Progresses in Organic Field Effect Transistors and Molecular Electronics

Weiping Wu, Wei Xu, Wenping Hu, Yunqi Liu*, Daoben Zhu**

(Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080)

Abstract

In the past years, organic semiconductors have been extensively investigated as electronic materials for organic field-effect transistors (OFETs). In this review, we briefly summarize the current status of organic field-effect transistors including materials design, device physics, molecular electronics and the applications of carbon nanotubes in molecular electronics. Future prospects and investigations required to improve the OFET performance are also involved.

Key words

Organic Semiconductors, Organic Field Effect Transistors, Mobility, Molecular Electronics

Organic field-effect transistor is a three terminal device whose characteristics can be modulated by the electrical field. It's composed of organic conjugated molecules as active channels, inorganic or polymer insulators as dielectric layers and metals or conductivity polymer as electrodes. Since the first OFET reported in 1986[1], organic field-effect transistors have drawn more and more attentions because of their low cost, flexibility as well as the cability for large area preparation. Bells Lab, IBM cooperation and many research institutes have ploughed into this field[2],[3]. In the past decade, many novel organic semiconductors were synthesized and device performances were significantly improved. Organic field-effect transistor is becoming a hot topic in organic electronics. Here, we present a few important progresses in organic field effect materials, device physics and molecular electronics based on our own results.

1   Device physics of organic field effect transistors

1.1 Basic principles of organic field-effect transistors

An organic field-effect transistor is a kind of device controlling the on/off states by applying a voltage on the gate electrode to form charge accumulation at the organic-dielectric interface. When the source-drain voltage V_{ds} equals to zero, no current forms in the channel as the charges along the channel are uniformly distributed. Once $V_{ds} < V_{gs} - V_{th}$ (here V_{gs} is the gate voltage and V_{th} is defined as the threshold voltage), charges get to be a gradient distribution along the channel so that the current can be controlled by the applied drain source electric field. Here, the device is operated in the linear mode, I_{ds} can be given by[4],

$$I_{ds} = \mu[(W/L)C_i (V_{gs} - V_{th})V_{ds} - 1/2V_{ds}^2]$$

If $V_{ds} > V_{gs} - V_{th}$, the device is operated under saturation region, I_{ds} is then given by,

$$I_{ds} = \mu(W/2L)C_i (V_{gs} - V_{th})^2$$

Here, μ is the field effect mobility, W is the channel width, L is the channel length, C_i is the capacitance of the insulator per unit area. The structure and output characteristics of OFET are resemble to that of inorganic MOS transistors, one difference lies in the mechanism of the charge

transportations. For example, for p type inorganic transistors, the minority carriers accumulate at the interface of the channel and the insulator when inversion occurs, however, organic field-effect devices have no inversion.

1.2 Parameters of organic field effect transistors

The most three important parameters of organic field-effect transistors are the mobility, on/off ratio, threshold voltage and the sub-threshold slope. The mobility determines the possible bit speed of the organic integrated circuits, mobility in the magnitude of 1 cm^2/V s is essential for high speed commercial applications. For other possible applications, mobility at least 0.01 cm^2/V s and on/off ratio larger than 10^3 are required[5]. The field mobility is related to the structures of the molecules, especially the conjugated degree and the aggregate status of the organic active materials[6]. The purity of the materials, the quality of source and drain contacts as well as the temperature have significant influence on the device performance[7]. Up to now, pentacene is the most ideal material for organic field-effect transistors, the highest performance of pentacene based OFET were reported by 3M cooperation with mobility up to 3.3 cm^2/V s and on/off ratio exceeded 10^6 by depositing pentacene films on the alumina substrate with phosphonohexadecane SAM layers[8], further investigations for the RFID tags were also taken based on this material[9].

On/off ratio is also critical for the applications in organic digital circuits, electronic papers and OFET driven OLEDs[10](E.g. for OLED driving, the mobility should be larger than 1 cm^2/V s and I_{on}/I_{off} >10^8, V_{th} be closed to 0 V). Materials purity, device optimization and the post processing such as annealing are the most common ways to improve the I_{on}/I_{off}[11]. Sirringhaus et.al[12] and Lin et.al[13] reported OFETs based on bis(dithienothiophene) and pentacene with I_{on}/I_{off} as high as 10^8. The threshold voltage V_{th} is determined by trap density near the organic-insulator interface and the quality of source drain contacts. Recently it is found that the dipole layer and the channel modification can also change the threshold voltage[14].

