

Perylene-based Pyrrolopyrone Derivatives as an n-Type Channel Materials

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Abstract

Perylene tetracarboxylic dianhydride derivatives have been well-known as an n-type channel material.¹ Here, we report perylene-based pyrrolopyrone derivatives as an n-type channel material. 1,8-naphthalene(1) and 1,2-phenylene(2)-based pyrrolopyrone derivatives were synthesized and characterized. Derivatives 1, 2 were soluble only in protic solvents with high acidity such as methanesulfonic acid and trifluoroacetic acid. Thin film transistors were fabricated by vacuum deposition and solution casting and electron mobility of the device were measured.

1. Introduction

Organic field-effect transistors (OTFTs) based on molecular and polymeric organic semiconductors are a focus of considerable current interest, motivated by 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 display (AMFPDs), organic light-emitting diodes, electrophoretic materials, 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, along with pentacene, the most promising p-type materials, due to their capacity for self-assembling into close-packed structures. As reported by different groups, when synthesized and purified according to optimized

procedures, oligothiophenes can reach field-effect mobilities of up to 0.1 cm²/Vs for, e.g., 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, with the most promising based on perfluorophthalocyanine and naphthalene skeletons.⁶

Perylene tetracarboxylic dianhydride derivatives the majority charge carriers are electrons in the conduction band, and this material is thus classified as n-type semiconductor.⁷ Considering these factors here, we report perylene-based Pyrrolopyrone derivatives as an n-type channel material. 1,8-Naphthalene(1) and 1,2-phenylene(2)-based pyrrolopyrone derivatives were synthesized and characterized.

2. Experimental

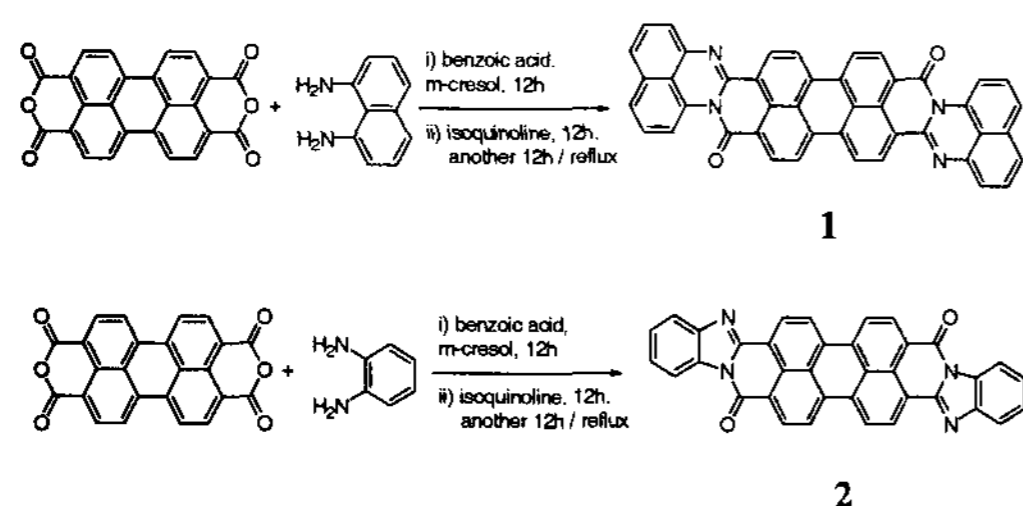
2-1. Synthesis

The perylene-based pyrrolopyrone derivatives 1, 2 were synthesized according to the following scheme depicted in Scheme 1.

Compound 1 Perylene tetracarboxylic dianhydride (2 g, 5.1 mmol), 1,8-diaminonaphthalene (2.42 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 °C under nitrogen for 12 h. Then isoquinoline (1.32 g, 10.2 mmol) was added and the heating was continued for another 12 h, and then the flask was heated for another 12 h. The reaction mixture was poured into methanol. The

precipitate was filtered off and washed with NaOH-solution and methanol several times. The precipitate was dried in vacuum oven. yield; 65 %. mp > 300 °C

Compound 2 The synthesis of compound 2 was conducted as described above; yield : 70 %. mp > 300 °C



Scheme 1 Synthetic scheme of pyrrolopyrone derivatives.

3. Results and Discussion

Scheme 1. illustrates the synthetic route of perylene-based pyrrolopyrone derivatives as an n-type channel material.

The products were analyzed by ¹H-NMR and FT-IR. ¹H-NMR spectrum of pyrrolopyrone derivatives showed in Figure 1.

