Organic thin-film transistors of phthalocyanines*

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Abstract: Organic thin-film field-effect transistors (OTFTs) are emerging as attractive candidates for low-price, large-area, and flexible circuit applications. A variety of organic compounds have been utilized as active semiconductor materials for OTFTs, among which phthalocyanine compounds have attracted considerable attention owing to their remarkable chemical and thermal stability as well as good field-effect performance. Here, we review recent results on the phthalocyanine-based OTFTs. The correlation between the crystal packing structure and the charge transport property is discussed, and we conclude with a description of the future prospects for phthalocyanine-based OTFTs.

Keywords: organic semiconductors; phthalocyanines; organic devices; transistors; analytical chemistry.

INTRODUCTION

Conventional inorganic field-effect transistors (FETs), which are the fundamental building blocks for numerous circuits, have exerted significant influence on the technological progress. During the past decades, the FET sciences have focused mainly on silicon-based devices, which require complicated fabrication such as high-temperature, ultra-clean condition, high-vacuum deposition, and photolithography. On the other hand, organic materials possess some interesting advantages over their inorganic counterparts including vapor/solution phase deposition under low-temperature, large-area coverage, good compatibility with different substrates and ease of molecular tailoring by chemical modification [1–7]. Therefore, organic thin-film field-effect transistors (OTFTs) have been proposed as an attractive alternative to inorganic FETs in some specific circuit applications such as radio frequency identification cards (RFIDs) [8–9], electronic paper [10], sensors [11–12], and switching devices for active matrix flat panel displays (AMFPDs) [13]. The prototype OTFT-based circuits have been demonstrated.


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OPERATION AND MATERIALS

A schematic diagram of an OTFT is shown in Fig. 1. It is a three-terminal device, in which the gate electrode is electrically insulated from the semiconductor through an insulating layer, and the source and drain electrode are connected with the semiconductor. For a given drain-source voltage, $V_{ds}$, the current flowing through the organic semiconductor shows a strong correlation with the applied gate voltage, $V_g$. That is, when no voltage is applied to the gate electrode, the drain-source current in the organic semiconductor is very low (device “off” state) due to lack of mobile charge carriers. Upon applying an appropriate $V_g$, the charge carrier can be electrostatically induced in the organic semiconductor at the semiconductor–insulator interface, and the drain-source current obviously increases, even by orders of magnitude (device “on” state). Hole and electron are the main carriers of p- and n-channel transistors, respectively.

The key parameters of OTFTs, including field-effect mobility, on/off current ratio, and threshold voltage, can be extracted from the drain-source current–voltage correlation of OTFTs. The basic relationship between drain-source current and voltage in the linear and saturated regions can be described using eqs. 1 and 2, respectively.

\[
I_{ds} = \frac{W}{L} \mu C_i (V_{gs} - V_T) V_{ds} \quad (1)
\]

\[
I_{ds} = \frac{W}{2L} \mu C_i (V_{gs} - V_T)^2 \quad (2)
\]

where $\mu$ is the charge mobility, $W$ and $L$ are the channel width and length, respectively, $C_i$ is the capacitance per unit area of the dielectric layer, and $V_T$ is the threshold voltage.

In order to achieve high-performance OTFTs, the following aspects are necessary for semiconductor materials: (1) good match of energy level between the organic semiconductor and electrode for charge-carrier injection; (2) efficient crystal packing, i.e., large $\pi$-orbit overlap and short intermolecular distance, for charge-carrier migration between neighboring molecules; (3) good self-assembling ability on the insulator surface to form proper molecule orientation, i.e., the $\pi$-stacking direction of organic semiconductor should be consistent with the charge-transporting direction; (4) good film-forming ability for the reduction of grain boundary; (5) high purity of organic semiconductor for avoiding the impurity as charge-carrier traps; and (6) good stability. The above five points are mainly related
to organic semiconductors for OTFTs. It should be noted that the optimal device structure and fabrication progress also play important roles in the device performance.

To date, a variety of organic semiconductors have been demonstrated to exhibit high field-effect performance, involving fused acene [14–18], oligothiophene [19,20], oligoselenophene [21], metallophthalocyanine [22–25], tetrathiafulvalene (TTF) derivatives [26–28], conjugated polymers [29,30], etc. Several papers have extensively reviewed the progress in OTFTs [1–4,31,32]. Here, we will mainly review recent results on the phthalocyanine-based OTFTs. Furthermore, the relationship between the crystal packing and charge transporting will be described, which not only explains the great difference in mobility of organic semiconductors with different packing structure, but also provides a guide to rational design of new organic compounds for high-performance OTFTs.