2   Organic semiconductor materials

Organic transistors are fabricated by thermal, spin coating, screen printing, pattern stamping using different organic semiconductors, insulators and electrodes[15]. For years, chemists are hammering at design and synthesis novel organic semiconducting materials with high mobility and superior stability. Early researches on OFETs were focused on oligothiophenes and polythiophenes, the earliest OFET was just fabricated by electrochemical polymerization of thiophenes[1]. Other conjugated small molecules, oligomers and their derivatives based on thiophenes, pyrroles, carbazoles, benans, fluorines and condensed-nuclei aromatics showed organic field-effect characteristics.

Organic small molecules are required to be conjugated and have coplanar conformation atoms to get better stacking for high transistors performance. The most ideal material so far is pentacene with high mobility above 1 cm^2 V^{-1} s^{-1}. In recent years, more and more materials with high mobility were synthesized. Li et. al[16] reported OFETs based on indolo[3,2-b]carbazoles with mobility of 0.2 cm^2/V s, Merlo et.al[17] found the mobility of hybrid acene-thiophene molecules was as high as 0.5 cm^2/V s, Naraso et. al[18] fabricated OFETs based on DN-TTF derivatives with mobility of 0.42 cm^2/V s. As for n type materials, Haddon et.al[19] fabricated OFETs based on C_{60} with electron mobility of 0.08 cm^2/V s in early years. In 2001, Patrick et. al[20] reported perylene derivatives with mobility of 0.6 cm^2/V s. In 2005, Ando et.al[21] and Letizia et. al[22] reported fluorin substituted n type organic semiconductors with electron mobility up to 0.3 cm^2/V s and 0.51 cm^2/V s. Not long ago, Gundlach et.al[23] synthesized an n type material with mobility as high as 0.6 cm^2/V s and applied it in logic gates. Chesterfield et.al[24] elevated the mobility of perylene derivatives to 1.7 cm^2/V s, Ando et.al[25] also reported another thiazole oligomers based n type material with high mobility up to 1.83 cm^2/V s. Besides, some organic polymers are also semiconductors, which are more easily to be synthesized and purified than small molecules. Polymer organic semiconductor devices can be prepared by spin coating, inject printing and screen printing. Generally, conjugated polymers form highly disordered

polycrystalline films, the mobility is relative low(around 10^{-7} to 10^{-2} cm^2/V s) as hopping between polymer chains determines the charge carrier transportations[26], [27]. Recently Roy et.al[28] reported polymer based OFETs with mobility as high as 10^{-1} cm^2/V s, but it was still one magnitude lower than small molecules.

We have synthesized tens of organic materials and their derivatives, such as asymmetrically substituted phthalocyanine, ladder tetraazapentacenes[29], cyclo pyrroles[30,31], condensed pentathienoacene[32,33]. We also fabricated organic field-effect transistors[34] and nano electron devices[35] based on these materials.

2.1 Pentacene like semiconducting compounds

So far, pentacene is thought to be one of the most ideal organic semiconductors, chemist and physical scientists have investigated it from molecule structure to the device physics in order to improve its mobility. It is widely accepted that good π-π conjugated and stronger molecule-molecule interactions are essential for higher mobility materials. Thus, substitutional pentacene like molecules are expected to have superior field effect performances.
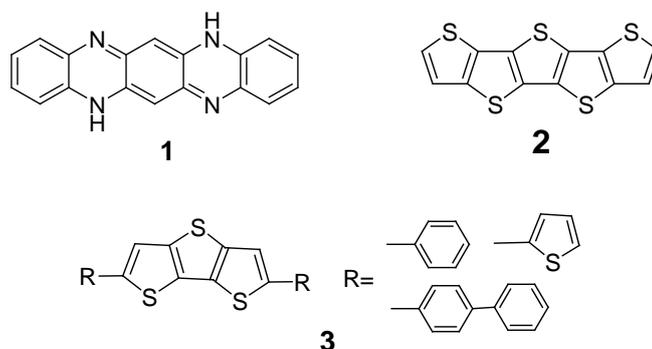

