Study of the Derivatives of Benzimidazole and Applications For Organic Thin Film Transistor

An-Chi Yeh

Department of Chemical and Material Engineering, Chengshiu University
No. 840, Chengcing Rd., Niaosong Dist., Kaohsiung City 83347, Taiwan R.O.C. acyeh1965@yahoo.com.tw

Abstract: This article reviews the development of the derivatives of benzimidazole and applications for organic thin film transistor. With special molecular structure that causes the gathering of holes by electric field can increase the carriers' mobility up to practical application stage.

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Keywords: organic thin film transistor; benzimidazole

I. Introduction

In recent years, the materials combined with the activity of organic semiconductor field effect that can be used for organic thin film transistors (OTFTs) are being extensively studied. Originally, it was considered in some of the initial stage of slow response or more low-end products such as gas detectors, flexible detector, electronic paper, smart card and electronic label tags. However, due to the efforts of researchers, the technology of developing new materials has been improved in synthesis of the field effect that causes carrier mobility increasing up to 0.5 ~ 2.4 cm^2/Vs [1]. This carrier mobility is higher than amorphous silicon rate (0.5 cm^2/Vs) and reaches the practical stage. It can be applied as control elements for the pixel-access devices in active matrix displays, flat panel display applications target [2], such as liquid crystal display light valve control device (TFT-LCD) and light-emitting display pixel circuit control circuit (TFT-OLED). The amazing activity based on recent reports that the organic material (Pentacene) of the carrier mobility was substantially increased to $10^5 cm^2/Vs$ [3]. It is not only beyond the low-temperature poly silicon (300 ~ 500cm^2/Vs) but also can compete with single crystal silicon. A new revolution for the material engineering and the development by the impending changes, the applications can be directly for the logic memory arrays, logical devices such as registers, processor and the integrated circuit etc.. Most of the silicon semiconductor industries can not develop the silicon products to the flexible substrate IC (Integrated circuits on flexible substrate) system. Even through pentacene molecule can only be obtained the phonon scattering [4, 5] at low temperature (10K), it is still excellent to reflect the capability of organic active materials being combined with a broad delocalization π-electron charges and which is very useful for the applications to the electronic transistor.

II. The Development of New Materials

Based on the molecular structure, materials used for organic thin film transistor can be classified into five categories including (1) aromatic rings class (2) Thiophenes (3) compounds containing electron-donating groups (4) compounds containing electron withdrawing groups and (5) metal complexes of these compounds. The first kind of organic materials is currently the best performing compounds. The typical one is Pantacene. At room temperature, the mobile rate could reach to 3.2 cm^2 / Vs. The majority of this kind of materials belongs to organic semiconductors that are p-type, however, it also can be used as n-type organic semiconductor in conditions [6, 7].

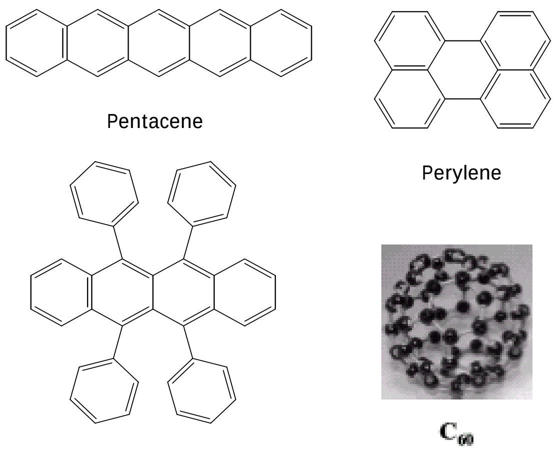


Fig. 1 Aromatic rings for organic thin film transistor materials

Study of the polycyclic aromatics, J.H. Schön, Ch. Kloc and B. Batlogg published a report in Organic Electronics in 2000 as "On the limits of intrinsic pentacene transistors" sets an example [3]. In this paper, organic semiconductor thin film devices was reported to be constructed by using of Pantacene thin film (Fig. 2 and Fig. 3) with the its essential characteristics to explore the limits of carriers' mobility. They pointed out in the report that the Pantacene with the limited monocrystal mobility at low temperatures can reach to $10^5 cm^2$ /Vs. In room temperature, thermal phonon scattering leads the mobility up to 3.2 cm^2 / Vs (Fig. 4) as an intrinsic property of the Pantacene.

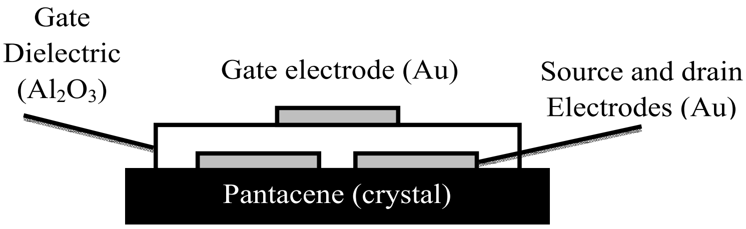


Fig. 2. Pantacene monocrystal transistor device (by J.H. Schön et al.)

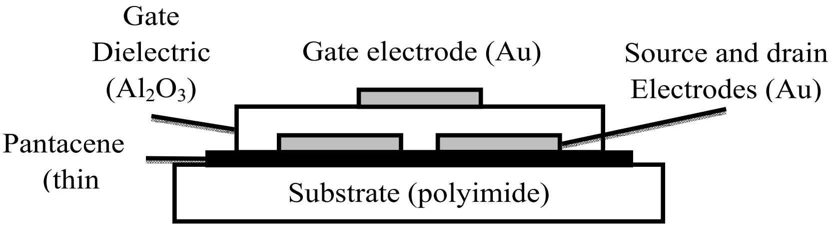


Fig. 3. Pantacene thin film transistor device (by J.H. Schön et al.)

