

New Air-Stable *n*-Channel Organic Thin Film Transistors

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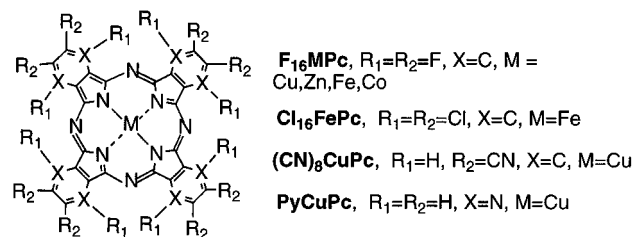
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Recently, there has been increased interest in organic and polymeric thin film field-effect transistors (FETs) due to their potential applications in low-cost memory cards and smart price tags and labels.^{1,2} Air-stable *n*-channel semiconducting materials are important components of *p*-*n* junction diodes, bipolar transistors, and complementary circuits.^{3,4} Up to date, most of the organic and polymeric semiconductors reported for FETs are *p*-channel materials, only very few compounds are found to function as *n*-channel semiconductors. Among them, C₆₀ and C₇₀ are reported to have the highest field-effect mobilities, ca. 0.08 cm² V⁻¹ s⁻¹.^{5,6} However, those devices are highly air-sensitive, which makes them difficult for practical applications. Some other materials are not only air and moisture sensitive but also have relatively low field-effect mobilities, such as 3,4,9,10-perylene-tetracarboxylic dianhydride (mobility 1.5 × 10⁻⁵ cm² V⁻¹ s⁻¹) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (mobility 0.003 cm² V⁻¹ s⁻¹).^{7,8} Tetracyanoquinodimethane (TCNQ) was previously found to have stable FET performance in air with a maximum mobility about 3 × 10⁻⁵ cm² V⁻¹ s⁻¹.⁹ Recently, Laquindanum et al. reported a TCNQ derivative namely 11,11-,12,12-tetracyanonaphtho-2,6-quinodimethane with higher mobility of ca. 0.003 cm² V⁻¹ s⁻¹.⁸

Metallophthalocyanines have been demonstrated to possess remarkable semiconducting properties.^{10,11} They have been widely studied as solar cells, optical limiters, and photoconductors.^{12,13} However, the transistor properties of these compounds

Chart 1. Electron-Transporting Metallophthalocyanines



have received less attention presumably because of their low reported mobilities (ca. 10⁻⁴ cm²/V⁻¹ s), e.g. in the case of nickel phthalocyanine (Ni-Pc).^{14–16} We have previously shown that it is possible to achieve high FET performance with copper phthalocyanine with a maximum field-effect mobility of ca. 0.02 cm² V⁻¹ s⁻¹.^{10,11} It is known that in order for a material to transport electrons (*n*-channel), it needs to have an accessible LUMO level for electron injection and sufficient π -overlaps to achieve reasonable charge carrier mobilities.¹⁷ Therefore, molecules with strong electron-withdrawing groups and extended π -systems are good candidates as *n*-channel semiconductors. In fact, copper octafluorophthalocyanine (F₈CuPc) has been found to form a rectifying junction with *p*-type unsubstituted MPcs.^{18,19} We have synthesized metallophthalocyanines with strong electron-withdrawing groups. Among them, hexadecahalogenated metallophthalocyanines were found to function as air-stable *n*-channel semiconductors with a maximum electron field-effect mobility of 0.03 cm² V⁻¹ s⁻¹. This is by far the highest electron mobility reported for air-stable *n*-channel organic semiconductors.

F₁₆CuPc, F₁₆ZnPc, F₁₉CoPc, and Cl₁₆FePc were purchased from Aldrich Chemical Co. F₁₆FePc,²⁰ (CN)₈CuPc,²¹ and PyCuPc²² were synthesized according to literature procedures. All phthalocyanines were further purified by sublimation twice at a pressure of 8 × 10⁻⁴ Torr or lower. The transistor device structure was the same as previously reported.^{10,11} An *n*-doped Si was used as substrate, with a gold contact that functioned as the gate and an oxide layer of 3000 Å as the gate dielectric having a capacitance per unit area of 10 nF/cm². The channel lengths of the devices were 25, 12, 4, and 1.5 μm. Semiconducting thin films were prepared by vacuum deposition at above 300 °C at a rate of 4 to 5 Å/s under a pressure of 2.0 × 10⁻⁶ Torr, and the thickness of the resulting films was between 500 and 600 Å. Different substrate temperatures for deposition were obtained by mounting the substrate to a heated copper block controlled by a temperature controller and measured by a thermocouple.

