Crystal structure of parallel-stacked peryleneimides and their application to organic FET devices

Kazuyuki Sato, Jin Mizuguchi*, Yoshimasa Sakai**, and Shinji Aramaki**; *Graduate School of Engineering, Yokohama National University, Yokohama, Kanagawa/Japan and **Mitsubishi Chemical Group Science and Technology Research Center, Inc., Yokohama, Kanagawa/Japan*

Abstract

Organic field-effect transistors (FETs) have recently attracted attention mainly because of the low fabrication cost. Parallel-stacked structure is considered favorable for realizing a high mobility along the stacked direction in organic FETs. Among our dipyridyl-peryleneimides synthesized previously for H_2 sensors (OPP, MPP, and PPP), two derivatives (OPP and PPP) are found to crystallize in this structure and are expected to show better FET characteristics than MPP. Therefore, the FET characteristics have been studied in the present investigation from the standpoint of the crystal structure. The FET devices based upon OPP and PPP exhibit n-type characteristics, showing a relatively high mobility of about 10^{-5} cm^2/Vs and "on/off" ratios of about 10^2; whereas only poor performance was observed for the MPP-based FET.

Introduction

Organic field effect transistors (FETs) have attracted much attention in recent years because of their several potential applications such as large-area coverage, structural flexibility, and especially low cost electronic devices [1]. They have been under widespread development for active-matrix flat-panel displays, sensors, and radio-frequency identification tags (RFIDs), making use of their advantages. The field-effect mobilities, μ, of the FETs with organic molecules are still much lower than those of the conventional FETs based upon inorganic materials. Because of this, new organic materials are being extensively studied in an attempt to achieve FET devices with high μ value [2].

A recent publication on pentacene [3] has pointed out that a conductivity path is achieved along the stacking axis due to the orbital overlap and that the parallel-stack structure is therefore favorable for realizing a high mobility in organic semiconductors. However, the complete parallel-stack (*i.e.* complete "atom/atom" contact) seems to be rather improbable because of the repulsive interaction between perfectly parallel-stacked molecules as shown typically by the structure of paracyclophanes [4]. For example, [2.2]paracyclophane has two benzene rings which are rigidly held together by the ethano bridges in *para* positions as shown in Fig. 1(a). X-ray structure analysis revealed that the two benzene rings are heavily deformed due to repulsive "out of phase" interactions between atomic orbitals (Fig. 1(b)). For this reason, the molecules arrange themselves to minimize the repulsive interaction along the stacking axis, in such a way to slip as to slide in a fashion "herringbone" (Fig. 2(a)), or to rotate in manner "*quasi* parallel-stack" (Fig. 2(b)). The herringbone structure is quite common in most organic semiconductors; whereas the *quasi* parallel-stack is rather rare, but is expected to provide us with a high mobility.