**PHTHALOCYANINES FOR OTFTS**

Unsubstituted (rigid) phthalocyanine compounds for OTFTs

Phthalocyanine (Fig. 2a), a compound with a 100-year history, is an 18 \( \pi \)-electron macrocyclic conjugated compound. Two hydrogen atoms in the center of phthalocyanine macrocycle can be substituted by different metal ions, i.e., phthalocyanine macrocycle can act as a host to a metal ion in its center cavity, to form metallophthalocyanine (Fig. 2b) (hereafter, phthalocyanine and metallophthalocyanine are referred to as Pc). Meanwhile, the 16 hydrogen atoms at the four outer benzene rings of Pc molecule can also be substituted by different groups to form Pc derivatives. Since the discovery of phthalocyanine in 1907 [33], Pc and their derivatives have been widely used in a variety of applications such as colorants (dyes or pigments), catalysts, and photoconducting materials in laser printers. More recently, Pc and their derivatives have been attracted in OTFTs due to their remarkable environmental stability and good field-effect property [22–25,34–69]. In this section, we describe recent results on the Pc-based OTFTs.

![Fig. 2 Molecule structure of (a) phthalocyanine and (b) metallophthalocyanine.](image)

Since the first report on OTFTs in 1986, considerable attention have been paid to the Pc (Table 1). In 1988, FETs based on scandium diphthalocyanine (ScPc\textsubscript{2}) with mobility of \( 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1} \) was reported. [34] Two years later, detailed research on diphthalocyanines compound (LuPc\textsubscript{2}, TmPc\textsubscript{2}) was carried out [35]. These studies yielded electron mobility of \( \sim 10^{-5} \) cm\(^2\) V\(^{-1}\) s\(^{-1} \) under vacuum. After annealing LuPc\textsubscript{2} exhibited ambipolar transport with improved mobility of \( 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1} \). Upon exposure to air, only p-type transport with the highest hole mobility of \( \sim 10^{-2} \) cm\(^2\) V\(^{-1}\) s\(^{-1} \) was obtained for TmPc\textsubscript{2}. Until 1996, Bao et al. reported a significant progress in Pc-based OTFTs [22]. They utilized copper phthalocyanine (CuPc) as an active layer to fabricate OTFTs and found the substrate tempera-
ture had great influence on the device performance. At the substrate temperature of 125 °C, CuPc exhibited the largest mobility of 0.02 cm$^2$ V$^{-1}$ s$^{-1}$. Subsequently, they exploited the field-effect property of phthalocyanine and a serial of bivalent metallophthalocyanine [36]. The influence of the central metal ion on the field-effect mobility under the same conditions was demonstrated.

Table 1 Summary of the field-effect performance of phthalocyanine compounds.