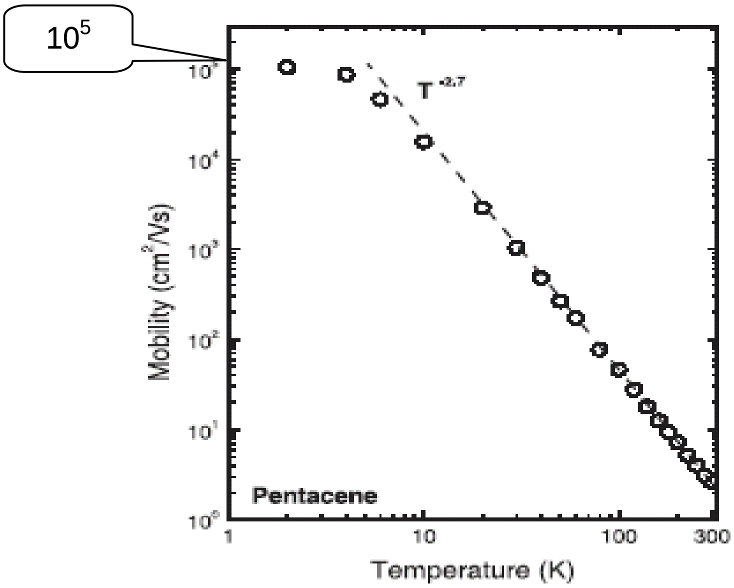


Fig. 4. Mobility vs. Temperature for Pantacene thin film transistor

Different film forming conditions for Pantacene transistor may affect its electrical characteristics (Fig. 5. and Fig. 6) majorly because the temperature influences the grain boundary energy barrier. Meanwhile, the gap of the lattice directly affect the energy barrier (Fig. 7) so that the grain boundary mobilityμ_{GB} can be negatively affected by the barrier energy, $\mu_{GB} = \mu_o \exp(-E_B/kT)$. In short, the characteristic of the crystal has the long term effect to the carriers' mobility and highly correlates the symmetry of the crystal lattice.

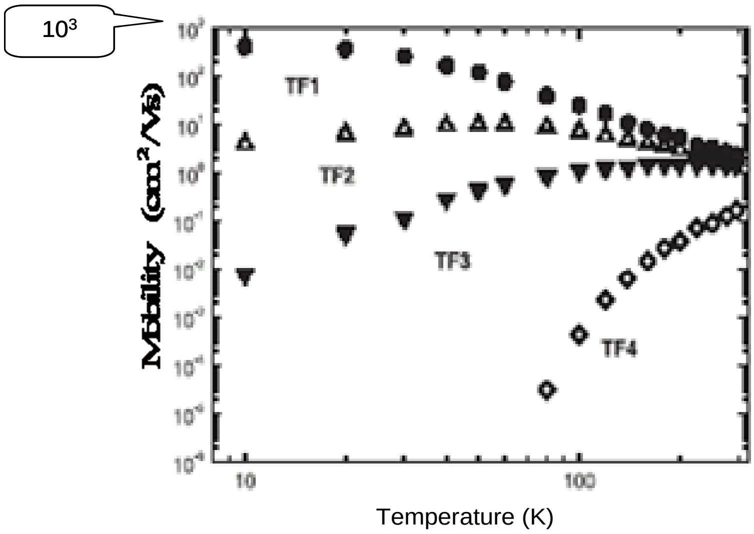


Fig. 5. The carrier-mobility in the Pantacene film transistors correlate with the temperature where TF4 (higher) to TF1 (lower) has been presented the film formation temperature on the substrate. (by J.H. Schön et al.)

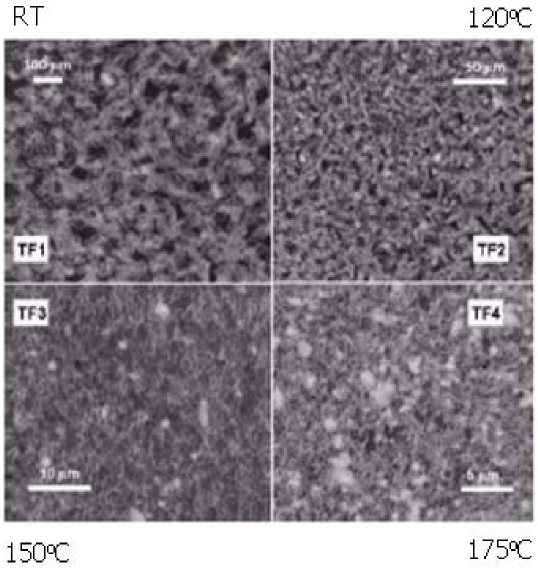


Fig. 6. The effect of the thin film formation temperature at different cons under crystallization of Pantacene (by J.H. Schön et al.)

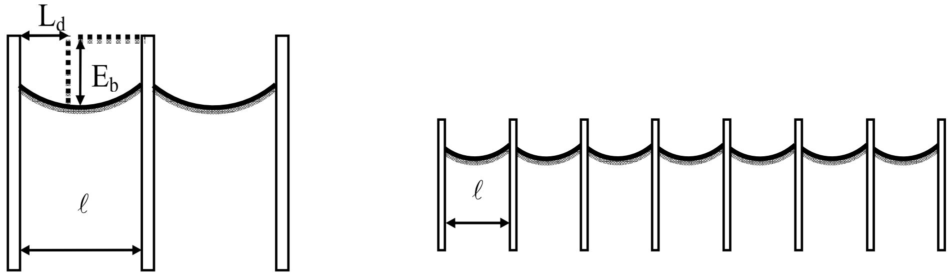


Fig. 7. The gap size of the lattice directly affects the grain barrier energy (by G. Horowitz et al.)

In this report, if the thermal phonon scattering can be overcome, increasing the operation temperature can be applied to high carriers' mobility rate. This can be done by material molecular structure design or by lowering intra-molecular charge transport node or expand the π electron set of unstable domain. Additionally, planar molecular structural and symmetrical molecules will benefit the lattice stack to reduce the barrier energy so that be able to increase the carriers' mobility including phonon scattering effects dominated bulk mobility (or called intragrain mobility) μ_B and crystallized characteristical dominated mobility (μ) where $\mu^{-1} = \mu_{GB}^{-1} + \mu_B^{-1}$ The second type of organic thin-film transistors materials for the thiophene compounds is depicted in Fig. 8. This is a kind of molecular having structural extensibility, formed by Tatrathiophene, Polythiophene and containing various derivative substituents. The standard type is Sexithiophene, and Octaithiophene. However, the rate of mobility can only be from 10^{-3} cm^2/Vs to 0.3 cm^2 / Vs. This serial compounds belongs to p-type organic semiconductor materials in majority [8-10]. The directional transmission of thiophenes is one of the hot topics for researches. Kinder et al. reported an article entitled "ordering and mobility in organic polymer carrier to thin film transistors" in 2004 [11] was an example to construct organic thin-film transistors by using of thiophene polymer. The result pointed out that the junction channel and the phenol molecular axial are related. If they oriented being in parallel, the carriers' mobility would be 4.4×10^{-3}cm^2 /V-s. But, if they oriented in vertical, the carriers' mobility would be 1.1×10^{-3}cm^2 /V-s of four times higher (Fig. 10.).

