitrogen atmosphere. The reaction mixture was stirred at  $70^\circ\text{C}$  for 5 h. After the reaction, the mixture was poured into water (200 mL), and then dichloromethane (200 mL) was added to it. The residual organic layer was separated and washed with water (200 mL $\times$ 2). After the removal of the solvent, the residue was purified via column chromatography on silica gel (hexane: chloroform=1:2). Yield: 52%; IR (KBr pellet,  $\text{cm}^{-1}$ ): 3040 ( $\text{sp}^2$  =C-H stretch), 2958, 2823 ( $\text{sp}^3$  C-H stretch), and 1446, 1376 (C=C stretch);  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ,  $\delta$  in ppm): 8.28 (s, 4H, Ar-H), 7.80 (m, 4H, Ar-H), 7.58 (t, 8H, Ar-H), 7.29 (t, 4H, Ar-H), 2.86 (t, 4H, Ar- $\text{CH}_2$ - $\text{CH}_2$ ), 1.89 (m, 4H, Ar- $\text{CH}_2$ - $\text{CH}_2$ ), and 1.11 (t, 6H,  $\text{CH}_3$ ).

## 2.3 Fabrication of an OTFT

TFTs were fabricated with glass substrates. For the gate electrode, a 70-nm-thick Al layer was prepared on a glass substrate via thermal deposition. Cross-linked polyvinylphenol (PVP) was used as the insulator, which was prepared by mixing the PVP with poly(melamine-co-formaldehyde) in propylene glycol monomethyl ether acetate (PGMEA). The bottom-contact source/drain electrode was fabricated by depositing 50-nm-thick Au. The channel length was 50  $\mu\text{m}$ , and the width was 100  $\mu\text{m}$ . The active layer with a thickness of over 60 nm was prepared by spin-coating a 3-wt% solution of compound 3 in chloroform.

## 3. Results and Discussion

A new pentacene derivative, 6,13-bis(4-propylphenyl)pentacene, was synthesized via the "organolithium reaction" method, as shown in Fig. 1. All the intermediate products obtained during the reaction steps were characterized via FT-IR and NMR spectroscopy. The results were in accordance with the expected formula. The three ranges of the solubility levels for 6,13-bis(4-propylphenyl)pentacene were classified in common organic solvents like chloroform, dichloromethane, tetrahydrofuran (THF), hexane, acetone, N,N-dimethylformamide (DMF), and toluene, at room temperature. The results are summarized in Table 1. Single circles, triangles, and cross signs were used, respectively, to represent the solubilities of more than 10 mg per mL (excellent solubility), between 5 and 10 mg per mL (good solubility), and less than 1 mg per mL (poor solubility). The obtained 6,13-bis(4-

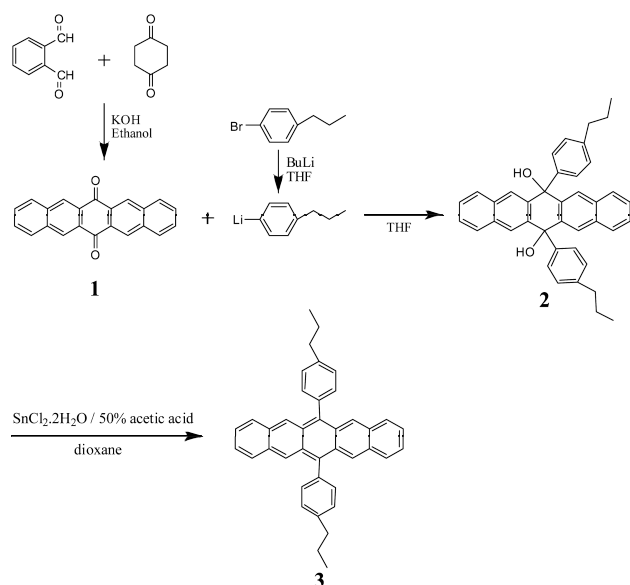


Fig. 1. Synthetic route to 6,13-bis(4-propylphenyl)pentacene.