<table>
<thead>
<tr>
<th>Phthalocyanine</th>
<th>$\mu$ (cm$^2$/Vs)$^a$</th>
<th>References$^b$</th>
<th>Phthalocyanine</th>
<th>$\mu$ (cm$^2$/Vs)$^a$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScPc$_2$</td>
<td>$10^{-3}$</td>
<td>[34]</td>
<td>TiOPc</td>
<td>10</td>
<td>[24,40]</td>
</tr>
<tr>
<td>LuPc$_2$</td>
<td>$3 \times 10^{-3}$</td>
<td>[35]</td>
<td>F$_{16}$CuPc</td>
<td>0.11</td>
<td>[23,25]</td>
</tr>
<tr>
<td>TmPc$_2$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>[35]</td>
<td>F$_{16}$ZnPc</td>
<td>$1.2 \times 10^{-3}$</td>
<td>[23]</td>
</tr>
<tr>
<td>CuPc</td>
<td>0.15</td>
<td>[22,25]</td>
<td>F$_{16}$CoPc</td>
<td>$4.5 \times 10^{-5}$</td>
<td>[23]</td>
</tr>
<tr>
<td>H$_2$Pc</td>
<td>$2.6 \times 10^{-3}$</td>
<td>[36]</td>
<td>F$_{16}$FePc</td>
<td>$5.8 \times 10^{-3}$</td>
<td>[23]</td>
</tr>
<tr>
<td>ZnPc</td>
<td>0.32</td>
<td>[36,25]</td>
<td>Cl$_{16}$FePc</td>
<td>$2.7 \times 10^{-5}$</td>
<td>[23]</td>
</tr>
<tr>
<td>NiPc</td>
<td>$8.9 \times 10^{-3}$</td>
<td>[36,38]</td>
<td>CN$_6$CuPc</td>
<td>c</td>
<td>[23]</td>
</tr>
<tr>
<td>PtPc</td>
<td>$1.5 \times 10^{-3}$</td>
<td>[36]</td>
<td>PyCuPc</td>
<td>c</td>
<td>[23]</td>
</tr>
<tr>
<td>CoPc</td>
<td>0.01</td>
<td>[36]</td>
<td>Cl$_{16}$CuPc</td>
<td>0.01</td>
<td>[37]</td>
</tr>
<tr>
<td>PbPc</td>
<td>$8.3 \times 10^{-4}$</td>
<td>[36]</td>
<td>Soluble Pcs</td>
<td>$1.7 \times 10^{-3}$</td>
<td>[63,67]</td>
</tr>
<tr>
<td>VOPc</td>
<td>1.5</td>
<td>[41,46]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The highest mobility in OTFTs reported to date.

$^b$References include the first literature on the field-effect property of the corresponding compound and the literature with highest mobility.

$^c$Compound cannot be sublimed.

Comparing the substantial progress of p-type Pc, the research on the n-type Pc lagged behind them. Until 1998, researchers [23] reported that modification of Pc cycles with strong electron-withdrawing groups such as F, CN could lower the lowest unoccupied molecular orbital (LUMO) energy level and thus facilitated the injection of electron. Through this strategy, Pc compounds were converted from p- into n-type. Furthermore, this kind of n-type materials exhibited good air stability, which was a very important advantage for n-type materials. The highest electron mobility of copper hexadecafluorophthalocyanine (F$_{16}$CuPc) was up to 0.03 cm$^2$ V$^{-1}$ s$^{-1}$. In 2006, another air-stable n-type field-effect performance of copper hexadecachlorophthalocyanine (Cl$_{16}$CuPc) was reported [37], which exhibited charge mobility of 0.01 cm$^2$ V$^{-1}$ s$^{-1}$ for thin film at the substrate temperature of 200 °C.

Since the pioneering work on the CuPc and F$_{16}$CuPc, these two compounds have been used as model p- and n-type compounds for OTFTs. There has been much research on CuPc and F$_{16}$CuPc-based OTFTs, and great progress has been achieved. Meanwhile, several other Pc compounds [38–43] were also applied to OTFTs, but they yielded low mobility and therefore failed to attract more attention.

Yan’s group has done a lot of work on the Pc-based OTFTs [39,44–50]. In 2004, they reported a specific device structure with source/drain electrodes sandwiched between CuPc and cobalt phthalocyanine (CoPc) layer, which increased mobility (up to 0.11 cm$^2$ V$^{-1}$ s$^{-1}$) and reduced threshold voltage [39]. They argued that the second layer (CoPc) can enhance charge injection from electrodes into semiconductors and thus improved device performance. Subsequently, in 2005, they investigated the field-effect performance of a composite of CuPc and NiPc, which yielded a mobility of 0.05 cm$^2$ V$^{-1}$ s$^{-1}$ [44]. Although the clear reason for the improvement of performance was not given, their results indicated that composites of conjugated molecules could also yield high mobility. Recently, they utilized para-hexaphenyl as ultra-thin buffer layer between the insulator and semiconductor [25]. They demonstrated that weak epitaxy growth (WEG) of semiconductor layer on the buffer layer led to highly oriented film. By using this WEG method, the device performance of several Pc compounds was significantly improved.
[highest mobility of 0.32 cm$^2$ V$^{-1}$ s$^{-1}$ for zinc phthalocyanine (ZnPc), 0.15 cm$^2$ V$^{-1}$ s$^{-1}$ for CuPc, and 0.11 cm$^2$ V$^{-1}$ s$^{-1}$ for F$_{16}$CuPc].