Figure 1 shows a current–voltage curve, obtained with a Hewlett-Packard (HP) 4145B analyzer, for copper hexadecafluorophthalocyanine (F₁₆CuPc) deposited at a substrate temperature of 125 °C with a 12 μm channel length. The film as-deposited performs as an *n*-channel transistor. The field-effect mobility calculated for the device shown in Figure 1a is 0.03 cm² V⁻¹ s⁻¹.²³ The on/off ratio (measured between points A and B as shown in Figure 1) for enhancement-mode-only operation is about 5 × 10⁴. The enhancement-depletion mode operation gives a higher (ca. 3 × 10⁵) on/off ratio. The value reported here is relatively high considering that neither the semiconducting layer nor the gate electrode is patterned.

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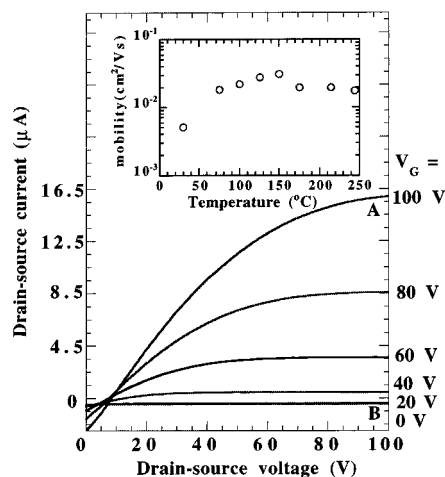


Figure 1. Drain-source current–voltage characteristics at different gate voltages of an *n*-channel transistor fabricated from $F_{16}CuPc$ at a substrate temperature of 125 °C for vacuum deposition. Inset: Field-effect mobilities of $F_{16}CuPc$ at different substrate temperatures for deposition.

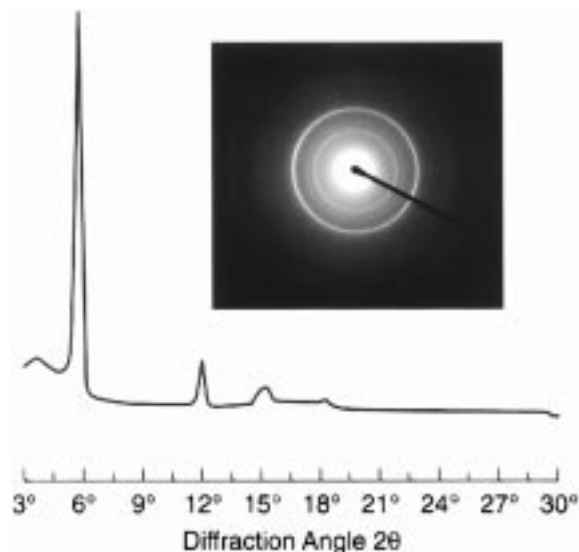


Figure 2. X-ray and electron (inset) diffractograms of $F_{16}CuPc$ deposited on SiO_2 .

We have prepared transistors at different substrate deposition temperatures (T_d). We found that the field-effect mobility is low, ca. 5×10^{-3} to $7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when T_d is at room temperature. The mobility is increased by almost 10 times at higher T_d . X-ray diffraction measurements (Figure 2) indicate that the as-deposited thin films of $F_{16}CuPc$ on Si/SiO_2 are highly ordered with a sharp diffraction peak at 2θ ca. 6.02° corresponding to an interplane distance of 14.6 Å, which is similar to the reflection from the (200) lattice planes of α -form $CuPc$, but in an expanded unit cell as is expected from the larger Van der Waals radius of F over H.¹⁰ The major peak visible under electron diffraction (Figure 2 inset) is around 3–4 Å, which corresponds to the π -stacking distance of the phthalocyanine rings. Therefore, the $F_{16}CuPc$ molecules are standing and essentially perpendicular to the SiO_2 surface; this renders the π -overlap direction of $F_{16}CuPc$ the same as the current flow direction, which provides an efficient path for charge transport. The mechanism for charge transport in these metallophthalocyanines and other polycrystalline organic semiconductors are believed to undergo a hopping mechanism at room temperature.²⁴ Therefore, the morphology of films can greatly affect charge carrier mobilities due to the grain boundary effect.^{10,24} In our case, it is found that the samples deposited at T_d above 75 °C are nodular with a mean diameter of about 50 nm. In contrast to our previous findings from $CuPc$,

