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# Material Design of Phenylenevinylene Oligomers for Organic Field-Effect Transistors

Tetsuo Tsutsui and Takeshi Yasuda

Institute for Materials Chemistry and Engineering, Kyushu University Kasuga-koen 6-1, Kasuga, Fukuoka 816-8580, Japan Phone: +81-92-583-7531 Email: tsutsui1020@fukuoka.email.ne.jp

#### 1. Introduction

In the application for organic field-effect transistors (OFETs), polycrystalline films of organic small molecules, such as acenes, heteroacenes, thiophene oligomers, fused oligothiophenes, thiophene-acene co-oligomers and so on, have been used. Thus, the molecular design of organic small molecules for OFETs has been focused on the intermolecular  $\pi$ - $\pi$  interactions, for high carrier mobility [1,2].

On the other hand, main-chain  $\pi$ -conjugated polymers, such as polythiophenes, polyphenylenes, polyfluorenes, and polyphenyvinlylenes, have been used for organic electronic devices. In the case of polythiophene derivatives for example, intermolecular  $\pi$ - $\pi$  stacking of aromatic rings has been assumed to be the origin of the high FET mobility, even though the traditional understanding of charge transport in linear extended  $\pi$ -conjugated chains is faster charge transport along extended  $\pi$ -electron systems [3]. In contrast, OFETs using polyfluorene derivatives, fast charge transport along main-chains have been reported [4]. For further understanding of the effect of inter-molecular  $\pi - \pi$ stacking and intra-molecular extended  $\pi$ -conjugation in OFETs, extended experimental studies and discussions based on well-defined model systems are required. In this paper, we focus our attention on one of the most popular and widely examined model skeletal structures, phenylenevinylene (PV).

### 2. Experimental

Variety of PV oligomers, unsubstituted PV oligomers with different numbers of repeat units, PV oligomers with attached donors or accepters, and PV oligomers with alkyl chain susbstitution were used. Typical examples of those oligomers used in this study are listed in Figure 1. OFETs were fabricated using a conventional vacuum sublimation, except for a few cases of spin-coating fabrication. In the cases of p-channel OFETs, fabricated devices were once exposed in an ambient condition and measurements were performed under vacuum. In the cases of n-channel OFETs, all experimental procedures were done under grove-box conditions with less than 1.0 ppm oxygen and water.

#### 3. Results and Discussion

The PV oligomer with methyl group at both ends (CH<sub>3</sub>-OPV) gave vacuum sublimed films composed of densely-packed submicron-size grains with a high degree of molecular order, in which long axis of oligomer chains was perpendicular to substrate. Field-effect hole mobilities as high as 0.13 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> were observed, indicating fast hole transport along the intermolecular  $\pi$ - $\pi$  stacking direction [5]. It was also shown that p-channel conduction in the oligo-PPVs changed to n-channel with the replacement of the methyl

group with trifluoromethyl group [6]. These observations were quite similar to those in conventional organic semiconductors.

Unsubstituted PV oligomer (3P2V) gave a FET hole mobility of  $5.7 \times 10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. When a substrate temperature was controlled at 45°C, the hole mobility increased up to 0.024. This meant that molecular order at the insulator-organic film boundary was the key to determine FET mobilities. The increase of the repeat units in PV oligomers brought about the increase of FET mobilities. 5P4V, for example gave the hole mobility of as high as 0.15 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>, which was comparable with that in CH<sub>3</sub>-OPV [7].

The addition of long alkyl chains in the ends of PV oligomers was effective for modifying processability of PV oligomers. In  $C_8H_{17}$ -OPV, a liquid crystalline phase

was observed above the 76°C, and annealing the vacuum-deposited film at 100°C was found to be effective for enhancing FET mobility. The hole mobility as high as  $0.15 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  was observed in C<sub>8</sub>H<sub>17</sub>-OPV [8].

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Figure 1. Chemical structures of phenylenevinylene oligomers used in this paper.