Fig.1 Pentacene like semiconducting molecules

(**1**) ladder tetraazapentacenes [29] (**2**) pentathienoacene [33] (**3**) dithieno[3,2-*b*:2′,3′-*d*]thiophene

[36]

We synthesized ladder tetraazapentacenes semiconductors(Fig.1 (**1**)) with mobility up to 0.02 cm^2/V s[29]. Recently, another pentacene like semiconducting compound pentathienoacene

was synthesized as shown in Fig.1 (**2**) by cooperation with Prof. Jingui Qin's group at Wuhan University. The energy gap E_g of pentathienoacene is 3.29eV（for pentacene it's only 1.85 eV), the decomposition temperature is 272℃ and the OFET mobility is 0.045 $cm^2/V\ s$, indicating pentathienoacene is a very promising material for high performance transistors with excellent stability[33]. We further fabricated transistors based on derivatives of dithieno[3,2-*b*:2′,3′-*d*]thiophene(Fig.1(**3**)). These fused thiophene derivatives exhibit excellent field-effect performances, with mobility as high as 0.42 $cm^2\ V^{-1}\ s^{-1}$, indicating they are a class of ideal building block for high organic field materials[36].

2.2 Ring and star shaped compounds

Ring shaped π conjugated molecules are a special class organic semiconductors which provide the possibility of conjugation dimensions extensions. Ring shaped molecules are important as they can easily be assembled to fabricate optical and electrical devices. We designed a serious of cyclopyrroles(Fig. 2) and prepared LB film based OFETs using them, the mobility of cyclo[4]pyrrole (Fig.2(**4**)) and cyclo[8]pyrrole (Fig.2(**6**)) were as high as 0.014 $cm^2/V\ s$ and 0.68 $cm^2/V\ s$, respectively[30,31].
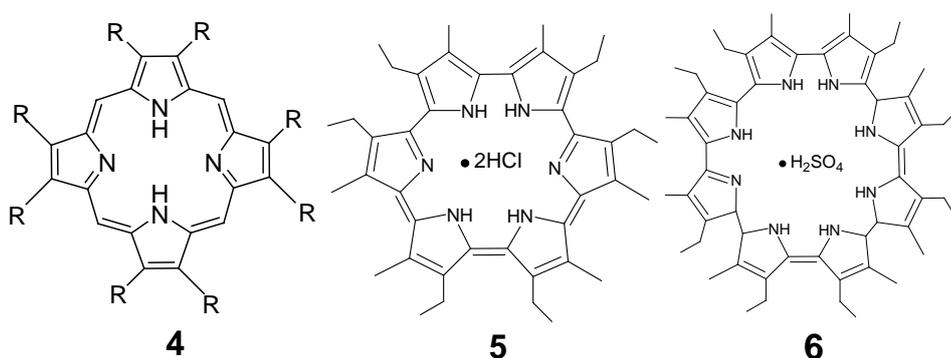

Fig2. Cyclopyrroles [30,31]

(**4**)cyclo[4]pyrrole (**5**)cyclo[6]pyrrole (**6**)cyclo[8]pyrrole

6

Organic complex compounds are drawing more and more attentions in optical and electrical devices. Phthalocyanine is a typical dye and optical electrical material which has been widely used in optical electrical devices. Its unique thermal stability makes it be an ideal field effect material that is suitable for potential commercial applications. We fabricated film[37], [38] and sinlge crystal[39] phthalocyanine based OFETs and sensors. The solubility of phthalocyanine is very limited, so we synthesized asymmetrically substituted phthalocyanines(Fig. 3(**7**)) and further fabricated LB film based diodes[40], transistors[41] and sensors[42] based on them.

Substitutions have great influence on the optical and electrical properties of organic semiconducting molecules. We cooperated with Prof. Jian Pei at Peking University and synthesized star shaped thiophene derivatives(Fig. 3(**8**))[32], the mobility reaches 1.03×10^{-3} cm^2/V s. Recently, we further synthesized pyrene based butterfly shaped molecules and used them as organic field active layers(Fig. 3(**9**)), the mobility of the device is 3.7×10^{-3} cm^2/V s[43]. These molecule design concepts establish the foundation for further design two and three dimension conjugated molecules.