Table 1. Solubility Test of 6,13-bis(4-propylphenyl)pentacene in Common Solvents at Room Temperature

CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	THF	Hexane	Acetone	DMF	Toluene
△	△	○	×	×	×	△

○: >10 mg/mL; △: 5~10 mg/mL; ×: <1 mg/mL

propylphenyl)pentacene showed excellent solubility in THF, good solubility in chloroform, dichloromethane, and toluene, and poor solubility in hexane, acetone, and DMF. It was previously reported that pentacene and other pentacene derivatives could be oxidized under the atmosphere, with room light [8, 9]. Thus, in this study, decolorization by irradiation was investigated for an examination of the oxidative stability of the pentacene derivative in a solution. The time-dependent UV-vis spectras of 6,13-bis(4-propylphenyl)pentacene in dichloromethane were measured to estimate their stability in a solution. Fig. 2 shows the UV-vis spectra of 6,13-bis(4-propylphenyl)pentacene, which show a characteristic vibrational finger-like absorbance in the 518, 558, and 602 nm wavelengths. The solution of 6,13-bis(4-propylphenyl)pentacene in dichloromethane gradually became colorless, and the peak intensity in the UV-vis spectra was decreased depending on the room light exposure period. The characteristic peaks of 6,13-bis(4-propylphenyl)pentacene disappeared after 50 min. The results indicate that 6,13-bis(4-propylphenyl)pentacene exhibits gradual degradation in a

solution, under room light. The solubility and oxidative stability can be increased, however, by introducing propylphenyl groups at the 6,13 position of pentacene, unlike the pentacene oxidized after 20 min in a toluene solution [10]. The electrical property of 6,13-bis(4-propylphenyl)pentacene was obtained in TFT, with a 50 μm channel length and a 100

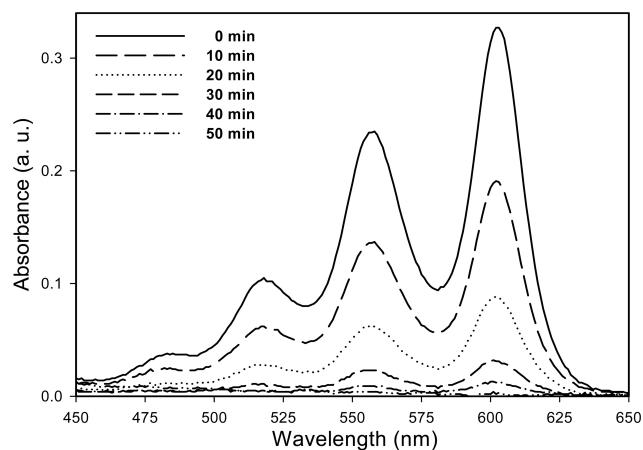
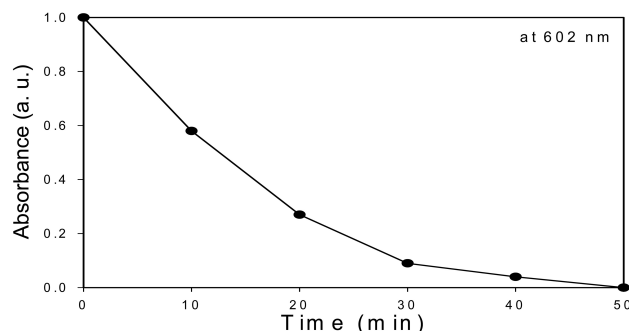


Fig. 2. Time-dependent UV-vis spectra of 6,13-bis(4-propylphenyl)pentacene in dichloromethane, under room light.

