Snake-Like Robot with Fusion Gait for High Environmental Adaptability: Design, Modeling, and Experiment
N-Type Semiconducting Behavior of Copper Octafluorophthalocyanine in an Organic Field-Effect Transistor

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Abstract: Based on the crystal structure analysis, the overlap integral between the frontier molecular orbitals of adjacent F8CuPcs in the one-dimensional chain is estimated: the overlap integral between the lowest unoccupied molecular orbitals is \(5.4 \times 10^{-3}\), which is larger than that in a typical n-type semiconducting material F16CuPc \((2.1 \times 10^{-3})\), whereas that between the highest occupied molecular orbitals is \(2.9 \times 10^{-4}\). Contrary to previous studies in air, we found that an organic field-effect transistor (OFET) composed of F8CuPc essentially shows clear n-type semiconducting behavior in vacuum.

Keywords: copper octafluorophthalocyanine; organic semiconductor; n-type semiconductor; OFET

1. Introduction

Metallophthalocyanines (MPcs) are widely used not only as organic dyes but also as organic semiconductors, owing to their high air and chemical stabilities. They are being actively studied as components of organic electronics, in applications such as organic field-effect transistors (OFETs), organic light-emitting diodes, and organic photovoltaic cells [1–3]. MPcs are used as hole transport/injection/extraction materials because the energy level of their highest occupied molecular orbital (HOMO), consisting of the \(\pi\) orbital of the phthalocyanine (Pc), matches well with the work function of ordinary hole injection/extraction electrodes such as Au or indium-tin-oxide (ITO) [4–6]. They show p-type semiconducting characteristics, with a field effect hole mobility of around \(10^{-2}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in thin film transistors and around 1 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in single crystal transistors [1,7].

Introduction of electron-withdrawing groups onto the peripheral benzene rings of Pc is a valid approach for tuning the electronic properties of MPcs. For instance, F16CuPc, a fully fluorinated CuPc shows n-type characteristics with an electron mobility comparable to its unsubstituted counterpart, CuPc, a p-type material [8,9]. Therefore, F16CuPc has been widely used as an n-type material in organic electronics [10–13].

For n-type organic semiconductors, in order to obtain a low energy barrier at the interface, the position of the lowest unoccupied molecular orbital (LUMO) should be close to the work function of the electrode. Moreover, a large \(\pi-\pi\) overlap of the LUMOs between the adjacent molecules in the crystal is preferred [14], because electron transport in the crystalline state occurs through the overlapped LUMOs. As for the LUMO level of F8CuPc (Figure 1), the reported value, \(-3.91\) eV [15], is similar to that of C60 and its derivatives [16,17]. This implies that the LUMO level of F8CuPc is positioned optimally to enable it to function as an n-type organic semiconductor, and that F8CuPc can
be potentially used as an electron transport/injection/extraction material in organic electronics, similar to C_{60}. Indeed, the junction between F_8CuPc and p-type MPc has been reported to exhibit a rectification effect [18,19]. In contrast, the highest occupied molecular orbital (HOMO) level of F_8CuPc has been reported to be −6.06 eV [15]. This value is far from the work function of Au or ITO [5,6]. Therefore, we expected F_8CuPc to be an n-type semiconductor. However, recently, thin film or single crystal transistors composed of F_8CuPc have been reported to show ambipolar characteristics in air [20,21].

![Structural formula of F_8CuPc.](image)

In this study, we grew a single crystal of F_8CuPc, and determined its crystal structure to estimate the π–π overlap between the frontier orbitals of adjacent molecules by the extended Hückel calculation. We have also examined the charge transport properties of OFETs based on F_8CuPc thin films, and discovered that the transistor is unstable in air, whereas it shows stable n-type transport properties in vacuum.

2. Materials and Methods

2.1. Synthetic and Crystallisation Procedures

All reagents were used as received without further purifications. 5.1 g (30 mmol) of CuCl_2·2H_2O (WAKO) was heated and dried under vacuum, and 5.0 g (30 mmol) of 4,5-difluorophthalonitrile (TCI) and 10 mL of N,N-dimethylformamide (Super Dehydrated grade, WAKO) were added. The mixture was refluxed under Ar for 6 h, and filtered. A bluish-purple powder of F_8CuPc was obtained, which was washed several times with acetone to yield 2.3 g (42%) of the product. Single crystals of F_8CuPc were grown from this, by vacuum sublimation at 380 °C under a pressure less than 40 Pa.

