

# Synthesis and Properties of New Pentacene Derivatives with Phenylethynyl Group

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## Abstract

*Pentacene has excellent semi-conducting characteristics. But pentacene practically used in OTFTs gives rise to problems mainly due to its sensitivity to oxygen and its very low solubility. In order to make up the problems, 6,13-disubstituted pentacene derivatives were synthesized and characterized. The properties of the compounds were characterized by FT-IR, NMR spectroscopy and UV-visible spectrophotometer. Now we are measuring the charge transport mobility and the on/off current ratios.*

## 1. Introduction

During the last few years, the development of organic thin film transistors (OTFTs) has attracted much interest. The production of OTFTs has been studied because organic molecules offer the opportunity of deposition over large surface areas and are compatible with flexible plastic substrates. Organic materials have the key advantage of potentially simple and low temperature thin film processing by using techniques such as spin coating, stamping or ink-jet printing methods. Thin film field-effect transistors using pentacene as the active semiconductor have shown a charge transport mobility in the range of  $0.005\text{--}2.1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and an on/off current ratios larger than  $10^8$ . But pentacene practically used in OTFTs gives rise to problems mainly due to oxidation and its very low solubility. In this study, we designed, synthesized (see Scheme 1) and characterized new pentacene derivatives.

## 2. Experimental

**Measurements.** The structure of compounds was characterized using FT-IR spectroscopy (Jasco, FT/IR-

300E with KBr pellet form), <sup>1</sup>H NMR spectroscopy (Bruker, DPX 200MHz). The <sup>1</sup>H chemical shifts are given in unit of  $\delta$  (ppm) relative the tetramethylsilane (TMS) where  $\delta$  (TMS)=0, and referenced to the residual solvent. The oxidative stability of pentacene derivatives was measured by UV-visible spectrophotometer (Mecasys, UV-3220).

**Synthesis.** All reagent-grade starting materials were purchased from Sigma-Aldrich Co. and TCI Co. Commercially available reagents and solvents were used without further purification, and silica gel (0.063~0.200mm) was purchased from Merck Co. for column chromatography.

**Synthesis of compound 1.** 1,4-cyclohexanedione (3.75 g, 33 mmol) and potassium hydroxide (7.5 g, 132 mmol) were dissolved in ethanol (100 ml) and the solution was cooled down to 0 °C. To the solution, o-phthalaldehyde (9 g, 66 mmol) was added. The reaction mixture was stirred for 1 h at 0 °C and for additional 1 h at 60 °C. After reaction, the product was collected by filtration and then washed with water (800 mL×2) and ethanol (800 mL×1) thoroughly.

**Synthesis of compound 3a.** A 2M solution of n-BuLi in cyclohexane (2 mL, 4 mmol) was added dropwise to a solution of 1-ethynyl-4-methylbenzene (0.34 g, 2.925 mmol) in dry THF (20 mL) at -78 °C under nitrogen. The solution was stirred for 50 min. After addition of 6,13-pentacenequinone (0.3 g, 0.975 mmol) to the solution, the obtained mixture was stirred for 1 h at -78 °C and for additional 7 h at room temperature. Tin(II) chloride dehydrate (2 g, 8.8 mmol) and 50% acetic acid (2 mL) were added to

the solution. The reaction mixture was stirred for 12 h at room temperature. The solution was poured into water (300 mL) and dichloromethane (300 mL) was added. The organic layer was separated and washed with water (300 mL $\times$ 2). After removal of the solvent, the residue was purified by column chromatography on silica gel using chloroform as an eluent to afford 6,13-bis(p-tolylethynyl)pentacene.

**Synthesis of compound 3b.** A 2M solution of n-BuLi in cyclohexane (2 mL, 4 mmol) was added dropwise to a solution of 4-ethynylanisole (0.39 g, 2.925 mmol) in dry THF (20 mL) at -78 $^{\circ}$ C under nitrogen. The solution was stirred for 50 min. After addition of 6,13-pentacenequinone (0.3 g, 0.975 mmol) to the solution, the obtained mixture was stirred for 1 h at -78  $^{\circ}$ C and for additional 8 h at room temperature. Tin(II) chloride dehydrate (2 g, 8.8 mmol) and 50% acetic acid (2 mL) were added to the solution. The reaction mixture was stirred for 12 h at room temperature. The solution was poured into water (200 mL) and dichloromethane (200 mL) was added. The organic layer was separated and washed with water (200 mL $\times$ 2). After evaporation of the solvent, the crude product was purified by column chromatography on silica gel using chloroform as an eluent to afford 6,13-bis((4-methoxyphenyl)ethynyl)pentacene.