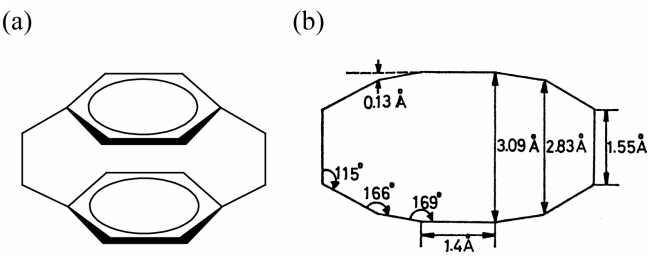

***Figure 1**. [2.2]Paracyclophane: (a) molecular conformation and (b) side view of the structure*

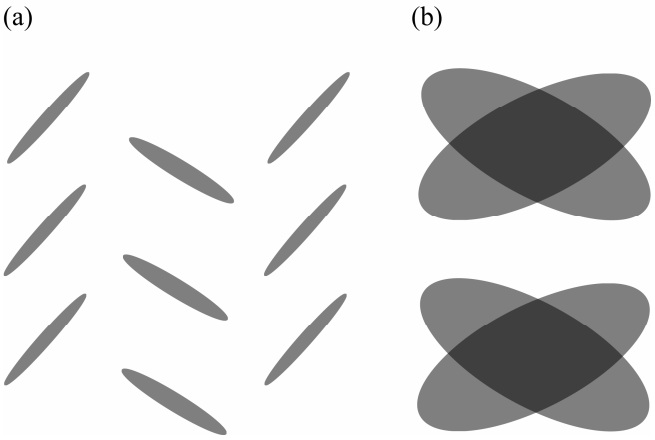

***Figure 2**. (a) "Herringbone" structure (side view) and (b) "quasi parallel-stack" structure (top view)*

We have previously synthesized novel dipyridyl-peryleneimide derivatives for H_2 gas sensors analyzed their crystal structure [5]. The pyridyl ring in which the N atom is positioned at the *ortho*, or *meta*, or *para* site is directly connected to the peryleneimide skeleton as shown in Fig. 3. These are called OPP, MPP, and PPP, respectively. Among these, OPP and PPP are found to crystallize in "*quasi* parallel-stack" structure. Therefore, we believed that OPP and PPP could basically exhibit better FET performance than MPP.

The objective of the present investigation is to study the FET characteristics of OPP, MPP, and PPP from the standpoint of the crystal structure.

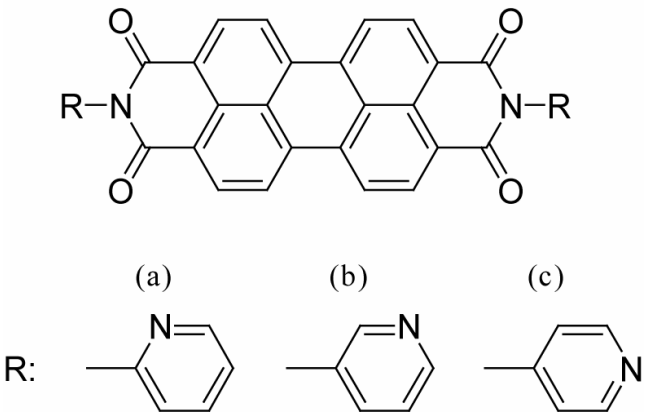

***Figure 3**. Molecular structure of peryleneimide derivatives: (a) OPP, (b) MPP, and (c) PPP*

Summary of the structure analysis

Table 1 details the crystallographic parameters for OPP [6], MPP [7], and PPP [8].

In the unit cell of OPP, there are two independent molecules, A and B. Both molecules A and B are characterized by C_i symmetry. Two pyridyl rings are twisted in the same direction with respect to the peryleneimide skeleton by 77.7° in molecule A and 72.8° in molecule B. Molecules A and B are stacked alternately with a tilt angle of about 39° shown in Fig. 4(a).

The molecule of MPP is characterized by C_i symmetry. Two pyridyl rings are twisted in the same direction by 54.9°. The molecules are stacked in a fashion "hunter's fence" (*viz.* when viewed from the side, the molecules, slipped by 45° within molecular stacks, cross each other in a fence like structure) along the *b* axis, as shown in Fig. 4(b).

Contrary to OPP and MPP molecules, the PPP molecule has C_2 symmetry. Therefore, two pyridyl rings are twisted in opposite directions by 74.5°. The molecules are stacked along the *c* axis with a tilt angle of 32° as shown in Fig. 4(c), and the molecular plane is exactly perpendicular to the stacking axis, showing a typical structure of "*quasi* parallel-stack".

Table 1: Crystallographic parameters for OPP, MPP, and PPP

	OPP (*ortho*)	MPP (*meta*)	PPP (*para*)
Formula	$C_{34}H_{16}N_4O_4$	$C_{34}H_{16}N_4O_4$	$C_{34}H_{16}N_4O_4$
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Pccn$
Molecular symmetry	C_i	C_i	C_2
Z	4	2	4
a (Å)	17.599(1)	15.422(2)	21.232(2)
b (Å)	7.1705(5)	3.8275(6)	15.890(2)
c (Å)	20.679(2)	19.282(3)	6.9311(8)
β (°)	111.004(5)	103.29(1)	-
Density (g/cm^3)	1.49	1.63	1.55
R_1	0.062	0.039	0.074