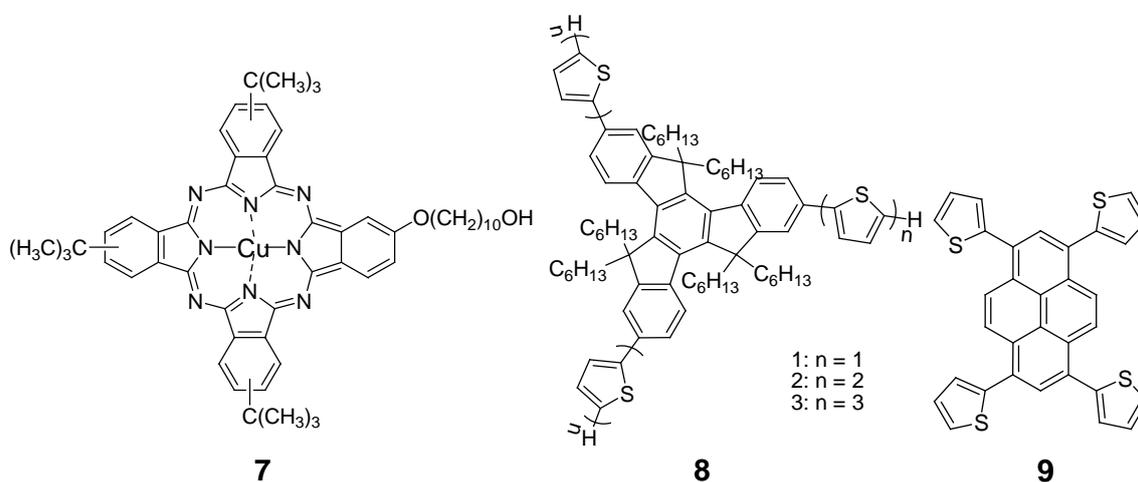**Fig3. Modified organic field effect materials**

(**7**) asymmetrically substituted phthalocyanine[38] (**8**)Star shaped[32]

and (**9**)butterfly shaped [43] organic semiconducing compounds

3   Novel field effect transistors

3.1 Field-effect transistors based on single molecules

It is an important field that utilizes single molecules to fabricate devices with determined properties, computing with molecules has been a dream of the chemist and physical scientist for years[44]. Studying the charge transfer inner as well as inter the molecules to find out the interactions between atoms and electrons, is very fundamental and important for fabricating single molecules devices(e.g. molecule rectifiers, molecule wires and molecule memories) and developing molecules electronics. We have also done some basic works in this field, recently we self assembled thioacetyl-end-functionalized poly(para-phenylene ethynylene) between gold nano-electrodes, and observed the light switching and transistor characteristics[35].

3.2 Organic field effect transistors based on Langmuir- Blodgett films

Langmuir-Blodgett (LB) technology is one of the most promising techniques for preparing thin films with the thickness of a few nanometers (a monolayer) on a solid substrate. It enables precise control of the monolayer thickness, homogeneous deposition of highly organized monolayer over large areas and allows making multilayer structures with varying layer composition. It has been widely used in the production of electrically, optically and biologically active components on a nanometer scale. The mobility of early OFETs based on LB films was very low, around $10^{-7}\sim 10^{-3}$ cm^2/V s only[45,46]. We worked together with Prof. Jianzhuang Jiang's group at Shandong University and synthesized heteroleptic bis(phthalocyaninato) rare earth complexes(Fig. 4(**10**)、(**11**)), the mobility of OFETs based on the LB films using the two compounds were 6.4×10^{-4} cm^2/V s and 1.7×10^{-3} cm^2/V s[47]. Recently, we designed amphiphilic tris(phthalocyaninato) rare earth triple-decker complexes and their field mobility reached $0.24\sim 0.60$ cm^2/V s, this work enhanced the performance of LB film based OFETs to a new level[48].