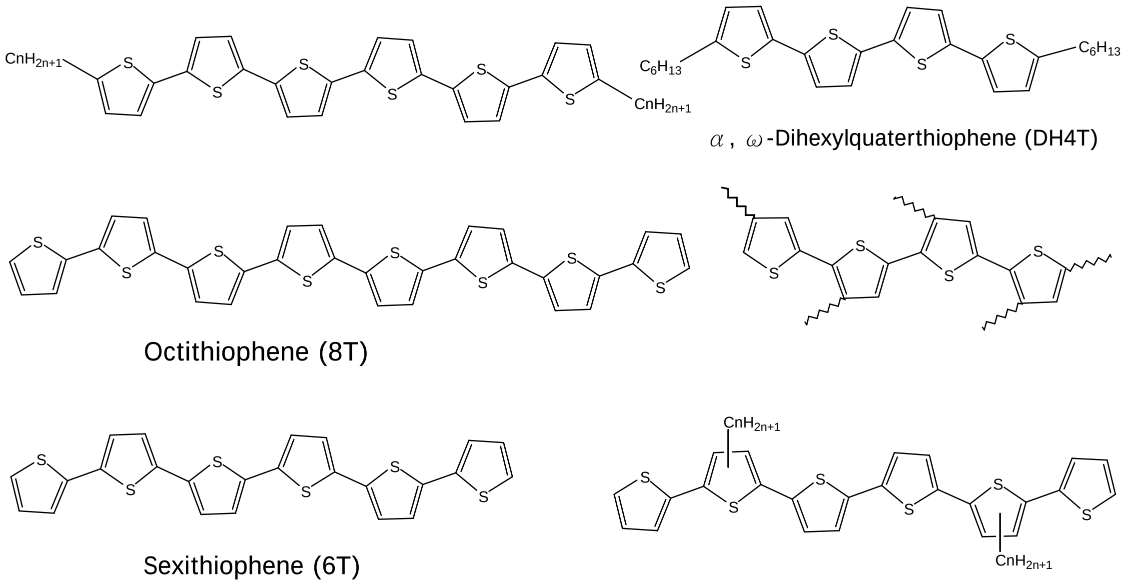


Fig. 8. The material structure of thiophene for organic thin-film transistor device

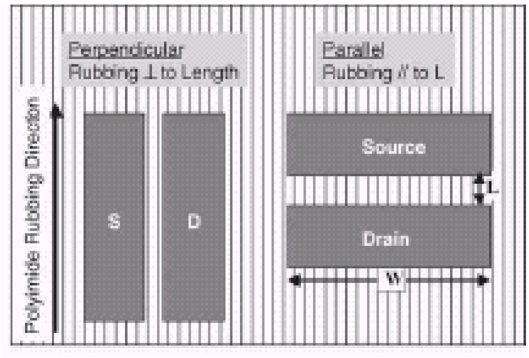


Fig. 9 The thiophene organic thin-film transistors (left: molecule axis perpendicular to the junction channel ; right: molecule axis parallel to the junction channel)

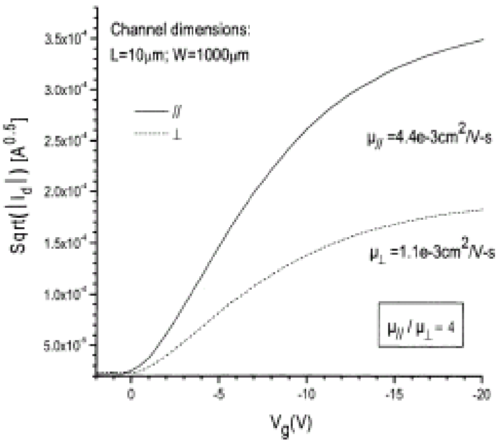


Fig. 10 The carriers' mobility of thiophene organic thin-film transistors

This article reported that the carriers moving parallel along the organic molecules π electronic un-localized space axis would be easier than the movement vertically along the axis. Therefore, the characteristic of carriers' mobility should be able to be justified by changing the distribution of the π electrons. The third type materials used for organic thin film transistor is containing electron donating group shown in Fig. 11. Those materials function as N-type. The carriers mobility is around 1×10^{-3} cm^2/Vs but they have the potential increasing the mobility if charge transfer can be strengthened. M. Iizuka et al. (200) used the compound of Tetramethyltetraselenafulvalene (TMTSF) as electron donor and Tetracyanoquinnodimethane (TCNQ) as electron acceptor to design different molecular structure with strong charge transfer successfully achieved the multiple stacked organic thin film transistor where the current can be higher up to two orders (Fig. 12 and 13).