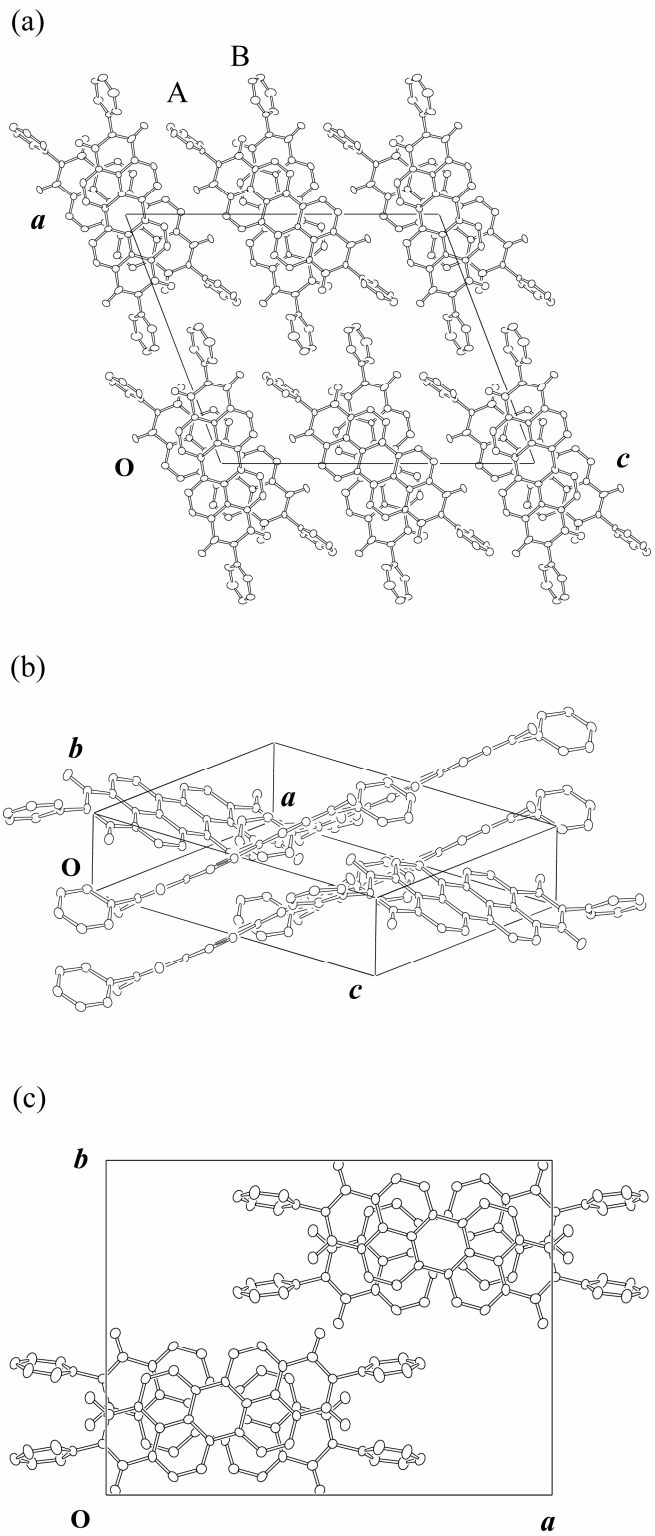

***Figure 4.** Molecular arrangement: (a) projection of OPP on to the (010) plane, (b) the packing arrangement of MPP, and (c) projection of PPP onto the (001) plane*

Experimental

Synthesis and purification of the material

OPP was synthesized by reaction of perylenetetracarboxylic dianhydride with 2-aminopyridine at 490 K in dimethylnaphthalene for 3 hours [9]. Likewise, MPP and PPP were synthesized with 3-aminopyridine and 4-aminopyridine, respectively. The products were purified three times by sublimation at 750 K, using a two-zone furnace [10].