M=Tb, Lu   R=C$_8$H$_{17}$

10

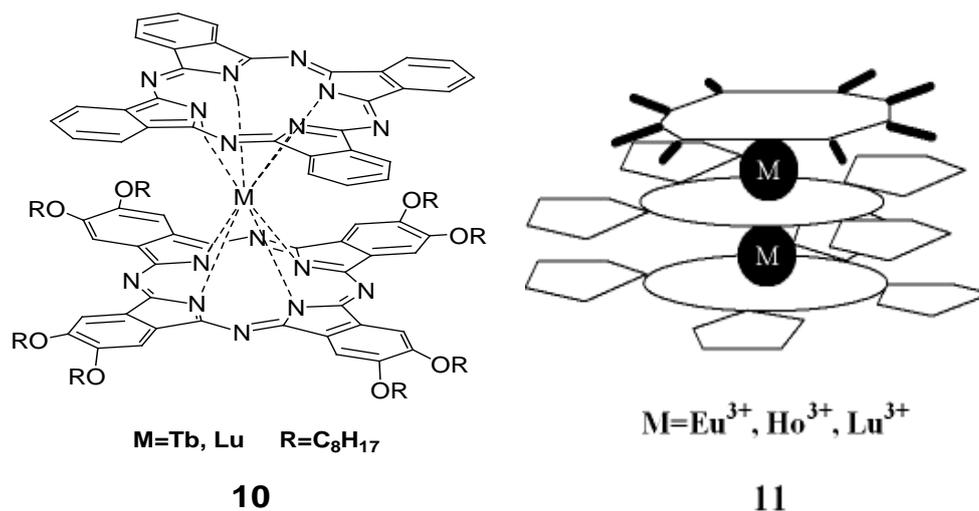**M=Eu^{3+}, Ho^{3+}, Lu^{3+}**

11

Fig4. The Layered rear earth complex

(**10**) heteroleptic bis(phthalocyaninato) [47] and (**11**) amphiphilic tris(phthalocyaninato) [48]

3.3 Carbon nanotube based transistors

Carbon nanotubes(CNTs) have enticed researchers since their discovery in 1991, offering an impressive combination of high strength and important electric properties. Strictly to say, carbon nanotubes do not belong to organic semiconductors, but they are often considered to be another aspect for organic electronics due to their significant meanings for micro and nano scale devices. Recently, CNTs have attached more and more attentions as they showed unique advantage and promising applications in flexible and organic composite transistors.

We fabricated the pillar-shaped and very interesting patterns of three-dimensionally aligned CNTs formed by pyrolysis of iron(**II**) phthalocyanine[49], and utilized them as the channel for transistors with mobility comparable to highly dopped silicon as high as 61.6 cm^2/V s[50] . We further doping CNTs with nitrogen[51] and fabricated field-effect transistors based on an individual CNx /C nanotube by focus ion-beam technology, with electron mobility as high as 3.84×10^3 cm^2/V s[52]. Temperature dependence of two-terminal transport experiments suggests that transportation was dominated by thermionic emission and tunneling through a 0.2 eV Schottky contact barrier[53].

Recently, we have prepared MWCNTs coated with crystalline multiwalled rare earth oxide[54], and zinc sulfide[55] achieving structures possible have applications in catalyse, high density storage and functional devices. Recently, we successfully coated the SWNTs by alumina as all around gate for the CNT based transistors[56]. We also functionalized SWNTs with thiol groups self-assembled on predefined gold contact pads by a solution-based orientational self-assembly method[57].

4   Potentials and applications and of OFETs

Organic field-effect transistors based on small molecules and polymer semiconductors will be extensively applied in electronic paper, RFID tags, OFET driving OLEDs[58]. In additional, investigations on trace matters and gas sensors using OFETs have been active for a long time since 1980s. Recently, OFETs were also used as mechanism sensors[59], not long ago pentacene based OFET arrays were modeled as human skins[60]. Other applications of OFETs such as the light[61] and photocurrent detectors[62] were realized. Prodigious progresses have been made in this field, however, several problems are still not solved. One is the development of OFETs with low operate voltage and high mobility, especially stable n type materials based OFETs. Another is the simplification of the device fabrication. There are also lots of unsolved theoretical issues on organic semiconductor charge carrier transportations. The model based on the inorganic MOS model is rough to explain OFET experimental results and should be further developed. Finally, single molecule and single electron organic devices should be further studied by intercrossing the organic material science and nano electronics. As the development of investigations and technologies, these issues will be understood more and more clearly, thus organic field-effect transistors will play more and more important roles in the new generation of devices.

Reference

[1] A. Tsumura, H. Koezuka, T. Ando. Applied Physics Letters, 1986, 49(18): 1210-1212.

[2] Z. N. Bao, J. A. Rogers, H. E. Katz. Journal of Materials Chemistry, 1999, 9(9): 1895-1904.