**Synthesis of compound 3c.** A 2M solution of n-BuLi in cyclohexane (2 mL, 4 mmol) was added dropwise to a solution of 1-ethynyl-4-pentylbenzene (0.51 g, 2.95 mmol) in dry THF (20 mL) at -78 $^{\circ}$ C under nitrogen. The solution was stirred for 50 min. After addition of 6,13-pentacenequinone (0.3 g, 0.975 mmol) to the solution, the obtained mixture was stirred for 1 h at -78  $^{\circ}$ C and for additional 8 h at room temperature. Tin(II) chloride dehydrate (2 g, 8.8 mmol) and 50% acetic acid (2 mL) were added to the solution. The reaction mixture was stirred for 12 h at room temperature. The solution was poured into water (200 mL) and dichloromethane (200 mL) was added. The organic layer was separated and washed with water (200 mL $\times$ 2). After removal of the solvent, the residue was purified by column chromatography on silica gel using chloroform as an eluent to afford 6,13-bis((4-pentylphenyl)ethynyl)pentacene.

### 3. Results and discussion

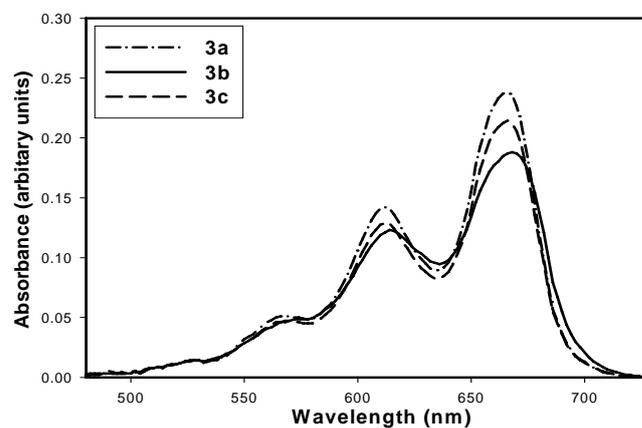
Pentacene derivatives were synthesized as shown in Scheme 1. The obtained compounds were characterized

by FT-IR and NMR spectroscopy. The results were in accordance with exported formula. The synthesized pentacene derivatives were soluble to organic solvents such as THF, dichloromethane and chloroform. In this study, we could increase the solubility and oxidative stability of pentacene by introducing substituent with phenylethynyl groups at 6, 13- position. Previously it was reported that pentacene and other pentacene derivatives could be oxidized under atmosphere with room light. Thus, decolorization by irradiation of room light was conducted to investigate the oxidative stability of the pentacene derivatives in solution. Figure 1 shows the UV-visible spectra of the pentacene derivatives which show a characteristic vibrational finger-like structure. Table 1 presents the calculated HOMO-LUMO gap by using  $\lambda_{\max}$ . The results exhibited lower band gaps than the band gap (2.12eV) of pentacene.

**TABLE 1. Optical properties for pentacene derivatives**

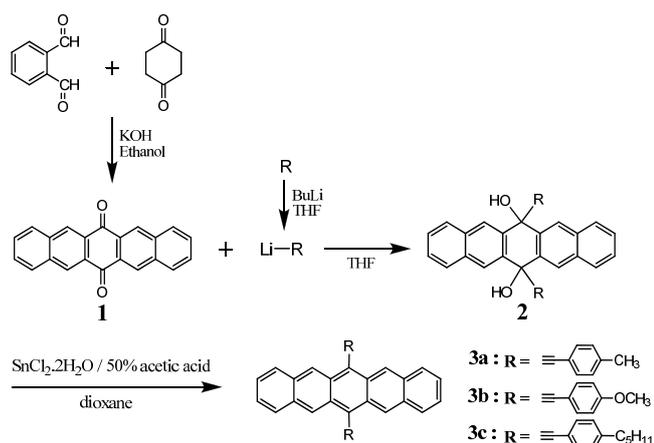
Compounds	$\lambda_{\max\text{abs}}$ (nm) <sup>a</sup>	HOMO-LUMO gap (eV)
<b>3a</b>	<b>666</b>	<b>1.86</b>
<b>3b</b>	<b>668</b>	<b>1.87</b>
<b>3c</b>	<b>666</b>	<b>1.86</b>

<sup>a</sup> Performed in dichloromethane.



**Fig. 1. UV-vis spectra of pentacene derivatives in dichloromethane.**

The solution of pentacene derivatives in dichloromethane gradually became colorless and the peak intensity in the UV-visible spectra was decreased depending upon exposure period at room light. The characteristic peaks of pentacene derivatives disappeared after 5 days as shown in Figure 5.



Scheme 1. Synthetic route to pentacene derivatives.

