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Air-stable ambipolar organic field effect transistors with heterojunction of pentacene and N,N' -bis(4-trifluoromethylben-zyl) perylene-3,4,9,10-tetracarboxylic diimide*

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Fabrication of ambipolar organic field-effect transistors (OFETs) is essential for the achievement of an organic complementary logic circuit. Ambipolar transports in OFETs with heterojunction structures are realized. We select pentacene as a P-type material and N,N'-bis(4-trifluoromethylben-zyl)perylene-3,4,9,10-tetracarboxylic diimide (PTCDI-TFB) as a n-type material in the active layer of the OFETs. The field-effect transistor shows highly air-stable ambipolar characteristics with a field-effect hole mobility of 0.18 $cm^2/(V{\cdot}s)$ and field-effect electron mobility of 0.031 $cm^2/(V{\cdot}s)$. Furthermore the mobility only slightly decreases after being exposed to air and remains stable even for exposure to air for more than 60 days. The high electron affinity of PTCDI-TFB and the octadecyltrichlorosilane (OTS) self-assembly monolayer between the SiO_2 gate dielectric and the organic active layer result in the observed air-stable characteristics of OFETs with high mobility. The results demonstrate that using the OTS as a modified gate insulator layer and using high electron affinity semiconductor materials are two effective methods to fabricate OFETs with air-stable characteristics and high mobility.

Keywords: organic heterojunction transistors, ambipolar, air-stable, high electron affinity
PACC: 7280L,7360,7340Q

1. Introduction

Organic field effect transistors (OFETs) have attracted considerable attention due to their extensive applications, such as radiofrequency identification tags, display drivers, smart cards and sensor arrays. A feature of almost all organic semiconductors is that even in their undoped state, often only unipolar transport,[1−10] i.e. either hole transport or electron transport, can be realized. The simultaneous transport of both types of carriers, however, could lead to a simplification in designing complementary logic circuits, which reduces power consumption and increases margins. As a consequence, a lot of effort has been made to fabricate and optimize the ambipolar OFETs.[11−15] The majority of ambipolar organic transistors so far are demonstrated based on bulk heterojunction systems where an electron transporting (n-channel) material is blended with a hole transporting(p-channel) material to form the heterogeneous ambipolar semiconductive layer. Bilayer-type ambipolar organic transistors based on the p/n heterostructure concept have also been demonstrated.

Pentacene ($C_{22}H_{14}$) has demonstrated the highest hole mobility of organic small molecules. Their planar shapes facilitate crystal packing and the extended π system over molecules enables the intermolecular overlap of the π system. The mobility of the single crystal pentacene could increase to 58 $cm^2/(V{\cdot}s)$ at 225 K and 35 $cm^2/(V{\cdot}s)$ at room temperature.[16] This property can compete with that of amorphous hydrogenated silicon (α-Si:H).

Perylene diimides (PTCDI) are among the most promising n-channel candidates due to their high elec-

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tron affinity and the large π-orbital overlap in the solid state. In contrast to their mother compound, perylene tetracaboxylic dianhydride (PTCDA), electron withdrawing substituents can be introduced at the imide nitrogen of PTCDI to stabilize field-induced electron transport by lowering the lowest unoccupied molecular orbitals (LUMO) of the resulting molecule. N,N'-bis(4-trifluoromethylben-zyl)perylene-3,4,9,10-tetracarboxylic diimide (PTCDI-TFB) is one of the air-stable n-type organic semiconductor materials with high mobility.[17]

The interface between the organic active layer and the gate dielectric material is a critical part of the field-effect device. Therefore, many methods of modifying the inorganic/organic interface were explored to improve the growth of ordered vapour deposited films. The characteristics of OTFTs can be improved by using a self-organizing material like OTS between the SiO_2 gate dielectric and the organic active layers.[18] The silane coupling agent octadecyltrichlorosilane (OTS) is a particularly interesting material because it can bond to oxide surfaces and has the ability to form a Si–O–Si bond which can influence the characteristics of insulator films. The OTS self-assembly monolayer not only depresses the surface roughness of the SiO_2 film but also reduces the leakage current, thereby acting as another insulator layer.