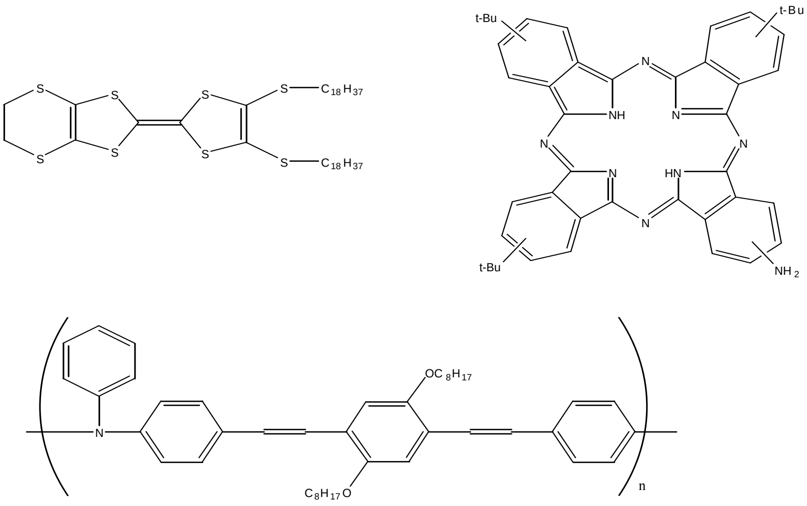


Fig. 11 Containing electron donating group compound for organic thin film transistor

The fourth type of thin film organic material is containing acceptor electron group structural compound shown in Fig. 14 [13, 14]. It functions as negative P-type material for the existing of withdrawing capability of the electron group in the structure. So far, the carrier mobility is still very low approximately from 1x10^{-7} to 1×10^{-3} cm^2/Vs but can be strengthen by charge transfer between the molecules up to two orders.

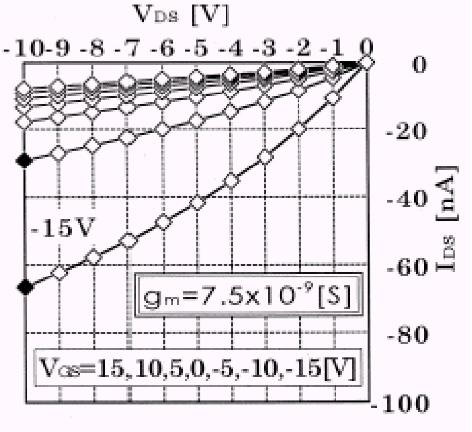


Fig. 12 I-V curve of single layer TMTSF thin film transistor (by M. Iizuka)

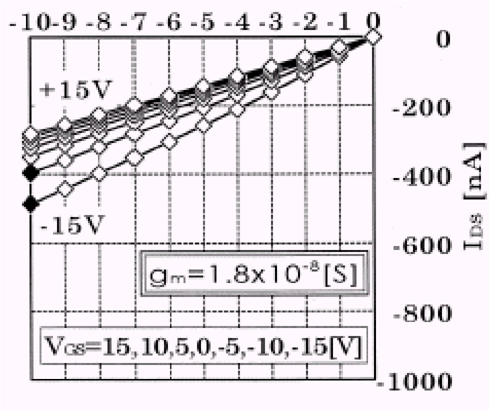


Fig. 13 I-V curve of TMTSF up-stacked TCNQ multilayer thin film transistor。

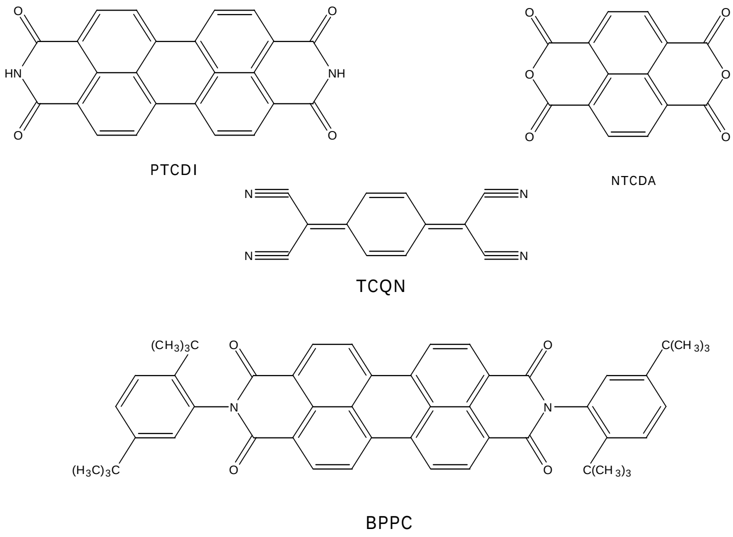
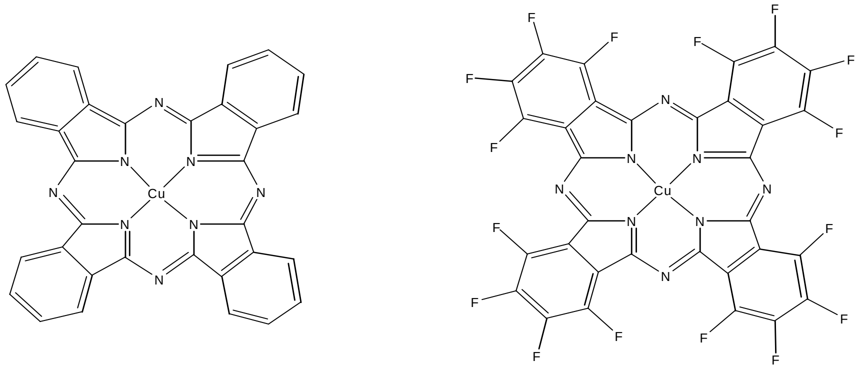


Fig. 14 Containing acceptor electron group structural compound for organic thin film transistor

The fifth class materials for organic thin-film transistors is metal complex compounds [15, 16]. This is a type of planar organic molecules.

Phthalocyanine is a standard type including CuPc, NiPc, benzene with 16-flubendazolum copper and so on. They can function as both p-type and n-type with the carrier mobility rate from 1×10^{-5} to 1×10^{-7} cm^2/Vs.



CuPc

$F_{16}CuPc$

Fig. 15 Metal complex compounds used for organic thin film transistor

III New Applications to OTFT

We have developed four derivatives of benzimidazole of new materials for thin film organic transistors such as 2-(naphtho[3,4] imidazol-2-yl)quinoline (NIQ), 2-(benzimidazol-2-yl) quinoline (BIQ), 2-(naphtha [3,4] imidazol-2-yl) pyridine (NIP), 2-(benzimidazol-2-yl) pyridine (BIP). It is shown in Fig. 16.