2.2. X-ray Diffraction (XRD) Measurements

Although single-crystal X-ray diffraction (XRD) measurements were performed and the molecular arrangement of F_8CuPc has been revealed in [21], the atomic coordinates are not available. Therefore, XRD data was collected for a single crystal of F_8CuPc, using an automated Rigaku Rapid system with the monochromated Cu-Kα radiation (λ = 1.54187 Å). The structure was solved using a direct method, using SIR2004 [22] and refined by a full-matrix least-squares technique with SHELXL-2014/7 [23] with anisotropic and isotropic thermal parameters for non-hydrogen and hydrogen atoms, respectively. The crystallographic data has been deposited at the Cambridge Crystallographic Data Centre (CCDC) as CCDC-1531473. Crystal data for F_8CuPc: Triclinic, P\overline{1}, a = 3.62740(10) Å, b = 12.7357(4) Å, c = 13.4538(4) Å, α = 95.079(9)°, β = 90.529(6)°, γ = 96.441(6)°, and V = 615.07(3) Å³, Z = 1, F(000) = 357, d_{cal} = 1.944 g cm⁻³, μ (CuKα) = 2.231 mm⁻¹ (λ = 1.54187 Å), R₁ = 0.0879, wR₂ = 0.2008, GoF = 0.999.

2.3. Fabrication of OFET and Measurement of the Transport Properties

A thin film organic field effect transistor composed of F_8CuPc was fabricated by the vacuum deposition of F_8CuPc on a SiO_2/n-Si substrate under a pressure less than 1 × 10⁻² Pa, where, n-Si and SiO_2 work as gate electrode and gate insulating layers, respectively. The deposition rate was ca. 0.05 nm s⁻¹, and the resulting thickness of the film was ca. 30 nm. Subsequently, 30 nm thick Al
electrodes were deposited on the F8CuPc film to serve as the source and drain electrodes, under a pressure less than $1 \times 10^{-3}$ Pa. Current–voltage characteristics were measured by an ADCMT 8252 electrometer in air or vacuum ($\sim 10^2$ Pa and less than $10^{-2}$ Pa).

3. Results and Discussion

The lattice constant of the F8CuPc crystal is consistent with those reported in [21]. The crystal structure is shown in Figure 2. F8CuPc forms a one-dimensional regular chain along the $a$-axis with an interplanar distance of 3.30 Å, which is smaller than the sum of the van der Waals radii of sp$^2$ carbons, suggesting a strong $\pi-\pi$ intermolecular interaction. As the charge transport in organic semiconductors occurs via the $\pi$-electrons, a strong $\pi-\pi$ intermolecular interaction in the crystalline state is desirable, which can be evaluated by the overlap integral in the conduction path consisting of $\pi$-orbitals. Using an extended Hückel calculation method (The extended Hückel calculation was performed using CAESAR 2 software developed by PrimeColor Software, Inc. (Raleigh, NC, USA) Default parameters were used for the calculations), the overlap integral between the $\pi$-orbitals of adjacent F8CuPcs in the one-dimensional chain along the $a$-axis were estimated: the overlap integral between the LUMOs was found to be $5.4 \times 10^{-3}$, which is comparable to that of molecular conductors consisting of MPcs [24], whereas that between HOMOs was $2.9 \times 10^{-4}$. In addition to the optimal position of the LUMO level, the $\pi-\pi$ overlap appears to favor electron transfer over hole transfer.

![Figure 2. One-dimensional molecular arrangement of F8CuPc along the a-axis.](image)

The carrier mobility of an organic thin film depends on the molecular orientation in the film. Figure 3 shows the X-ray diffraction pattern of the F8CuPc film deposited on a SiO$_2$/n-Si substrate. A peak at $2\theta = 6.56^\circ$, corresponding to (001) plane was observed, indicating that the crystallographic $c$-axis of F8CuPc in the as-deposited film is perpendicular to the substrate surface. This orientation is favorable for charge transport between the source and drain electrodes of an OFET (vide infra), because the $\pi-\pi$ overlap between adjacent F8CuPc molecules in the one-dimensional chain lies on the substrate.