In this paper, we focus on the dependence of carrier transport characteristics on the heterostructure of ambipolar OFETs using PTCDI-TFB and pentancene as p- and n-type organic semiconductors, respectively. We succeed in observing ambipolar carrier transport in the OFET performances. The hole mobility and the electron mobility are as high as 0.18 $cm^2/(V{\cdot}s)$ and 0.031 $cm^2/(V{\cdot}s)$ in the saturation region, respectively. Furthermore, the OFETs exhibit long-term air-stable characteristics.

2. Experiment

The chemical structure of PTCDI-TFB and its relevant energy levels are schematically shown in Fig.1. The structure of top-contact OFET based on an PTCDI-TFB/pentacene heterostructure is shown in Fig.2. A heavily p-doped Si wafer with an aluminum back contact acts as a gate electrode and substrate. The gate insulator consists of a thermally grown SiO_2 layer with a thickness of 250 nm. The substrate, immersed in a 1:1 mixture of concentrated H_2SO_4 and H_2O_2 (30% water solution) for 10 min, was washed separately in hot and cold de-ionized water several times and dried in an infrared oven. Then the SiO_2 surface was treated with OTS by immersing the sample in a 0.5% solution of CH_3Cl:C_6H_{12} (1:3) for 12 h at room temperature in an anhydrous ambient. This process is shown in Fig.3. The cleaning process took place under the irradiation of UV, which is an important step to activate a Si–OH bond and make the reaction process easy. A 40 nm thick pentacene film was first deposited at a substrate temperature of about 60 °C, a base pressure of 5×10^{-4} Pa and a growth rate of 0.05 nm/s. For an ambipolar operation, a 30 nm thick PTCDI-TFB layer was then sublimed onto the pentacene at a substrate temperature of 60 °C, a rate of 0.05 nm/s and a base pressure of 5×10^{-4} Pa.

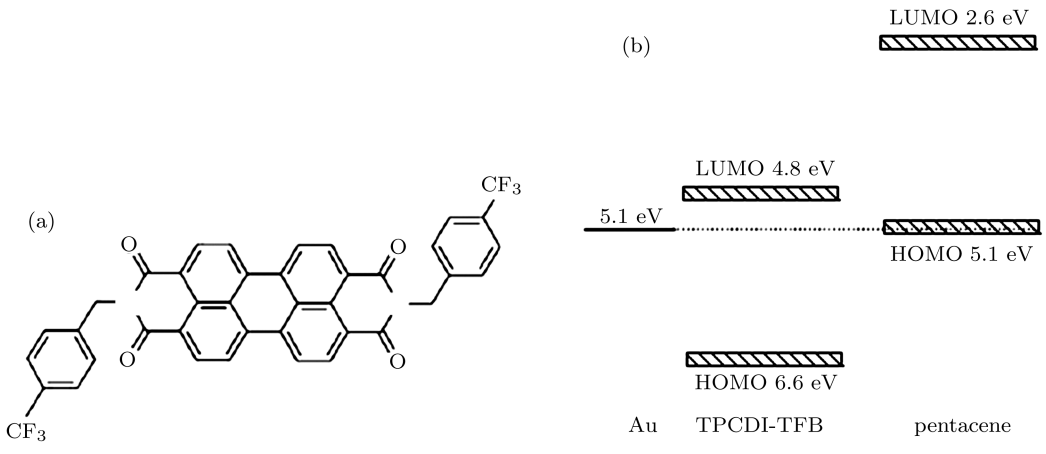


Fig.1. Chemical structures of PTCDI-TFB (a) and molecular orbital energy level diagram for PTCDI-TFB, pentacene and gold (b).