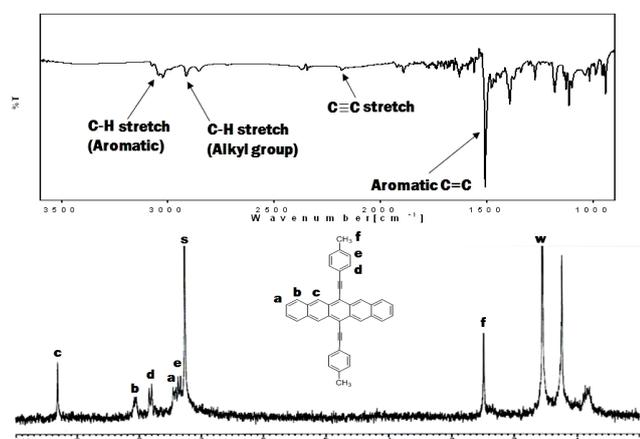
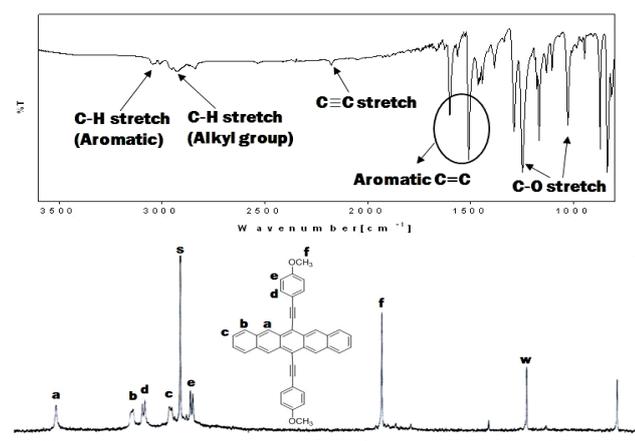
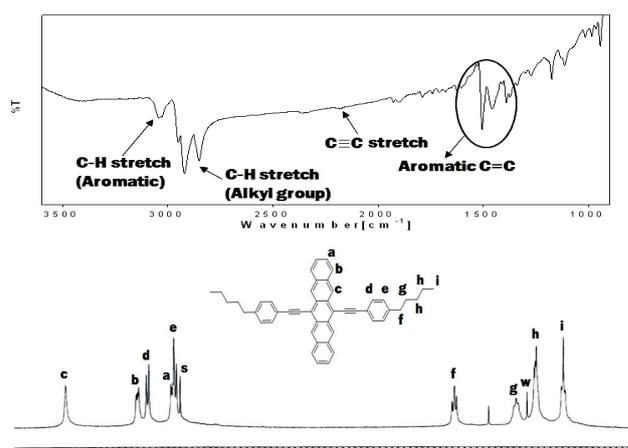
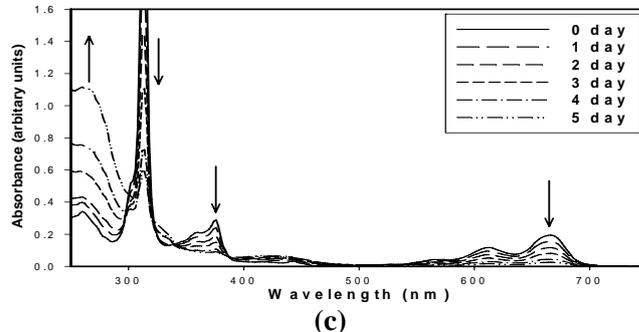
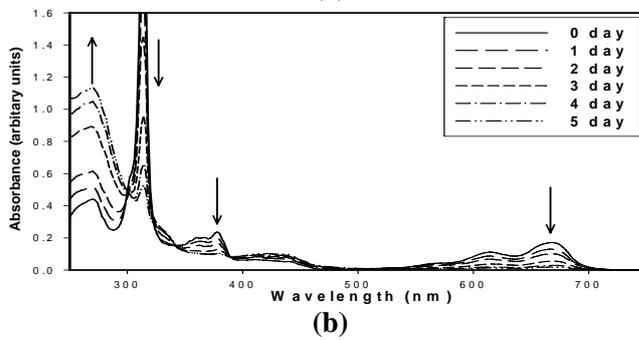
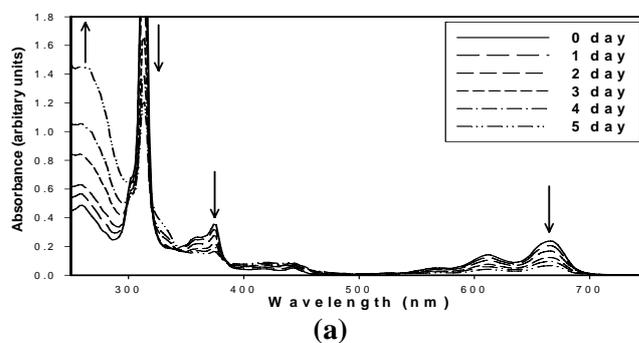
Fig. 2. IR (KBr pellet) and NMR (solvent =  $\text{CDCl}_3$ ) spectra of compound 3a.Fig. 3. IR (KBr pellet) and NMR (solvent =  $\text{CDCl}_3$ ) spectra of compound 3b.Fig. 4. IR (KBr pellet) and NMR (solvent =  $\text{CDCl}_3$ ) spectra of compound 3c.

Fig. 5. Time-dependent UV-vis spectra of pentacene derivatives in dichloromethane under room light; (a) compound 3a; (b) compound 3b; (c) compound 3c.

#### 4. Summary

New pentacene derivatives with phenylethynyl groups have been synthesized and characterized. The pentacene derivatives were soluble to organic solvents such as chloroform, THF and dichloromethane. Although the pentacene derivatives were still oxidized in solution under a room light, we could increase the stability of pentacene to light by introducing substituent with phenylethynyl groups.

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#### 5. References

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