Fabrication of the FET

The FET structure is depicted as shown in Fig. 5. A SiO_2-layer of about 300 nm was thermally grown on heavily doped *n*-type Si-substrate which serves as the gate electrode. On top of SiO_2, the source and drain electrodes made of Au/Cr were prepared by photolithographic technique. The channel length and the channel width are was 10 and 500 μm, respectively. After that, each thin layer of peryleneimides was applied by vacuum evaporation to the thickness of about 70 nm at room temperature (Tokyo Vacuum Co. Ltd.: model EG240).

The *I-V* characteristics of the FETs were measured at room temperature under vacuum on an Agilent 4155C semiconductor parameter analyzer.

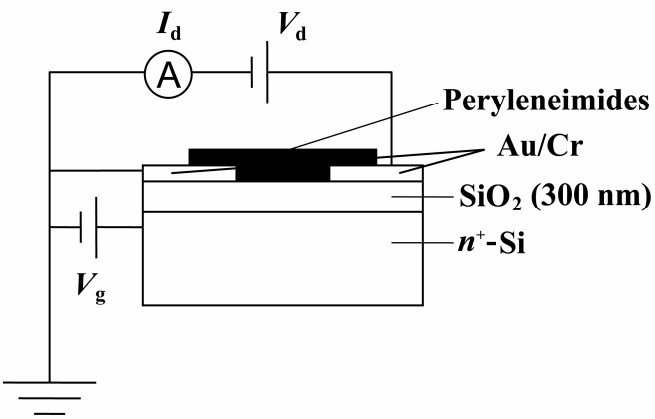

Figure 5. *Device structure of organic FET*

Results and Discussion

FET characteristics

Figure 6(a) shows the "drain current"-"drain voltage" (I_d-V_d) plot based upon OPP, which is typical of the FET characteristics composed of a linear region at low V_d and a saturation region at a high V_d. The positive sign of both the drain and gate voltage (V_d and V_g) indicates an electron transport. The mobility (μ) calculated from the slope of the $I_{sat}^{1/2}$-V_g plot in the saturated region is 8.1×10^{-6} cm^2/Vs, and the threshold voltage V_t of the devices is 4.2 V. Furthermore, the "on/off" ratio is 150 in OPP that is defined as the ratio of the drain current at V_g = 50 V to that at V_g = 30 V while the drain voltage is kept constant at V_d = 30 V.

Figure 6(b) shows I_d-V_d plot of the FET based upon MPP. The drain current increases nearly linearly and no saturation is recognized at higher drain voltages. Consequently, the "on/off" ratio is quite small. This result suggests that the interface between the electrode and MPP makes an ohmic contact, indicating that the inversion layer is not formed under the applied gate voltage.

Figure 6(c) shows I_d-V_d plot of the FET based upon PPP. The present FET characteristic is quite similar to those of OPP. The FET is of the *n*-type and the mobility, V_t, and the "on/off" ratio are 2.2×10^{-6} cm^2/Vs, 4.6 V, and 46, respectively.

The above results show clearly that the FET devices based upon OPP and PPP are by far superior to that of MPP. In other words, the *quasi* parallel-stack structure is effective in improving the mobility value.