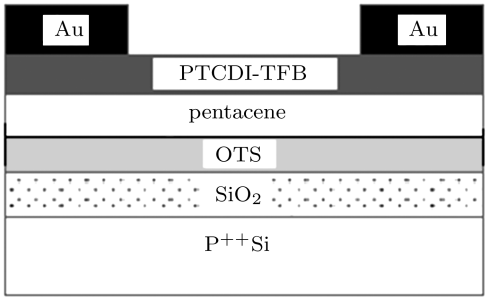


Fig.2. Schematic structure of OFET based on an PTCDI-TFB/pentacene heterostructure.

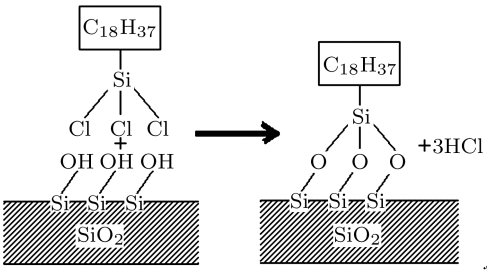


Fig.3. Chemical process between OTS and the surface of OH.

The electron mobility of the PTCDI-TFB thin film on SiO_2 is generally lower than the hole mobility of the pentacene thin film on SiO_2. In the case of hole transport, carriers are injected from the source/drain electrodes into pentacene through the PTCDI-TFB layer which acts as a charge injection barrier. Therefore, the thickness of the PTCDI-TFB thin film must be carefully controlled within a range of 30–45 nm.[18] Note that even though the field-induced two-dimensional (2D) charge channel is independent of the PTCDI-TFB film thickness, experimentally efficient n-channel operation requires films to be about 30 nm thick or more. Finally, Au source and drain electrodes each with a thickness of 100-nm were separately vacuum-deposited through a shadow mask. The current–voltage characteristics of OFETs were measured by using a piece of transistor detection equipment which is made by ourselves. All experiments were carried out in air at room temperature.

3. Results and discussion

Figure 4 shows source–drain current (I_D) vs source–drain voltage (V_{DS}) characteristics of OFET with a bi-layer heterostructure under several different negative and positive gate voltages. It can be seen that the gate voltage V_G can typically control the value of the source-drain current I_D. A typical ambipolar operation can be observed. The P-channel operational characteristics of the ambipolar FET are different from those of FET with only a pentacene layer. At negative gate voltage $|V_G| < 30$ V, unusual characteristics are observed. When V_{DS} is negatively increased, a steep increase in current is observed without current saturation for $|V_{DS}| - |V_G| > 20$ V. Such a steep increase in current is a typical characteristic of ambipolar operation in OFETs.[19,20] This suggests that an n-channel is formed in the PTCDI-TFB molecules due to the electron injection from the drain electrode. In this voltage range with $|V_{DS}| - |V_G| > 20$ V, the gate contact is biased positively with respect to the drain contact. As the drain contact is energetically favourable for electron injection into PTCDI-TFB, an accumulation layer of electrons is expected to form in the PTCDI-TFB layer on the pentacene layer. Therefore, the current increase is attributed to the injection of electrons into the PTCDI-TFB layer and the transport of electrons in a channel formed close to the pentacene layer. Similarly, at positive gate voltages, i.e. $|V_G| > 30$ V, n-channel operational characteristics of the ambipolar FET identical to those of FET with only one PTCDI-TFB layer are observed. For $|V_G| < 30$ V and $|V_{DS}| - |V_G| > 40$ V, an increase in nonsaturated I_{DS} can also be observed, which originates from drain-induced holes. The carrier mobility (μ) of the ambipolar FET in the saturation regime may be estimated from the relation between the saturated source-drain current $I_{DS,sat}$ and V_G,