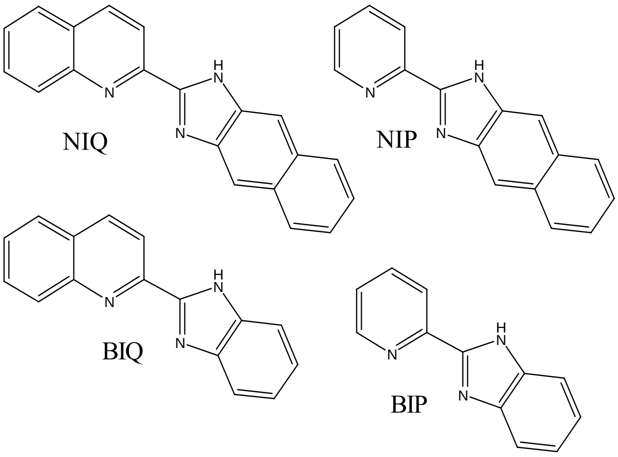
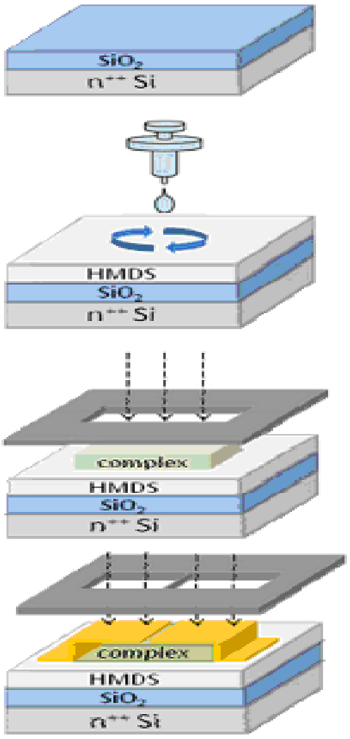


Fig. 16 New materials that we developed in our Lab for organic thin film transistor

Generally, the organic thin film design process with Bottom-Source-Drain Contact OTFT (BC-OTFT) has been used in our lab. The construction of the transistor device is to use silicon wafer being washed by soak water, acetone, distill water, isopropanol solvent and then put into sonic oscillators for 10 minutes. Taking distill water, hydrogen peroxide solution (30%), ammonia (29%) with the ratio 5:1:1 for lye and distill water, hydrogen peroxide solution (30%), hydrochloric acid (37%) ratio 5:1:1 for acid. Putting wafer in lye, acid respectively, and then put the surpluses soaking ultrasound oscillators for ten minutes dried with nitrogen (N2) placing into vacuum drying oven 30 minutes (120^{o}C). Complete the cleaning steps, it should be followed by six methyl two silicon nitrogen 1,1,1,3,3,3 - Hexamethyldisilazane, polyurethanes (MHDS spin) spin coating for the film. The electrodes can be deposited by thermal evaporation method. The width of the channel is 10mm and the length is 50μm. We should be very careful to avoid and check the shadow effect shown in Fig. 17



Clean the substrate and put into oven
at 120° pre-heating for thirty minutes

Spin coating HMD film at speed of
1000 rpm for 10 seconds and
6000 rpm for 60 seconds

Select appropriate mask to define the active
layer region for thermal evaporation

Chamber pressure: 1.0×10^{-6} torr
Plating rate :0.54 Å / sec

Using of appropriate Au mask for
thermal evaporation

Chamber pressure: 1.0×10^{-6} torr
Plating rate :2~3 Å / sec

Fig. 17 Schematic drawing of the design process by using of Bottom-Source-Drain Contact OTFT

By using of the derivatives of benzimidazole as new materials for thin film organic transistors, both NIQ and BIQ molecules have internal hydrogen bonds to be as planar structural bonding and stacked as 3-D structure (Fig.18, 19). The derivatives of benzimidazole of new materials observation of V-VIS (Fig. 20) has shown that the solidified derivatives of benzimidazole of molecules can have the effect of intermolecular charge transfer (ICT) for the effective stacking of π electron and π orbital.

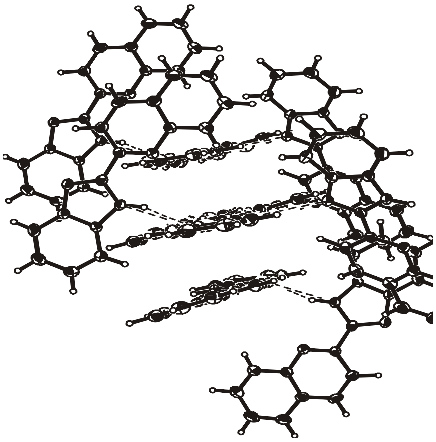


Fig. 18. 3-D stacking structure of BIQ

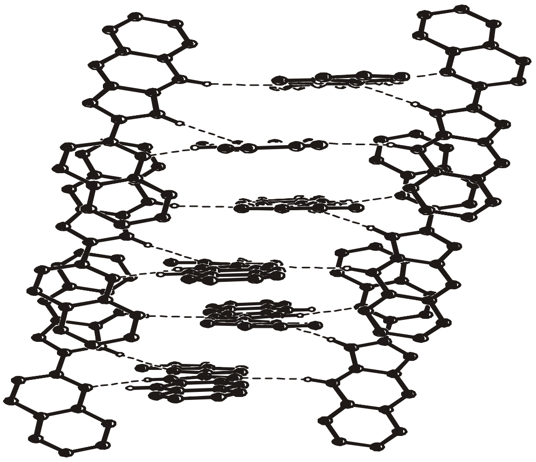


Fig. 19. 3-D stacking structure of NIQ

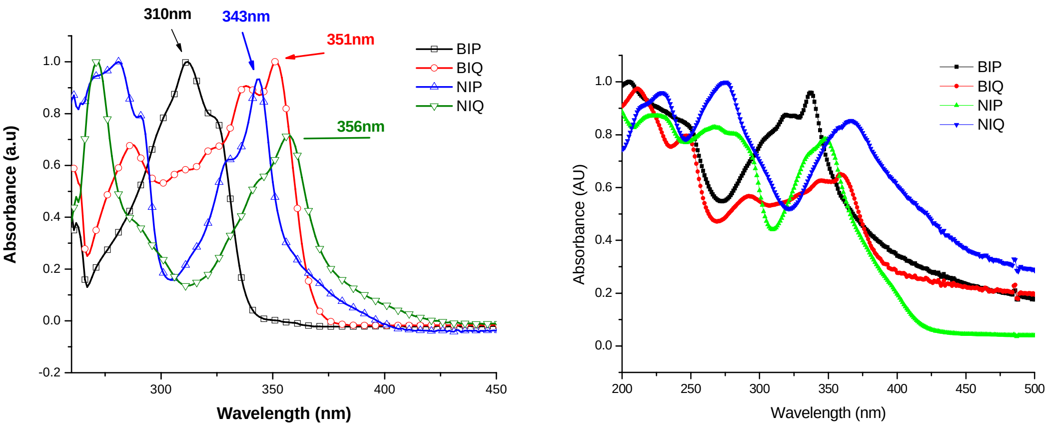


Fig. 20. The V-VIS spectrum for the derivatives of benzimidazole, left one is for solution sample and the right one is for thin film sample