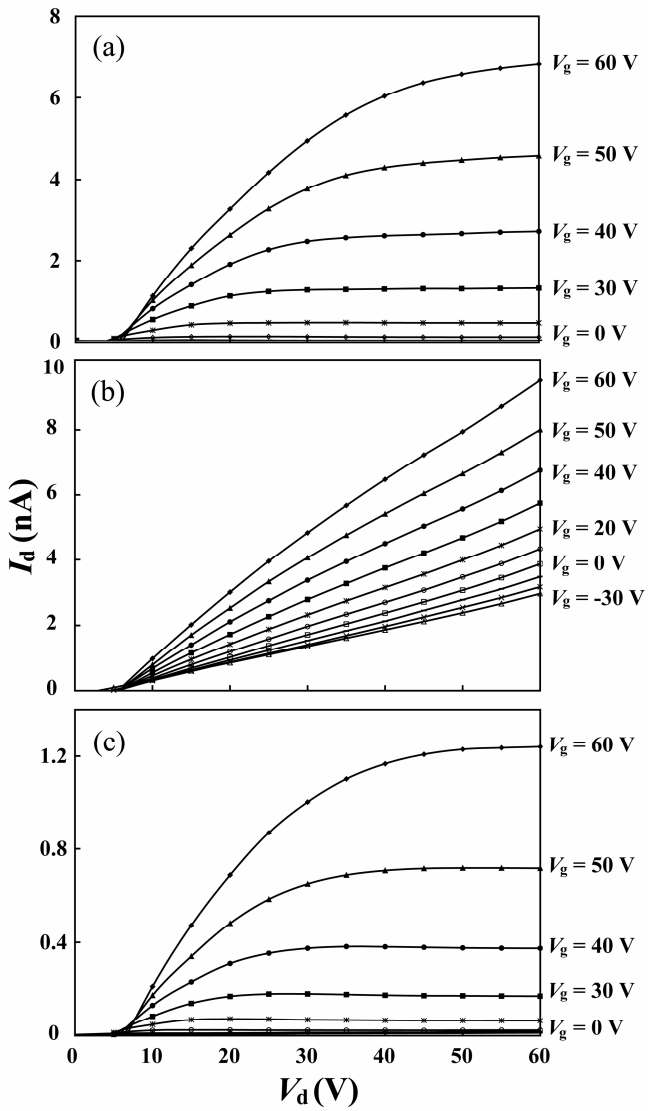

Figure 6. *I-V characteristics of FETs: (a) OPP, (b) MPP, and (c) PPP*

Conclusions

Organic FETs have been fabricated on the basis of three kinds of peryleneimide derivatives: OPP, MPP, and PPP. OPP and PPP, which possess "*quasi* parallel-stack" structure, exhibit *n*-type characteristics, showing a relatively high mobility of about 10^{-5} cm^2/Vs and "on/off" ratio of about 100. OPP and PPP with *quasi*

parallel-stack structure are found to show significantly better FET characteristics than MPP with absence of the parallel-stacked structure.

References

[1] C. D. Dimitrakopoulos and P. R. L. Malenfant: Organic Thin Film Transistors for Large Area Electronics, Adv. Mater., 14, 99 (2002).

[2] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radik, and W. Weber: High mobility polymer gate dielectric pentacene thin film transistors, J. Appl. Phys., 92, 5259 (2002).

[3] J. H. Schön, Ch. Kloc, and B. Batlogg: Hole transport in pentacene single crystals, Phys. Rev. B, 63, 245201 (2001).

[4] A. Ishitani and S. Nagakura: Electronic absorption and electron spin resonance spectra of the benzene and paracyclophane anions, Mol. Phys., 12, 1 (1967).

[5] K. Sato, K. Hino, H. Takahashi, and J. Mizuguchi: Hydrogen gas sensor based upon perylene-imide derivatives, Int. J. Intell. Syst. Technol. Appl., 3, 52 (2007).

[6] J. Mizuguchi, K. Hino, K. Sato, H. Takahashi, and S. Suzuki: *N*,*N*'-Di–2–pyridylperylene-3,4:9,10-bis (dicarboximide), Acta Cryst., E61, o437 (2005).

[7] J. Mizuguchi, K. Hino, K. Sato, H. Takahashi, and S. Suzuki: *N*,*N*'-Di–3–pyridylperylene-3,4:9,10-bis (dicarboximide), Acta Cryst., E61, o434 (2005).

[8] K. Hino, K. Sato, H. Takahashi, S. Suzuki, and J. Mizuguchi: *N*,*N*'-Di–4–pyridylperylene-3,4:9,10-bis (dicarboximide), Acta Cryst., E61, o440 (2005).

[9] M. Herbst and K. Hunger: Industrial Organic Pigments (Third Edition), (VCH, Weinheim, 2004).

[10] J. Mizuguchi: Electronic characterization of *N*,*N*'-bis(2-phenylethyl)perylene-3,4:9,10-bis(dicarboximide) and its application to optical disks, J. Appl. Phys., 84, 4479 (1998).

Author Biography

Kazuyuki Sato received his Bachelor of Engineering in 2005 and his Master of Engineering in 2007, both from Yokohama National University. He is currently in the PhD course for applied physics at the same university. His research interest includes structure analysis of organic pigments and their electronic applications.