$$I_{DS,sat} = \frac{W}{2L}\mu C(V_G - V_T)^2. \quad (1)$$

Here, W represents the channel width of 8 mm, L the channel length of 200 μm, μ the field-effect mobility, C the gate capacitance per unit area of the double insulating layer. The capacitance of the double insulating layer could be considered as two capacitors in series. The corresponding value of the effective capacitance is 8 nF/cm^2. Moreover, the threshold voltage V_T is derived from the linear slope of the square root of I_{DS} vs V_G represented by the abscissa in Fig.5. From drain current–voltage (I_D–V_{DS}) characteristics shown in Fig.4, the field-effect hole mobility of 0.18 cm^2/(V·s) and the electron mobility of 0.031 cm^2/(V·s), can be extracted from the saturation region. These values are less than those of the single layer structure. It is known that mobilities of the bi-layer structure devices tend to lower because

the morphology of the first organic layer is changed by the deposition of the second organic layer. In addition, it is unclear whether formula (1) is applicable for this system, because the gate electric field may not sufficiently influence the second organic layer.

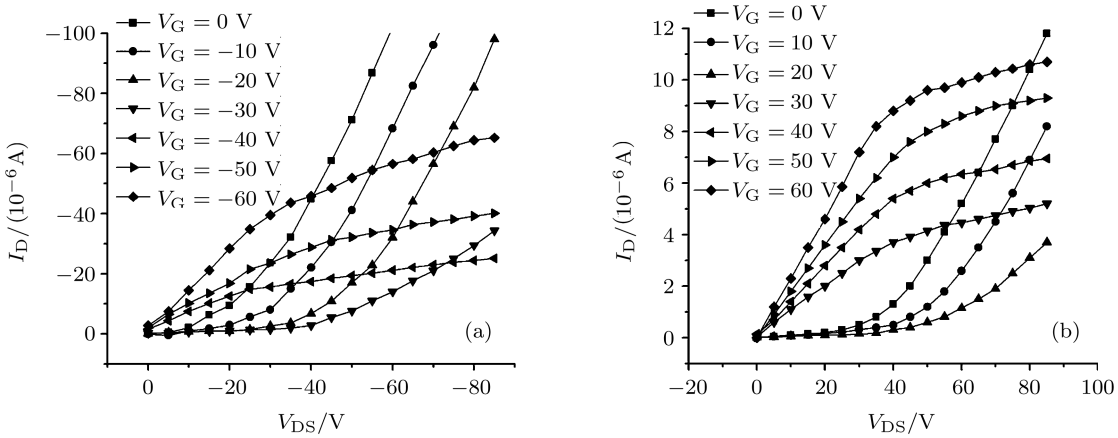


Fig.4. Drain current–voltage (I_D–V_{DS}) characteristics of a heterostructure OFET working separately in hole-enhancement mode (a) and in electron-enhancement mode (b).