![Figure 3. X-ray diffraction pattern of an F8CuPc film deposited on a SiO$_2$/n-Si substrate.](image)

An OFET composed of F8CuPc was fabricated using a SiO$_2$/n-Si substrate and Al electrodes. Figure 4 shows a schematic of the fabricated transistor and its current-voltage characteristics measured.
in air. F8CuPc shows an n-type semiconducting behavior. However, parabolic current-voltage curves exhibiting a large hysteresis were obtained, although the first half of each measurement was consistent with the current-voltage characteristics reported previously [20]. Furthermore, the results could not be reproduced in repeated measurements. Figure 5 shows the current–voltage characteristics measured in vacuum (~10\(^{-2}\) Pa). Compared to the measurement in air, it is obvious that the instability is rather suppressed. These features indicate that the F8CuPc transistor is unstable in air, and therefore, it is difficult to evaluate the transistor characteristics under air. In fact, we could not observe the reported ambipolar characteristics under air [20,21] even when Au was used as the source and drain electrodes. On the other hand, Figure 6 shows the current–voltage characteristics measured under high vacuum (under a pressure less than 10\(^{-2}\) Pa). F8CuPc shows a typical, stable n-type semiconducting behavior in vacuum, and the field effect electron mobility in the thin film transistor was calculated to be 7.9 \(\times\) 10\(^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) (on/off ratio being 3.6 \(\times\) 10\(^{3}\)). Obviously, the p-type characteristics could not be found in high vacuum, irrespective of the source and drain electrodes.

![Schematic diagram of an F8CuPc film transistor](image)

**Figure 4.** (a) Schematic of an F8CuPc film transistor; (b) current-voltage characteristics of the F8CuPc film transistor measured in air; and (c) those obtained from repeated measurements; these were performed immediately after the first.
Indeed, a recent study on a single-crystal transistor of F\textsubscript{16}CuPc demonstrated that the field effect electron mobility could be obtained for F\textsubscript{8}CuPc, if a single crystal is used. The field effect electron mobility of 7.9 × 10\textsuperscript{-4} cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} is almost 10 times lower than that of the F\textsubscript{16}CuPc film transistor; Bao et al. reported a field effect electron mobility of 5 × 10\textsuperscript{-3} cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} for the F\textsubscript{16}CuPc thin film transistor [8], and we too obtained a similar value with our measurement system. As for the electron transport, the overlap of the LUMOs is responsible for the transport. In the case of F\textsubscript{16}CuPc, the overlap integral between the LUMOs of adjacent F\textsubscript{16}CuPcs in the one-dimensional chain could be estimated to be 2.1 × 10\textsuperscript{-3}, according to the crystal data in [26]. Despite the larger overlap integral between the LUMOs, the F\textsubscript{8}CuPc film transistor shows smaller electron mobility compared to that of the F\textsubscript{16}CuPc film transistor. The lower electron mobility in the F\textsubscript{8}CuPc film transistor could be attributed to the relatively low crystallinity in the as-deposited film, as indicated by the broad diffraction peak observed in Figure 3, whereas sharp diffraction peaks suggesting high crystallinity were observed in the F\textsubscript{16}CuPc film [8]. When a single crystal of F\textsubscript{16}CuPc was used, the field effect electron mobility of the F\textsubscript{16}CuPc transistor increased by two orders of magnitude [9].

Figure 5. Current–voltage characteristics of the F\textsubscript{8}CuPc n-channel transistor in vacuum (~10\textsuperscript{2} Pa).

![Figure 5](image1.png)

Figure 6. Current–voltage characteristics of the F\textsubscript{8}CuPc n-channel transistor in high vacuum (less than 10\textsuperscript{-2} Pa).

![Figure 6](image2.png)
This implies that higher field effect electron mobility could be obtained for F$_8$CuPc, if a single crystal is used. Indeed, a recent study on a single-crystal transistor of F$_8$CuPc demonstrated that the field effect electron mobility of F$_8$CuPc is comparable to that of F$_{16}$CuPc [21], even though the measurements were performed in air.

4. Conclusions

Based on the crystal structure analysis, we have estimated the overlap integral between the LUMOs of adjacent molecules along the $a$-axis of the one-dimensional regular chain of F$_8$CuPc, and discovered that it is larger than that in a typical n-type semiconducting material F$_{16}$CuPc. The X-ray diffraction pattern shows a peak attributable to (001) plane, implying that the one-dimensional chain in the as-deposited F$_8$CuPc film lies on the substrate. A field-effect transistor composed of an F$_8$CuPc film on a SiO$_2$/n-Si substrate clearly shows n-type semiconducting behavior with the field effect electron mobility of 7.9 x 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ in vacuum, while being unstable in air. The larger overlap integral between the LUMOs in F$_8$CuPc compared to that in F$_{16}$CuPc implies that the electron mobility of F$_8$CuPc could potentially exceed that of F$_{16}$CuPc. Considering the LUMO level and the electron transport properties, F$_8$MPcs are good candidates for n-type semiconduction in organic electronics.

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References


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