Ling and his coworkers [51] reported that the soft contact lamination method could avoid the thermal and penetration damage to organic semiconductors during the preparation of metal electrodes by thermal evaporation. By this method, the mobility of 0.08 cm$^2$ V$^{-1}$ s$^{-1}$ for F$_{16}$CuPc could be obtained. Okuda et al. [52] used high-permittivity PbZr$_{0.5}$Ti$_{0.5}$O$_3$ as an insulator layer to fabricate CuPc-based OTFTs. Their devices achieved low-voltage operation. Additionally, Liu’s group [53,54] and others [55–58] also exploited Pc-base OTFTs from various aspects such as polymeric blend insulator, crystal size effect on mobility, surface modification of insulator, etc.

Moreover, ambipolar OTFTs based on Pc have also been extensively investigated [49,50,59–62]. Ambipolar transistors are key components for complementary metal-oxide-semiconductor (CMOS) logic circuits, which possess the advantages of low power dissipation and good noise margin. Utilization of organic ambipolar transistors can further simplify the design and fabrication of CMOS circuits. In view of the above considerations, together with the features of Pc compounds, it is therefore significant to investigate Pc-based ambipolar transistors. Because CuPc and F$_{16}$CuPc possess similar molecular shape and crystal packing structure as well as comparable performance, it is convenient to obtain ambipolar transport by using these two compounds. Ye et al. [59] adopted laminated structure to fabricated ambipolar transistors. They argued that CuPc and F$_{16}$CuPc could be grown through an intermediate phase layer to form homostructure. Wang et al. [49,50] claimed that, in the CuPc/F$_{16}$CuPc heterojunction, there might be charge transfer from CuPc to F$_{16}$CuPc, which resulted in a dipolar layer in the interface of CuPc/F$_{16}$CuPc. This dipolar layer could act as a new conductive channel, which could improve field-effect mobility and shift the threshold voltage. Furthermore, ambipolar transport has been observed in single phthalocyanine compound by special electrode metals [60], under special measurement conditions [34,40,42,61] or by insulator hysteresis [62].

Despite the progress in Pc-based unipolar and ambipolar transistors, the performance of Pc is still inferior to that of some other popular organic semiconductors (such as pentacene and 6T) as well as some new synthesized semiconductors [14–18,26–28]. Until recently, our group [40] demonstrated that titanyl phthalocyanine (TiOPc, Fig. 3), a nonplanar, polar, and pyramide-like molecule, exhibited very excellent field-effect performance with mobility up to 10 cm$^2$ V$^{-1}$ s$^{-1}$ and good environmental stability under air condition. The mobility of TiOPc was higher than that of other Pc compounds, and was one of the highest mobility for the organic semiconductors reported to date. We concluded that the high performance of TiOPc mainly stemmed from its ultra closed π-stacked structure and edge-on molecular orientation on the insulator substrate. At the same time, Wang et al. [46] reported the high performance of vanadyl phthalocyanine (VOPc, a TiOPc’s analog) with mobility of 1.5 cm$^2$ V$^{-1}$ s$^{-1}$. They attribute the high performance to the WEG mode, which was similar to their other report [25]. They did not give a reason for the high performance of VOPc from its crystal packing structure.

**Substituted (soluble) phthalocyanine compounds for OTFTs**

Until now, the performance of unsubstituted Pc rivals or exceeds that of commercial inorganic amorphous silicon transistors. However, these thin films of unsubstituted Pc were almost obtained by thermal evaporation under vacuum, which were unfavorable to fulfill the cost advantage of OTFTs. It is desirable to fabricate thin film with solution-based deposition progress such as dipping, spin-coating, and printing, which will require soluble semiconductors. Generally, chemical structure modification by introducing flexible groups into the rigid Pc macrocycle can improve the solubility. However, spin-coating with these soluble small molecules is still difficult due to their low viscosity. Up-to-date, Langmuir–Blodgett (LB), and dipping technologies were applied to fabricate OTFTs based on some soluble Pc. Our group previously investigated the field-effect performance of a series of asymmetrically substituted Pc by LB technology [63–67]. Locklin et al. reported OTFTs based on water-soluble
cationic and anionic phthalocyanine derivatives using a layer-by-layer deposition technique [68]. Field-effect measurement indicated that their alternating multilayer showed ambipolar-like behavior, which came from “an ion-modulated electrical conduction mechanism”. Until now, most of the soluble Pc-based devices exhibited low mobility, which may have arisen from the fact that the flexible group increased steric hindrance of Pc molecules and reduced their ability to form an ordered packing structure. It is therefore highly desirable to develop soluble Pc without loss of field-effect performance. There might be two useful ways to overcome the low mobility of soluble Pc: (1) introduction of special substituted groups which cannot only increase the solubility of Pc but also facilitate to form ordered packing structure; and (2) development of soluble polymer Pc. In addition, it was noted that soluble Pc-based OTFTs have been used in sensors due to the sensitivity, selectivity, and stability of Pc [69].