[3] C. D. Dimitrakopoulos, D. J. Mascaro. IBM Journal of Research and Development, 2001, 45(1): 11-27.

[4] S. M. Sze Semiconductor Devices, Physics, and Technology,John Wiley & Sons: New York, , 1985p 490.

[5] M. Kitamura, T. Imada, Y. Arakawa. Applied Physics Letters, 2003, 83(16): 3410-3412.

[6] K. Xiao, Y. Liu, Y. Guo, et al. Applied Physics a-Materials Science & Processing, 2005, 80(7): 1541-1545.

[7] H. E. Katz, Z. N. Bao, S. L. Gilat. Accounts of Chemical Research, 2001, 34(5): 359-369.

[8] T. W. Kelley, L. D. Boardman, T. D. Dunbar, et al. Journal of Physical Chemistry B, 2003, 107(24): 5877-5881.

[9] P. F. Baude, D. A. Ender, M. A. Haase, et al. Applied Physics Letters, 2003, 82(22): 3964-3966.

[10]G. H. Gelinck, H. E. A. Huitema, E. Van Veenendaal, et al. Nature Materials, 2004, 3(2): 106-110.

[11]L. Torsi, A. Dodabalapur, H. E. Katz, et al. In Materials Research Society Symposium Proceedings 1995; Vol. 377, p 695-700.

[12]H. Sirringhaus, R. H. Friend, X. C. Li, et al. Applied Physics Letters, 1997, 71(26): 3871-3873.

[13]Y. Y. Lin, D. J. Gundlach, T. N. Jackson. Annual Device Research Conference Digest,

1996,80-81.

[14] Y. Abe, T. Hasegawa, Y. Takahashi, et al. Applied Physics Letters, 2005, 87(15): 153506.

[15] M. M. Ling, Z. N. Bao. Chemistry of Materials, 2004, 16(23): 4824-4840.

[16] Y. N. Li, Y. L. Wu, S. Gardner, et al. Advanced Materials, 2005, 17(7): 849-853.

[17] J. A. Merlo, C. R. Newman, C. P. Gerlach, et al. Journal of the American Chemical Society, 2005, 127(11): 3997-4009.

[18] Naraso, J. I. Nishida, S. Ando, et al. Journal of the American Chemical Society, 2005, 127(29): 10142-10143.

[19] R. C. Haddon, A. S. Perel, R. C. Morris, et al. Applied Physics Letters, 1995, 67(1): 121-123.

[20] R. L. M. Patrick, D. D. Christos, D. G. Jeffrey, et al. Applied Physics Letters, 2002, 80(14): 2517-2519.

[21] S. Ando, J. I. Nishida, H. Tada, et al. Journal of the American Chemical Society, 2005, 127(15): 5336-5337.

[22] J. A. Letizia, A. Facchetti, C. L. Stern, et al. Journal of the American Chemical Society, 2005, 127(39): 13476-13477.

[23] D. J. Gundlach, K. P. Pernstich, G. Wilckens, et al. Journal of Applied Physics, 2005, 98(6): 064502.

[24] R. J. Chesterfield, J. C. McKeen, C. R. Newman, et al. Journal of Physical Chemistry B, 2004, 108(50): 19281-19292.

[25] S. Ando, R. Murakami, J. Nishida, et al. Journal of the American Chemical Society, 2005, 127(43): 14996-14997.

[26] A. Zen, J. Pflaum, S. Hirschmann, et al. Advanced Functional Materials, 2004, 14(8): 757-764.

[27] A. R. Murphy, P. C. Chang, P. VanDyke, et al. Chemistry of Materials, 2005, 17(24): 6033-6041.

[28] V. A. L. Roy, Y. G. Zhi, Z. X. Xu, et al. Advanced Materials, 2005, 17(10): 1258-1261.

[29] Y. Q. Ma, Y. M. Sun, Y. Q. Liu, et al. Journal of Materials Chemistry, 2005, 15(46): 4894-4898.

[30] H. Xu, G. Yu, W. Xu, et al. Langmuir, 2005, 21(12): 5391-5395.

[31] H. Xu, Y. Wang, G. Yu, et al. Chemical Physics Letters, 2005, 414(4-6): 369-373.

[32] Y. M. Sun, K. Xiao, Y. Q. Liu, et al. Advanced Functional Materials, 2005, 15(5): 818-822.