Table 1. Summary of Field-Effect Mobilities ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for Different Substituted Metallophthalocyanines

MPc	$T_d = (30 \text{ }^\circ\text{C})$	$T_d = (125 \text{ }^\circ\text{C})$	$T_d = (215 \text{ }^\circ\text{C})$
$F_{16}CuPc$	5×10^{-3}	0.03	0.02
$F_{16}ZnPc$	1.7×10^{-5}	4.6×10^{-4}	1.2×10^{-3}
$F_{16}CoPc$	1.8×10^{-6}	4.5×10^{-5}	4.3×10^{-5}
$F_{16}FePc$	5.5×10^{-4}	5.8×10^{-3}	2.1×10^{-3}
$Cl_{16}FePc$	no field-effect	2.7×10^{-5}	<i>a</i>
$(CN)_8CuPc$	<i>b</i>	<i>b</i>	<i>b</i>
$PyCuPc$	<i>b</i>	<i>b</i>	<i>b</i>

^a Compound desorbs at this temperature. ^b Compound cannot be sublimed.

the nodules do not change to large, separated crystals around 150 °C but remain in good contact, becoming only more elongated. Thus, the good mobilities at high T_d may be a result of the very smooth, flat films, with close contact of the elongated nodules. On the other hand, samples deposited at 30 °C also consist of nodules but much more three-dimensional, rough, with poor contacts. This probably contributes to its lower mobility.

We have also studied other metallophthalocyanines with different metal coordinations and their mobility data are summarized in Table 1. It can be seen that the field-effect mobility is strongly dependent on the metal coordination and the substrate temperature for deposition. An iron hexadecachlorophthalocyanine ($Cl_{16}FePc$) was tested and it showed much lower field-effect mobility compared to the corresponding $F_{16}FePc$. The low mobilities of $Cl_{16}FePc$ might be related to its very poorly ordered films upon deposition, for which we observed no crystallographic diffraction peak by X-ray measurements and only very diffused ring patterns by electron diffraction. $(CN)_8CuPc$ and $PyCuPc$ were previously reported to be *n*-type conductors.²⁵ However, none of them can be vacuum sublimed: they both decomposed before they could be sublimed. $(CN)_8CuPc$ is very soluble in polar solvents such as DMF or acetone. We were able to obtain uniform films by casting from acetone solution, but no field-effect behavior was observed.

Most importantly, all the above halogenated phthalocyanine devices are very stable in air. The same field-effect mobilities as in vacuum (10^{-3} Torr) can be obtained when measured in air. The devices can be stored in open air for more than half a year without substantial change in mobilities or on/off ratio. To our knowledge, these are the only *n*-channel organic semiconducting materials that are stable in air and also have field-effect mobilities greater than $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Electron-withdrawing groups are known to lower the HOMO and LUMO energy levels of molecules. The LUMO level of $F_{16}MPc$ has previously been shown to be ca. 1.6 eV lower than its unsubstituted counterpart by UPS measurement and UV–vis data and this makes it less susceptible to oxidation.²⁶ In addition, since all the $F_{16}MPcs$ adopt the edge-on conformations in their thin films the fluorine atoms are in contact with air and could help to block moisture from penetrating through the films.

In summary, we have demonstrated that air-stable *n*-channel transistors with high field-effect mobilities can be realized with hexadecafluorinated metallophthalocyanines. With these materials, it is now possible to fabricate high-performance all-organic complimentary circuits and ring oscillators. In addition, these materials should also be of great interest as *n*-channel semiconductors in photovoltaic devices and electron-transporting materials in light-emitting diode (LED) applications.

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