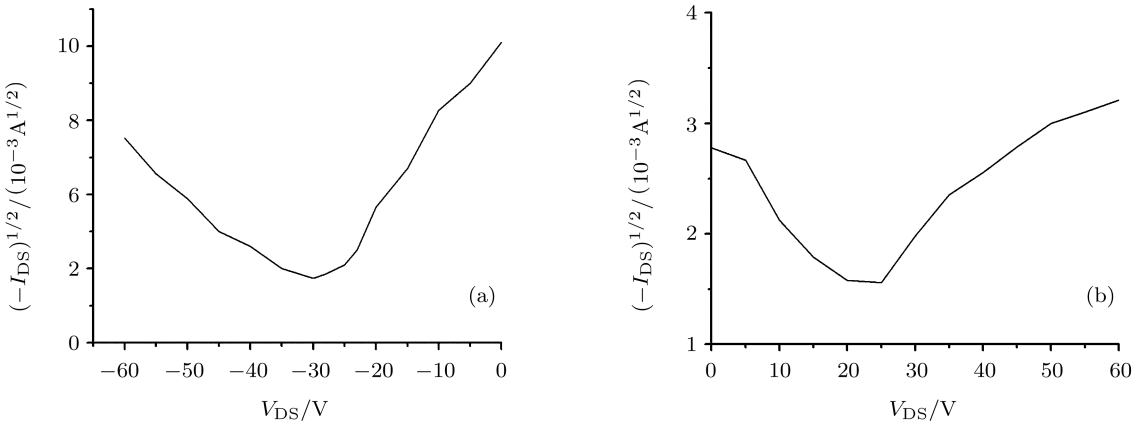


Fig.5. Transfer characteristics of heterojunction FET separately under positive and negative gate biases. (a) $V_{DS} = -60$ V, (b) $V_{DS} = 60$ V.

From Figs.6(a) and 6(b) it can be seen that the OTS-treated SiO_2 layer is flater than the bare SiO_2 layer and a considerable difference in surface roughness is observed and the OTS shows rather good surface modification. The OTS layer improves the surface roughness of the SiO_2: the roughness of the insulator is critical to the performance of OFETs. It is well known that the smooth surface is favourable for the growth of an organic thin film active layer. The OTS hydrophobic surface also makes less bipolar and increases the adhesion of the organic semiconductor to the substrate, which minimizes traps and defects at the interface between the insulator and the organic semiconductor for better carriers transportation.

The air stability of these ambipolar OFETs was monitored by measuring the performance as a function of time (Fig.7). The OFET device was stored in dark and ambient laboratory air conditions. Compared with the initial value, the mobility shows a reduction of 3.2% for electrons and 2.1% for holes after a storage for 10 days, but no further change was observed even after a storage for more than 60 days. It can be seen from Fig.7 that the ambipolar OFETs exhibit long-term air-stable characteristics. There exist several possible mechanisms explaining the stable operation of the OFET in air. 1) As reported earlier, the air stability of PTCDIs FETs is thought to be strongly related to the molecular packing and morphology of the thin films. The densely packed PTCDI cores together with the closely packed fluorocarbon may provide a kinetic barrier for the diffusion of O_2 and H_2O into the channel region.[21,22] 2) Cosseddu *et al*[23] have recently shown that the use of a pentacene

layer on the dielectric polymer can improve the n-type transport due to the fact that n-type material grows more uniform crystalline. 3) A comparison between the electron affinities and air stabilities indicates that OFETs based on n-type materials with electron affinities above 4.6 eV operate stably in air.[24−33] The high electron affinity of PTCDI-TFB with 4.8 eV, which prevents the injected electrons in the OFETs from being caught by traps resulting from environmental contaminants such as O_2 and H_2O that have penetrated into the channel region. 4) The OTS self-assembly monolayer improves the organic/inorganic interface, which optimizes the growth behaviour of the organic semiconductor. The outstanding air-stability may make this transistor an attractive candidate for organic CMOS IC.