[33] K. Xiao, Y. Q. Liu, T. Qi, et al. J. Am. Chem. Soc., 2005, 127(38): 13281-13286.

[34] Y. Q. Liu, W. P. Hu, W. F. Qiu, et al. Sensors and Actuators B-Chemical, 2001, 80(3): 202-207.

[35] W. P. Hu, H. Nakashima, K. Furukawa, et al. Journal of the American Chemical Society, 2005, 127(9): 2804-2805.

[36] Y. M. Sun, Y. W. Ma, Y. Q. Liu, et al. Advanced Functional Materials, 2006, 16(3): 426-432.

[37] W. P. Hu, Y. Q. Liu, S. Q. Zhou, et al. Thin Solid Films, 1999, 347(1-2): 299-301.

[38] K. Xiao, Y. Q. Liu, G. Yu, et al. Synthetic Metals, 2003, 137(1-3): 991-992.

[39] Q. X. Tang, H. X. Li, M. He, et al. Advanced Materials, 2006, 18(1): 65-68.

[40] S. Q. Zhou, Y. Q. Liu, W. F. Qiu, et al. Advanced Functional Materials, 2002, 12(1): 65-69.

[41] W. P. Hu, Y. Q. Liu, Y. Xu, et al. Synthetic Metals, 1999, 104(1): 19-26.

[42] W. P. Hu, Y. Q. Liu, Y. Xu, et al. Thin Solid Films, 2000, 360(1-2): 256-260.

[43] Hengjun Zhang, Ying Wang, Kuizhan Shao , et al. Chemical Communications, 2006, 353(7): 755 - 757.

[44] L. Fu, L. C. Cao, Y. Q. Liu, et al. Advances in Colloid and Interface Science, 2004, 111(3): 133-157.

[45] W. P. Hu, Y. Q. Liu, Y. Xu, et al. Mol. Cryst. Liquid Cryst., 1999, 337511-514.

[46] K. Xiao, Y. Q. Liu, X. B. Huang, et al. Journal of Physical Chemistry B, 2003, 107(35): 9226-9230.

[47] W. Su, J. Z. Jiang, K. Xiao, et al. Langmuir, 2005, 21(14): 6527-6531.

[48] Y. L. Chen, W. Su, M. Bai, et al. Journal of the American Chemical Society, 2005, 127(45): 15700-15701.

[49] X. B. Wang, Y. Q. Liu, D. B. Zhu. Advanced Materials, 2002, 14(2): 165-167.

[50] K. Xiao, Y. Q. Liu, P. A. Hu, et al. Applied Physics Letters, 2003, 83(1): 150-152.

[51] P. Hu, K. Xiao, Y. Q. Liu, et al. Applied Physics Letters, 2004, 84(24): 4932-4934.

[52] K. Xiao, Y. Q. Liu, P. G. Hu, et al. Applied Physics Letters, 2003, 83(23): 4824-4826.

[53] K. Xiao, Y. Q. Liu, P. A. Hu, et al. Journal of the American Chemical Society, 2005, 127(24): 8614-8617.

[54] L. Fu, Z. M. Liu, Y. Q. Liu, et al. Advanced Materials, 2004, 16(4): 350-352.

[55] J. M. Du, L. Fu, Z. M. Liu, et al. Journal of Physical Chemistry B, 2005, 109(26): 12772-12776.

[56] L. Fu , Y. Q. Liu, Z. M. Liu, et al. Advanced Materials, 2006, 18(2): 181-185.

[57] X. L. Li, Y. Q. Liu, D. C. Shi, et al. Applied Physics Letters, 2005, 87(24): 243102.

[58] H. Sirringhaus, N. Tessler, R. H. Friend. Science, 1998, 280(5370): 1741-1744.

[59] D. Grzegorz, B. Ulrich, W. Rainer, et al. Journal of Applied Physics, 2005, 97(9): 093708.

[60] T. Someya, T. Sekitani, S. Iba, et al. PNAS, 2004, 101(27): 9966-9970.

[61] N. Yong-Young, K. Dong-Yu, Y. Kiyoshi. Journal of Applied Physics, 2005, 98(7): 074505.

[62] M. Breban, D. B. Romero, S. Mezhenny, et al. Applied Physics Letters, 2005, 87(20): 203503.