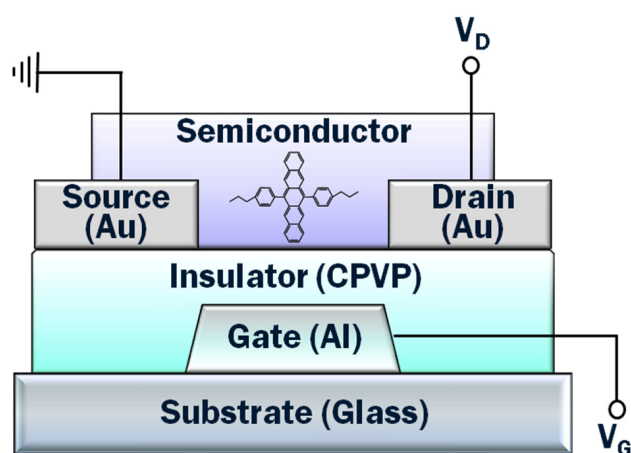
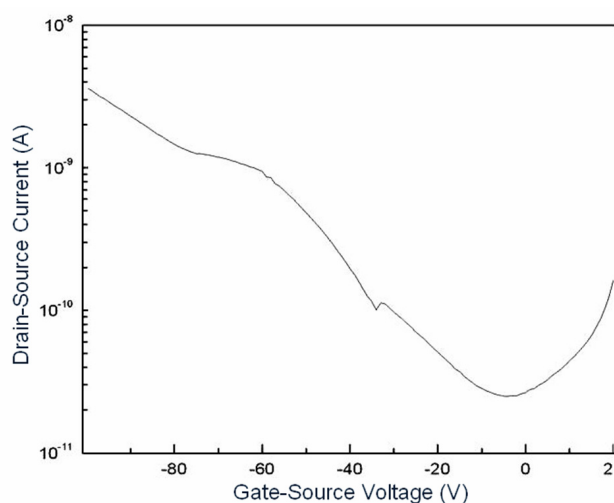


Fig. 3. Schematic cross-section of a pentacene derivative TFT with bottom contact.



**Fig. 4.** Drain-source current as a function of the gate-source voltage. Channel L/W: 50  $\mu\text{m}$ /100  $\mu\text{m}$ .

$\mu\text{m}$  width. The charge transport mobility was  $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , and the on/off ratio was  $10^2$ . It was envisioned that if an attempt would be made to optimize the device configuration, there would be room for the further enhancement of the OTFT performance, using the soluble pentacene derivative as a semiconductor material.

#### 4. Conclusions

In this study, a new pentacene derivative with propylphenyl groups was synthesized and characterized. The 6,13-bis(4-propylphenyl)pentacene was found to be soluble in

common organic solvents like chloroform, dichloromethane, THF, and toluene. 6,13-bis(4-propylphenyl)pentacene was completely oxidized in a solution after 50 min, under room light. It was found that the stability of pentacene when subjected to light can be increased by introducing propylphenyl substituents. The charge transport mobility of 6,13-bis(4-propylphenyl)pentacene was  $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , and its on/off ratio was  $10^2$ .

#### References

- [ 1 ] M. Halik, H. Klauk, U. Zschieschang, G. Schmid, C. Dehm, M. Schutz, S. Maisch, F. Effenberger, M. Brunnbauer and F. Stellacchi, *Nature* **431**, 963 (2004).
- [ 2 ] A. Maliakal, K. Raghavachari, H. Katz, E. Chandross and T. Siegrist, *Chem. Mater.* **16**, 4980 (2004).
- [ 3 ] H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.* **34**, 359 (2001).
- [ 4 ] G. Horowitz, R. Hajlaoui, R. Bourguiga and M. Hajlaoui, *Synth. Met.* **101**, 401 (1999).
- [ 5 ] C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer and G. G. Malliaras, *Org. Lett.* **7**, 3163 (2005).
- [ 6 ] Y. M. Wang, N. Y. Fu, S. H. Chan, H. K. Lee and H. N. C. Wong, *Tetrahedron* **63**, 8586 (2007).
- [ 7 ] N. Vets, M. Smet and W. Dehaen, *Tetrahedron Lett.* **45**, 7287 (2004).
- [ 8 ] O. Katsuhiko, T. Hiroaki, H. Takao, Y. Akihiro, S. Katsuhiko, E. Katsuya, T. Masaaki, N. Junichi and Y. Yoshiro, *Tetrahedron* **63**, 9699 (2007).
- [ 9 ] F. De Angelis, M. Gaspari, A. Procopio, G. Cuda and E. Di Fabrizio, *Chem. Phys. Lett.* **468**, 193 (2009).
- [ 10 ] Y. Li, Y. Wu, P. Liu, Z. Prostran, S. Gardner and B. S. Ong, *Chem. Mater.* **19**, 418 (2007).