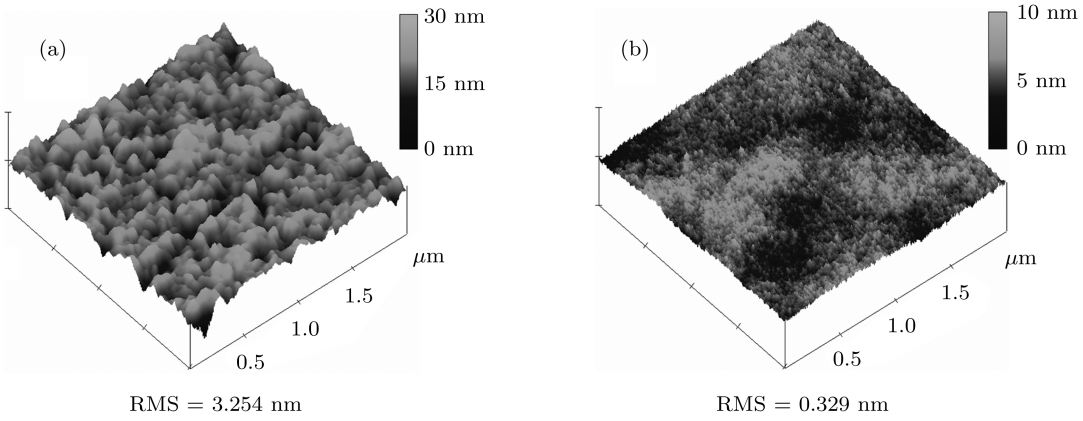


Fig.6. AFM images of the OTS-untreated SiO_2 surface (a) and the OTS-treated SiO_2 surface (b).

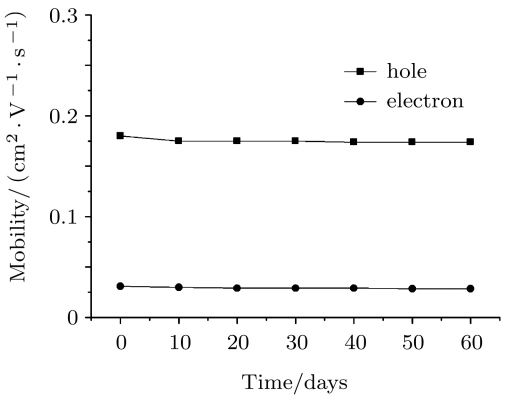


Fig.7. Field-effect mobilities of electron and hole vs time for the ambipolar OFETs to be stored in dark and ambient laboratory air conditions.

4. Conclusions

We have demonstrated highly air-stable ambipolar OFETs based on a pentacene and PTCDI-TFB heterostructure. The hole mobility and the electron mobility are as high as 0.18 $cm^2/(V{\cdot}s)$ and 0.031 $cm^2/(V{\cdot}s)$ in the saturation region, respectively. In particular, the ambipolar OFETs exhibit air-stable operation. There exist several versions that can account for the observed air-stable characteristics of the OFET, i.e. the OTS self-assembly monolayer improves the interface between the gate insulator and organic semiconductor; the use of a pentacene layer on the dielectric polymer can improve the PTCDI-TFB transport due to the fact that PTCDI-TFB material grows more uniform crystalline; the high electron affinity of PTCDI-TFB probably avoids the capture of the injected electrons by the traps resulting from environmental contaminants such as O_2 and H_2O that have penetrated into the channel region. The results demonstrate that using the OTS as a modified gate insulator layer and using the high electron affinity semiconductor materials are effective methods to fabricate OFETs with air-stable characteristics.

References

[1] Xie Y Q, Guo J H, Peng J B, Cao Y and Wang Y 2005 *Acta Phys. Sin.* **54** 3424 (in Chinese)

[2] Lü W, Peng J B, Yang K X, Lan L F, Niu Q L and Cao Y 2007 *Chin. Phys.* **16** 1145

[3] Zhou J G, Yang K X, Zhou J L, Peng J B and Cao Y 2007 *Jpn. J. Appl. Phys.* **46** 913

[4] Zhou J L, Zhang F J, Lan L F, Wen S S and Peng J B 2007 *Appl. Phys. Lett.* **91** 253507

[5] Yuan G C, Xu Z, Zhao S L, Zhang F J, Jiang W W, Huang J Z, Song D D, Zhu H N, Huang J Y and Xu X R 2008 *Acta Phys. Sin.* **57** 5911 (in Chinese)

[6] Dong G F, Liu Q D, Wang L D and Qiu Y 2008 *Chin. Phys. Lett.* **25** 3375

[7] Tao C L, Zhang X H, Dong M J, Liu Y Y, Sun S, Ou G P, Zhang F J and Zhang H L 2008 *Chin. Phys.* B **17** 0281