Based upon the carrier mobility of organic materials is related to solidified molecules via the effect of intermolecular charge transfer (ICT) from stacking of π electron and π orbital, we further set up a reliable evaluation by checking the purity and size of grain for the new material of thin films. The optimized condition in our lab is to use the evaporation rate at 0.5 Å /sec for the thin film deposition thickness around 100 nm. We have observed those criteria are the best base for constructing the minimum roughness and most complete grain productions that can be key factor to affect the molecular characteristics and the carrier mobility. The SEM observations of all BIP, BIQ, NIP, NIQ thin films are depicted in Fig.21

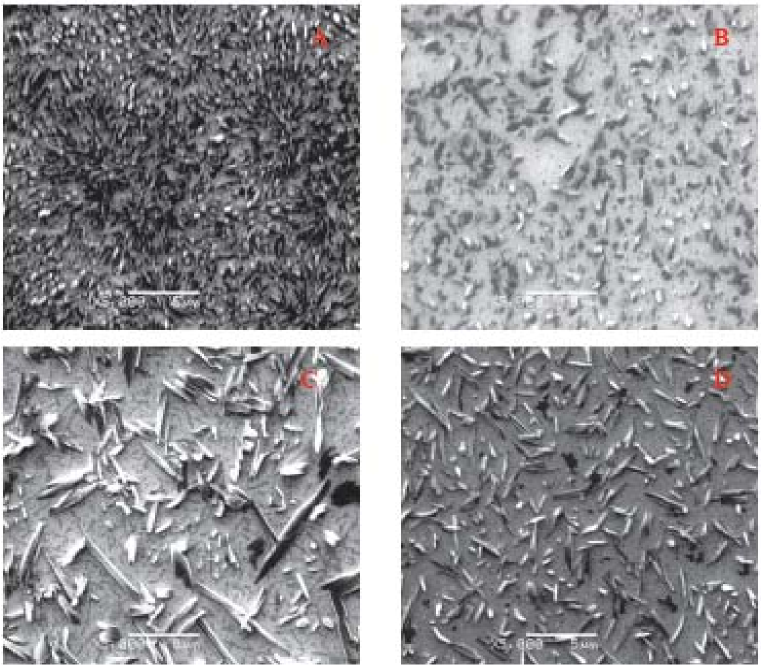


Fig. 21. SEM observation of (A) BIP device (B) BIQ device (C) NIP device (D) NIQ device with thickness of 100nm

Structure of metal-semiconductor-metal (MSM) has been used to anticipate the carrier mobility. The process is simple but effective by using of ITO thin film as electrode to predict the carrier mobility. The detail structure is like a sandwich structure as Glass/ITO/organic semiconductor/u (shown in Fig. 22). The sample thickness is 100 nm. This structure is thus also similar to the Schottky diode. When the reverse bias is added in the structure the depletion area will be increased. Meanwhile, if bias is added unto another side, due to the ohm contact the current should be increased very quick and cause the diode being breakdown.

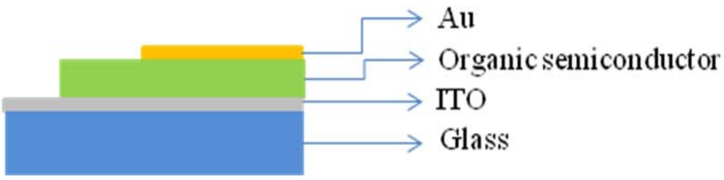


Fig. 22. Device structure of metal-Semiconductor-metal

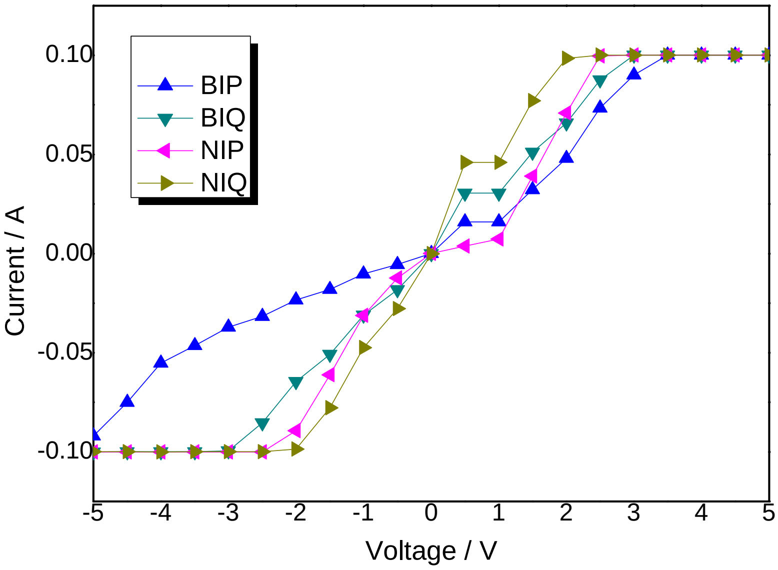


Fig. 23. I-V curve of four derivatives of benzimidazole using MSM device

From the I-V curev for MSM in Fig 23, it is revealed the resistance should be as BIP>BIQ>NIP>NIQ. Therefore, we can predict the carrier mobility could be as NIQ > NIP > BIQ > BIP which is fit our experimental results. The charge transfer in derivatives of benzimidazole (BIP, BIQ, NIP and NIQ) can strengthen the carrier mobility. The I-V curves of derivatives of benzimidazole (BIP, BIQ, NIP and NIQ) the thin film transistor and the characteristics of transconductance are depicted in Fig. 24 ~27.