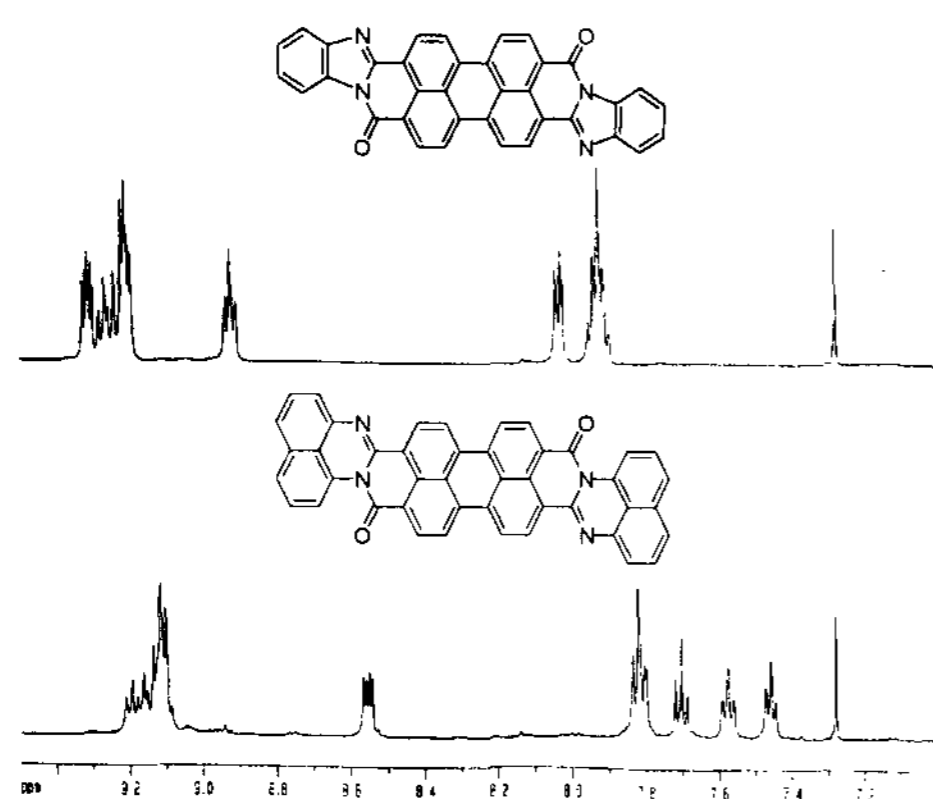


Figure 1. ¹H-NMR spectra of pyrrolopyrone derivatives. (CF₃COOD)

Compound 1, 2 were soluble only protonic solvents with high acidity such as methane sulfuric acid and trifluoroacetic acid.

Thermal analysis results are showed in Figure 2. Glass transition temperature was not detected to 300 °C. The TGA thermograms showed that 5 % weight loss in nitrogen were above 560 °C.