STRUCTURE–PROPERTY RELATIONSHIP
All of the Pc compounds possess similar molecular structure except the central metal ion, but they exhibit field-effect mobility in the range of $10^{-5}$ to 10 cm$^2$ V$^{-1}$ s$^{-1}$. What can account for such a great difference in mobility among various Pc compounds? Here, we will illustrate the reason from the aspect of the relationship between the crystal structure and charge transport.

Theoretical calculation and experimental studies have demonstrated that the charge transport between conjugated molecules is modulated by intermolecular interaction, i.e., strong intermolecular π-π interaction is favorable to obtain high mobility [24,70–73]. Generally, the intermolecular interaction is primarily related to the π-orbit overlap and relative orientation between adjacent molecules. Structure analysis indicates that there are, in principle, two crystal packing structures commonly adopted by conjugated aromatic molecules, i.e., herringbone structure and π-stacked structure. The former structure was adopted by a majority of conjugated molecules, while the conjugated molecules with π-stacked structure are relatively scarce. However, compared with the herringbone structure, the π-stacked structure possesses a larger π-orbit overlap and shorter intermolecular distance and thus facilitates higher mobility [24,72,73]. In the following text, we will take CuPc and TiOPc, which adopt herringbone and π-stacked structures, respectively, as examples to illustrate the relationship between the crystal structure and charge transport, and clarify the reason for such a great difference in mobility among various Pc compounds.

Figures 4a and 4b show the crystal packing structure of CuPc and TiOPc, respectively. In CuPc’s herringbone structure, which was also adopted by most of planar Pc, the adjacent molecules are packed with two modes (face-to-face and edge-to-face) in the 2-dimensional directions. Since the charge trans-
port in the 2-dimensional layer [74–76], the herringbone structure with edge-to-face packing mode minimizing the \( \pi \)-orbit overlap is unfavorable to achieve high mobility. Whereas the TiOPc molecules are packed with face-to-face \( \pi \)-stacked structure with significant \( \pi \)-orbit overlap and short intermolecular distance (3.145 Å in the convex pair and 3.221 Å in the concave pair), which are obvious features for strong intermolecular interactions. Accordingly, it is reasonable that CuPc only exhibits moderate mobility, while high mobility can be obtained in TiOPc.

Our laboratory also used quantum mechanics to quantitatively analyze the mobility of TiOPc and CuPc [24]. An incoherent hopping transport model was used to describe the mobility of TiOPc and CuPc. In this mode, two major parameters (the electronic coupling and reorganization energy) determined charge mobility. In principle, large electronic coupling and small reorganization energy are efficient for high mobility. In our study [24], the largest electronic coupling and hole reorganization energy for TiOPc were calculated to be 0.143 and 0.079 eV, respectively. On the other hand, the corresponding values for CuPc were 0.048 and 0.17 eV, respectively. Thus, theoretical calculation not only further indicated TiOPc should have higher mobility than CuPc but also confirm the \( \pi \)-stacked structure was more favorable to obtain high mobility than herringbone structure.

PROSPECTS

Since the discovery of phthalocyanine, large numbers of Pc and their derivatives have been obtained, and their physical, chemical, optical, electrical, and magnetic properties have also been intensively investigated. Pc compounds have become a kind of important functional material for modern technology. More significantly, some Pc compounds have been demonstrated to be excellent candidates for OTFTs.
From now on, the research on the Pc-based OTFTs might mainly focus on the following four aspects: (1) exploring new p- and n-type high-performance compounds from the known Pc family; (2) further optimizing the Pc-based devices structure, and investigating the relative phenomena and mechanism; (3) designing and synthesizing new n-type Pc compounds with high performance and good stability; and (4) developing soluble Pc with good field-effect performance, which can be processed by solution-based technologies.

REFERENCES