[8] Yuan G C, Xu Z, Zhao S L, Zhang F J, Jiang W W, Song D D, Zhu H N, Li S Y, Huang J Y, Huang H and Xu X R 2008 *Chin. Phys.* B **17** 1887

[9] Lu X F, Majewski L A and Song A M 2008 *Organic Electronics* **9** 473

[10] Cao Q J, Zhang Y M, Zhang Y M, Lu H L, Wang Y H, Chang Y C and Tang X Y 2007 *Chin. Phys.* **16** 1097

[11] Yuan G C, Xu Z, Zhao S L, Zhang F J, Jiang W W, Song D D, Zhu H N, Li S Y, Huang J Y, Huang H and Xu X R 2008 *Chin. Phys.* B **17** 1887

[12] Yamane K, Sawamoto A, Hotta S and Yanagi H 2008 *Thin Solid Films* **516** 2758

[13] Shi J W, Wang H B, Song D, Tian H K, Geng Y H and Yan D H 2008 *Thin Solid Films* **516** 3270

[14] Sakanoue T, Yahiro M, Adachi C, Takimiya K and Toshimitsu A 2008 *J. Appl. Phys.* **103** 094509

[15] Rongbin Y, Mamoru B, Kazunori S and Kunio M 2008 *Solid-State Electronics* **52** 60

[16] Dodabalapur A, Torsi L and Katz H E 1995 *Science* **268** 270

[17] Hosoi Y, Tsunami D, Ishii H and Furukawa Y 2007 *Chem. Phys. Lett.* **436** 139

[18] Lin Y Y, Gundlach D J, Nelson S F and Jackson T N 1997 *IEEE Trans. Electron Devices* **44** 1325

[19] Meijer E J, Leeuw D W, Veenendaal E, Huisman B H and Blom P W M 2003 *Nat. Mater* **2** 678

[20] Dodabalapur A, Katz H E, Torsi L and Haddon R C 1996 *Appl. Phys. Lett.* **68** 1108

[21] Jones B A, Ahrens M, Yoon M H, Faceehetti A, Marks T J and Wasielewski M R 2004 *Angew. Chem.* (Int. Ed.) **43** 6363

[22] Dimitrakopoulos C D and Malenfant PR L 2002 *Adv. Mater.* **14** 99

[23] Cosseddu P, Bonfiglio A, Salzmann I, Rabe J P and Koch N 2008 *Organic Electronics* **9** 191

[24] Wheland R C and Gillson J L 1976 *J. Am. Chem. Soc.* **98** 3916

[25] Brown A R, Leeuw D M, Lous E J and Havinga E E 1994 *Synth. Met.* **66** 257

[26] Peisert H, Knupfer M, Schwieger T, Fuentes G G, Olligs D, Fink J and Schmidt T 2003 *J. Appl. Phys.* **93** 9683

[27] Allemand P M, Koch A and Wudl F 1991 *J. Am. Chem. Soc.* **113** 1050

[28] Kobayashi S, Takenobu T, Mori S, Fujiwasa A and Iwasa Y 2003 *Appl. Phys. Lett.* **82** 4581

[29] Malenfant P R L, Dimitrakopoulos C D, Gelorme J D, Kosbar L L, Graham T O, Curioni A and Andreoni W 2002 *Appl. Phys. Lett.* **80** 2517

[30] Sakamoto Y, Suzuki T and Kobayashi M 2004 *J. Am. Chem. Soc.* **126** 8138

[31] Inoue Y, Sakamoto Y, Suzuki T, Kobayashi M, Gao Y and Tokito S 2005 *Jpn. J. Appl. Phys.* **44** 3663

[32] Facchetti A, Mushrush M, Katz H E and Mark T J 2003 *Adv. Mater.* **15** 33

[33] Facchetti A, Yoon M H , Stern C L, Hutchison G R, Ratner M A and Marks T J 2004 *J. Am. Chem. Soc.* **126** 13480