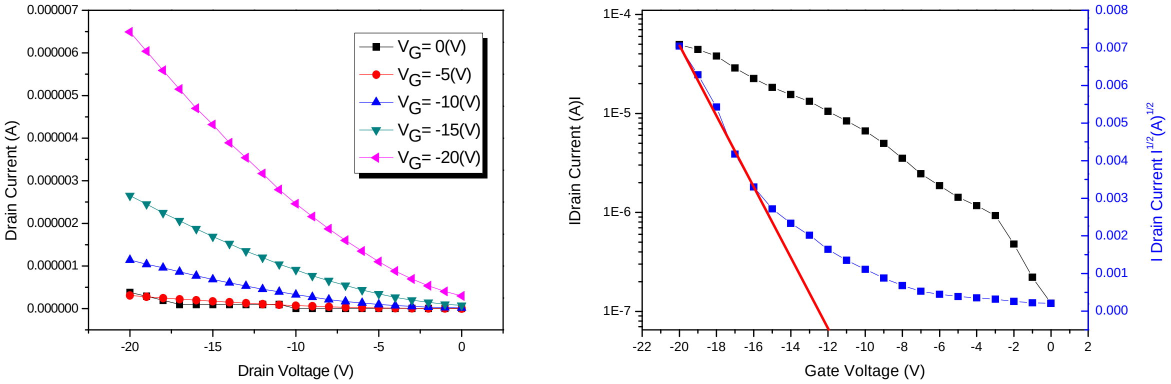


Fig. 24. I-V (left) and transconductance (right) curves of BIP thin film transistor

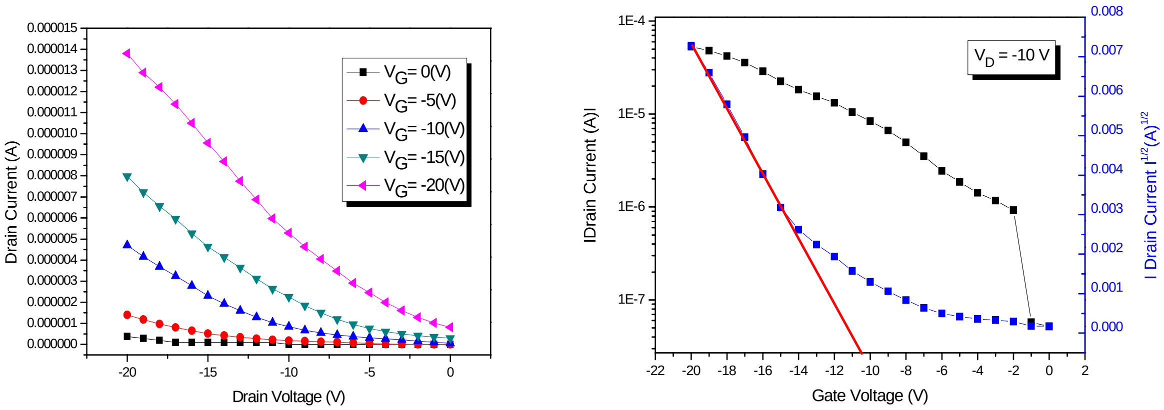


Fig. 25. I-V (left) and transconductance (right) curve of BIQ thin film transistor

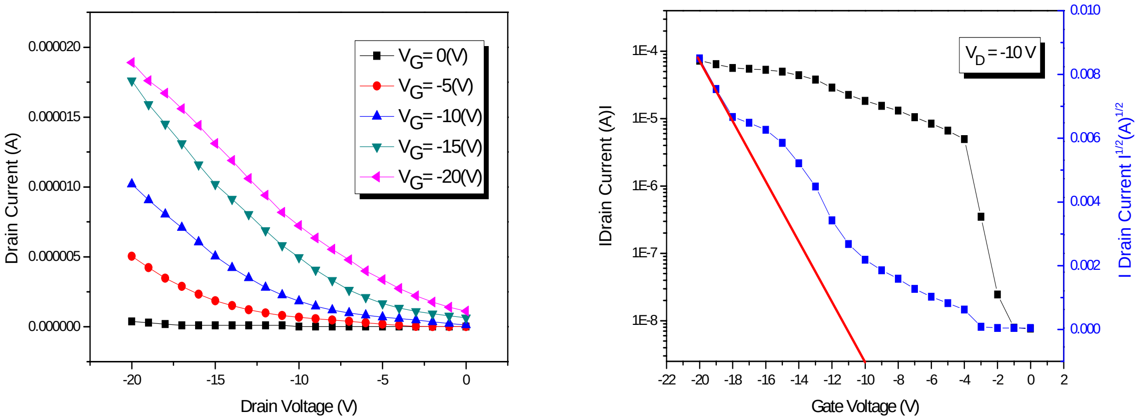


Fig. 26. I-V (left) and transconductance (right) curve of NIP thin film transistor

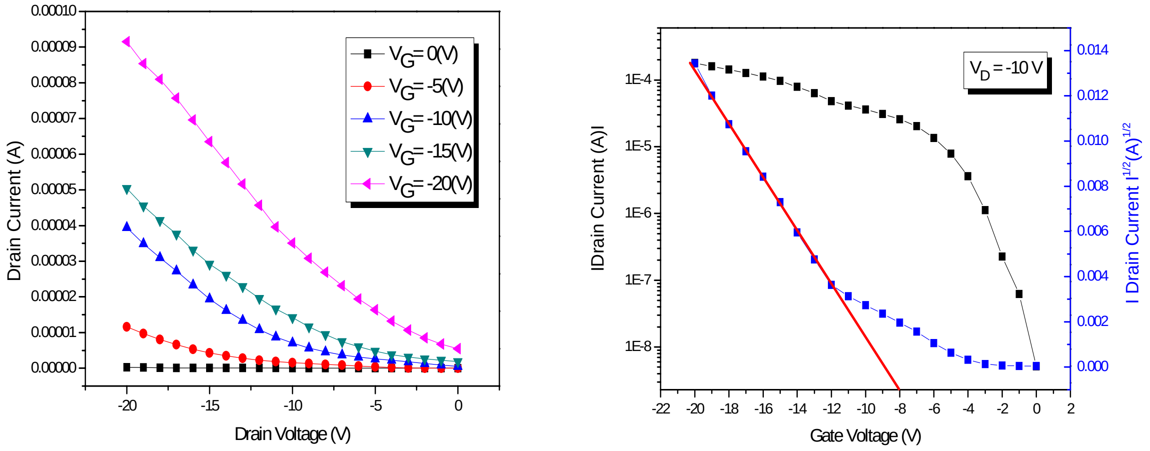


Fig. 27. I-V (left) and transconductance (right) curve of NIP thin film transistor