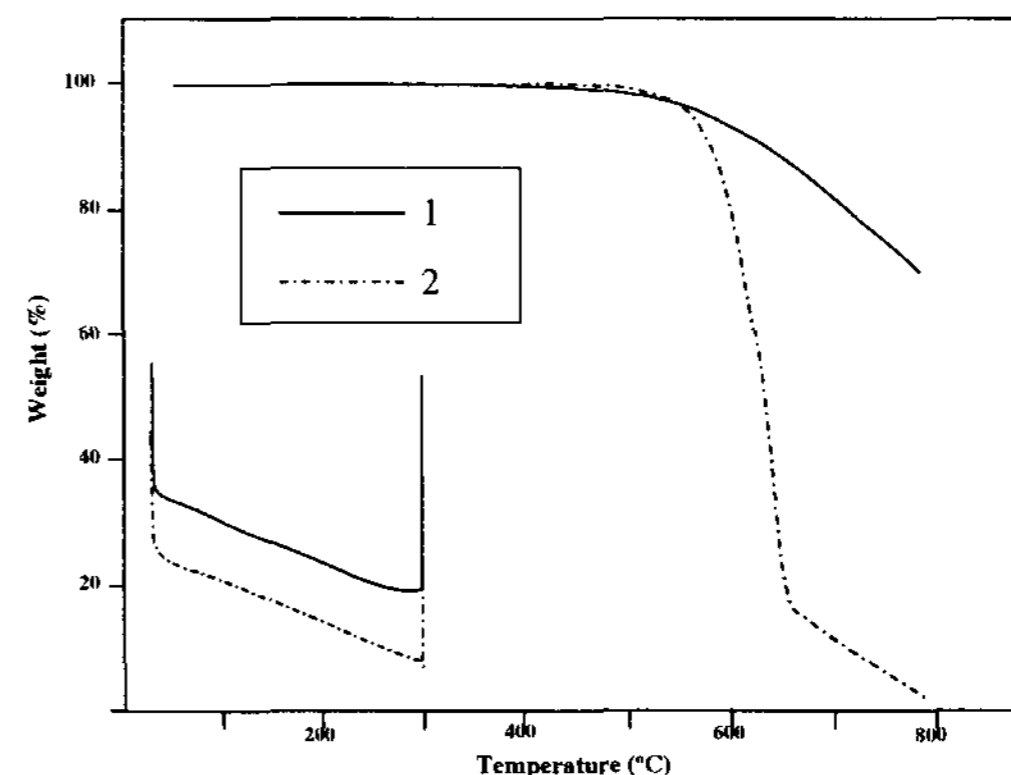


Figure 2. TGA and DSC curves of pyrrolopyrone derivatives.

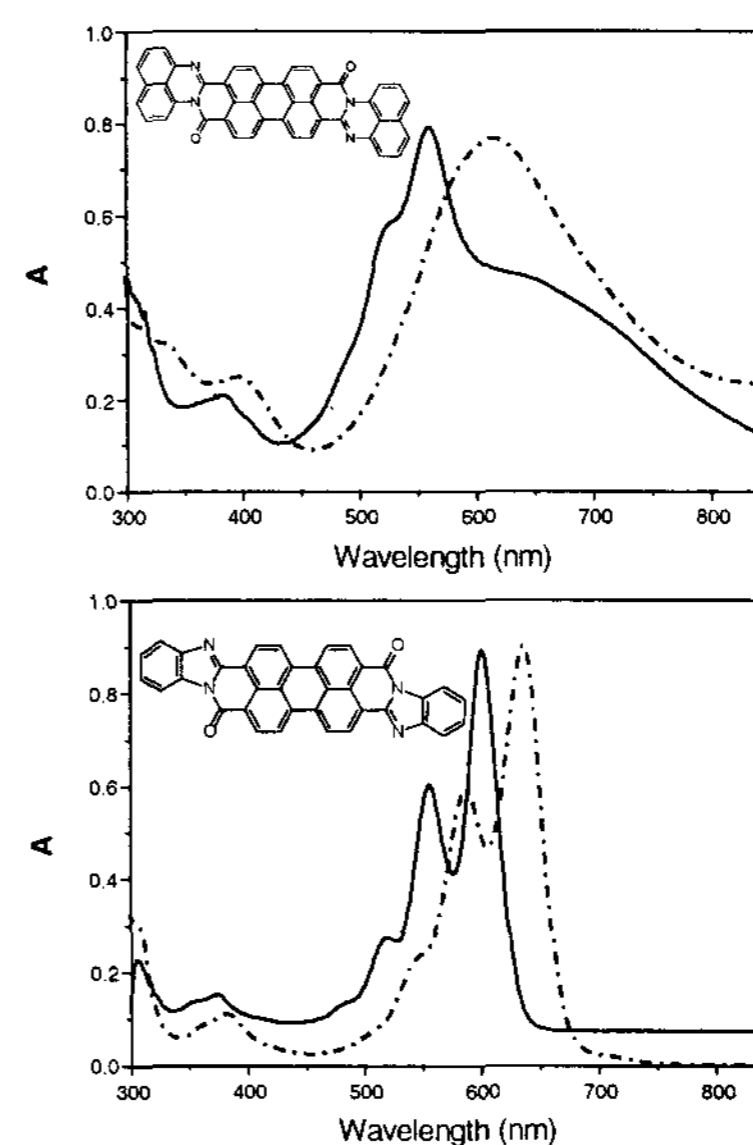


Figure 3. UV-vis spectra of pyrrolopyrone derivatives. (solid line: trifluoroacetic acid, dot line: sulfuric acid)

UV-vis spectrum of pyrrolopyrone derivatives showed in Figure 3 dissolved in sulfuric acid and trifluoroacetic acid. All products showed red shift in sulfuric acid solution. The maximum absorption peaks of the compound 1 and compound 2 are 562(sulfuric

acid), 615 nm(trifluoroacetic acid) and 556, 601(sulfuric acid), 588, 637 nm(trifluoroacetic acid), respectively.

Solution PL spectrum of compound 1 is illustrated Figure 4. The maximum emission peak is at 628 nm, which corresponds to red light.

