Air stable organic semiconductors towards flexible organic field-effect transistors

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1. Introduction

Plastic electronics requires high performance as well as sustainable organic semiconductor materials. Many strategic syntheses of organic materials have been reported and investigated in their potential performance as active material for organic field-effect transistor. One of the issues is the stability as well as the low mobility for transport characteristics of organic semiconductors. Towards designing high stability of semiconductor characteristics in ambient atmosphere, large band-gap in the electronic structure is a possible important characteristics toward stable transport in ambient condition.

This paper introduces new functional materials, having stable p-type as well as n-type transport organic semiconductors. These provide possible candidates of materials for complimentary logic circuit on flexible substrate.

2. Experimental

Materials

Pyrene derivatives were synthesized according to the literature. In this study, thiophenes substituted pyrene compound were used for p-type semiconductor. A chemical structure used in this study is shown below.

Chemical structures of synthesize pyrene-thiophene (PyTP) derivatives

Absorption spectra

Absorption spectra were observed in chloroform solution. Doping characteristics were also investigated in the mixture of PyTP with tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).

Electrochemical characteristics

Electron affinity level(EA) was estimated with electrochemical procedure according with the following equation.

$$EA = E_{oxd}^{onset} + 4.4$$
 [eV]

Cyclicvoltammetry (CV) has been carried out in 0.1M Tetrabutylammonium tetrafluoroborate (TBABF₄) dissolved in dichloromethane. Absorption spectra were observed in chloroform solution. Doping characteristics were also investigated in the mixture of PyTP with tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).

Device fabrication

Top contact OFET was fabricated in this study. Pyrene derivatives were deposited on 300nm thick SiO₂ coated p-doped Si wafer as substrate, which was supplied in the Center for Microelectronic Systems (CMS), Kyushu Institute of Technology. Capacitance of 10nF/cm² was used for estimating field-effect mobility. Si/SiO2 substrates were silanized with octade-cyltrichlorosilane (ODTS). A flexible OFET was also fabricated by using polyethylene naphthalate (PEN) film (Teijin DuPont, Teonex). Polyimide (PI) was used for gate-insulator (Kyocera Chemical, KEMIT-ITE). Au electrodes were vacuum deposited on top of the organic semiconductor through a Ni shadow mask, by which source and drain electrodes with 20um long and 2mm wide channel. For investigating the hole

injection effect, F4-TCNQ buffer layer was also deposited underneath the Au electrodes.

PyTP was deposited in vaccuo at 4 x 10⁻⁶ torr, by which a 50nm thick organic layer was formed on Si/SiO₂ substrate.

3. Results and Discussion

Figure 1 shows solution spectra of PyTP, PyTP with F4-TCNQ and F4-TCNQ dissolved in chloroform.

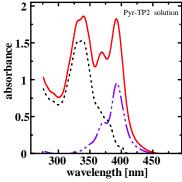


Figure 1. Absorption spectra of mixture of PyTP with F4-TCNQ (solid line) and PyTP solution (dotted line) and F4-TCNQ solution (dot-dash line), respectively.

As can be seen in this Fig., the mixture solution shows a simple addition of both spectra, indicating that there is no clear CT in this system. LUMO level of F4-TCNQ being reported to be around 5.4 eV, the HOMO level of PyTP is possibly lower than that. A large band-gap of around 3.4 eV was estimated in PyTP.

CV measurement clarified the oxidation potential to be around 5.6 eV according with the estimation of HOMO level with onset voltage of the oxidation potential. These values are consistent with the absorption spectra.

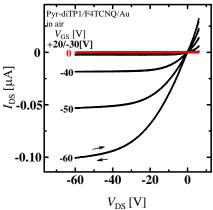


Figure 2: output characteristics of OFET consisted of PyTP as active layer with F4TCNQ/Au as top electrodes.

Figure 2 shows output characteristics of PyTP. It was found that very fine with no hysteresis characteristics were found. The results indicate that the PyTP possesses are very stable FET characteristics even in their electrostatic mode. This suggests that PyTP has a large potential utilizing for logic circuit holding a stable on state.

Large band-gap of PyTP will provide very stable p-OFET characteristics. Besides, hole injection was prevented. An acceptor buffer layer insertion will promote the hole injection in such large band-gap p-type transport organic semiconductor.

Table I: FET parameters with or w/o buffer layer

$\mu (x10^{-4} \text{ cm}^2/\text{Vs})$		$V_{ m th}({ m V})$	
w/o	F4-TCNQ	w/o	F4-TCNQ
1.9	2.3	-41	-25

Table I shows the FET parameters collected in OFETs consisted of PyTP as active layer. It was found that the insertion of F4-TCNQ layer promoted both of the threshold voltage as well as the field-effect mobility. Decrease of contact resistance possibly explains all those change in the FET performances

It was more emphasized that the mobility was almost stationary even after one moth exposure of the device in ambient condition. These facts indicate that PyTP is very stable in their semiconductor characteristics even in air exposure.

Stable semiconductor characteristics of PyTP promote more practical expansion of organic semi-conductor into electronic devices even in their low FET performances.

4. Conclusion

We developed an air stable organic semiconductor, pyrene-thiophene derivative. A large band-gap with low HOMO level was found in the material. Air stable transport characteristics will be attributed to their low HOMO level electronic structure.

Acknowledgements

The present study was financially supported by the Research Foundation for the promotion of Academic-Industrial collaboration Project, Kitakyushu City.