The observation has shown that the derivatives of benzimidazole (BIP, BIQ, NIP and NIQ) functions all as p-type material to sense the accumulation of holes and transport enhancement mode with carrier mobility rate (μ_{FET}) between 0.117 to 0.336 cm^2/V-s.

Table I.
Electrical characteristics under the atmosphere of the OTFT made by BIP, BIQ, NIP and NIQ

Materials	**μ_{FET} (cm^2/V$_S$)**	**V$_{th}$ (V)**	**I$_{ON}$/I$_{OFF}$ ratio**	**S (V/decade)**
BIP	0.117	-12	4.11×10^2	7.653
BIQ	0.129	-10.5	1.02×10^3	6.645
NIP	0.230	-10	9.45×10^3	5.031
NIQ	0.336	-8	3.50×10^4	4.401

From the experimental results, it is observed that when we use the idea of device of MSM to predict the sequence of carrier mobility, we can get consistent outcomes. In our new derivatives of benzimidazole compounds including pyridine ring and imidazole ring, for those two aromatic groups we observe an interesting phenomena, when more aromatic rings, pyridine ring (p) and imidazole ring (I) involved, the carrier mobility increased as NIQ (2P+3I) > NIP (1P+3I)> BIQ (2P+2I) > BIP (1P+2I). In NIP (1P+3I)and BIQ (2P+2I), they have four aromatic rings. The carrier mobility of NIP (1P+3I), μ_{FET} = 0.230 cm^2/V$_S$, which is about btwo times more than BIQ (2P+2I), μ_{FET} = 0.129 cm^2/V$_S$ because the connection of pyridine ring and imidazole ring are single bond which may decrease the effective capability from the π-π conjugation of aromatic. Therefore, since the NIP (1P+3I), located at imidazole ring side, there has three aromatic ring in which effective capability of π-π conjugation of aromatic is larger than BIQ (2+2) two aromatic ring. Furthermore, if the numbers of pyridine ring or imidazole ring is less, the carrier mobility can't increase lot like BIQ (2P+2I) μ_{FET} = 0.129 $cm^2/V_{S,}$ comparatively, just be a little bit higher than BIP (1P+2I) μ_{FET} = 0.117 in about 0.012 cm^2/V_S. When the number of pyridine ring or imidazole ring is larger, the carrier mobility can increase a lot. However, if the number of pyridine of NIQ (2P+3I) μ_{FET} = 0.336 cm^2/V_S in compare with NIP (1P+3I) μ_{FET} = 0.23 appears higher, for instance 0.106 cm^2/V_S which is about 1.5 times more than the carrier mobility of NIP. As the carrier mobility of NIQ is 0.336$cm^2/V_{S,}$ the materials are good for OTFT**.** Conclusively, we can adjust the number of pyridine ring or imidazole ring to increase the carrier mobility.

References

[1]. Y.-Y. Lin, D.J. Gundlach, S.F. Nelson, and T.N. Jackson, IEEE Transactions on Electron Devices, Vol 44, pp.1325-1331, AUG. 1997.
[2]. A. Tsumura, H. Koezuka, T. Ando, Appl. Phys. Lett. 49(1986) 1210.
[3]. J.H. Schon, Ch. Kloc, B.Batlogg, Organic Electronics, 1(2000) 57.
[4]. S.M. Sze, Physics of Semiconductor Devices, Wiley, New York, 1981, P.442.
[5]. J.H. Schon, S. Berg, Ch. Kloc, B.Batlogg, Proceedings of the Materials Research Society Fall Meeting, Boston, 1999, Vol.599.
[6]. Y.-Y. Lin, D.J. Gundlach, S.F. Nelson, and T.N. Jackson, IEEE Electron Devices Letters, Vol 18, pp.606-608, DEC. 1997.
[7]. M.H. Choo, W.S. Hong, Seongil Im, Thin solid Film 420-421 (2002) 492.
[8]. Francis Garnier, Gilles Horowitz, Denis Fichou, Abderrahim Yassar, Synthetic Metals, 81, pp.163-171, 1996.
[9]. Luisa Torsi, Microelectronics Reliability 40 (2000) 779.
[10]. D. Fichou, F. Demanze, G. Horowitz, R.Hajlaoui, M Constant, F. Garnier, Synthetic Metals 85 (1997) 1309.
[11]. L. Kinder, J. Kanicki, P. Petroff, Synthetic Metals 146 (2004) 181.
[12]. M. Iizuka, Y. Shiratori, S. Kuniyoshi, K. Kudo, K. Tanaka, Appl. Surface Svience, 130, pp. 914-918. 2000
[13]. T. Suga, M. Iizuka, S. Kuniyoshi, K. Kudo, K. Tanaka, Synthetic Metals 102 (1999) 1050.
[14]. L. Torsi, A. Dodabalapur, N. Cioffi, L. Sabbatini, P.G. Zambonin, Sensors and Actuators B 77 (2001) 7.
[15]. J. Yuan, J. Zhang, J. Wang, D. Yan, W. Xu, Thin Solid Film 450 (2004) 316.
[16]. K. Kudo, M. Iisuka, S. Kuniyoshi, K. Tanaka, Thin Solid Films 393 (2001) 362.
[17]. C. D. Dimitrakopoulos and P. R. L. Malenfant, "Organic thin film transistors for large area electronics" Adv. Mater., 2002, 14, 99-117.

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