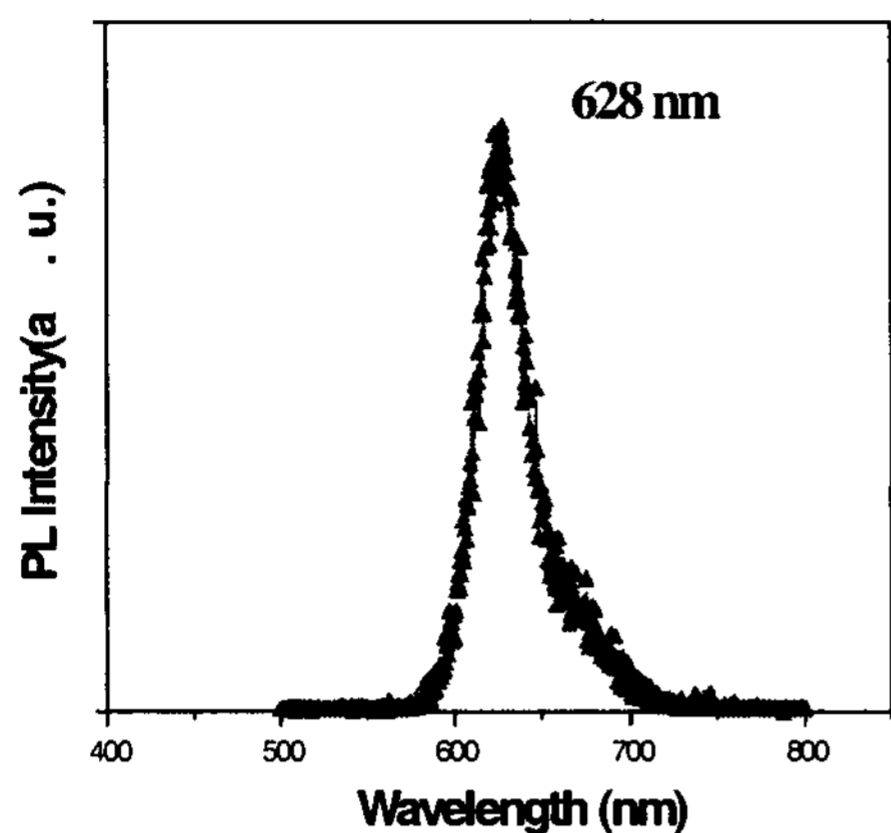


Figure 4. Solution PL spectrum of compound 2. (trifluoroacetic acid)

Thin film transistors were fabricated by vacuum deposition and solution casting and electron mobility of the device were measured.

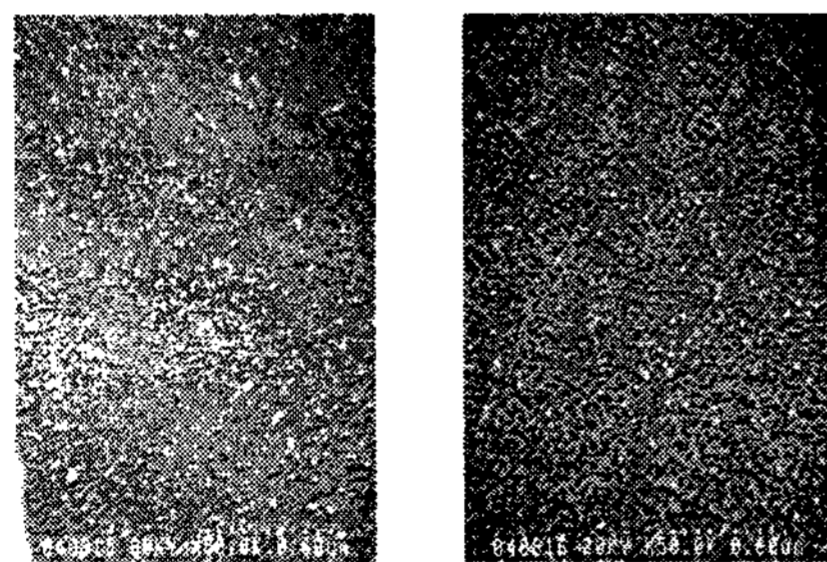


Figure 4. SEM micrographs of 500 Å thick films of compound 2 grown on SiO₂(left) and Au substrates(right).

Electron mobility was not detected for compound 1. However, in case of compound 2 the electron mobility was found resulting in a value of 10^{-6} cm²/Vs for vacuum deposition and 10^{-7} cm²/Vs for solution casting.

4. Acknowledgements

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5. References

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