Fluorination of Metal Phthalocyanines: Single-Crystal Growth, Efficient N-Channel Organic Field-Effect Transistors, and Structure-Property Relationships

Hui Jiang¹, Jun Ye², Peng Hu¹, Fengxia Wei¹, Kezhao Du¹, Ning Wang¹, Te Ba², Shuanglong Feng¹ & Christian Kloc¹

¹School of Materials Science and Engineering, Nanyang Technological University, 639798 Singapore, ²Institute of High Performance Computing, Agency for Science, Technology and Research, 138632 Singapore.

The fluorination of p-type metal phthalocyanines produces n-type semiconductors, allowing the design of organic electronic circuits that contain inexpensive heterojunctions made from chemically and thermally stable p- and n-type organic semiconductors. For the evaluation of close to intrinsic transport properties, high-quality centimeter-sized single crystals of F₁₆CuPc, F₁₆CoPc and F₁₆ZnPc have been grown. New crystal structures of F₁₆CuPc, F₁₆CoPc and F₁₆ZnPc have been determined. Organic single-crystal field-effect transistors have been fabricated to study the effects of the central metal atom on their charge transport properties. The F₁₆ZnPc has the highest electron mobility (1.1 cm² V⁻¹ s⁻¹). Theoretical calculations indicate that the crystal structure and electronic structure of the central metal atom determine the transport properties of fluorinated metal phthalocyanines.

Devices based on organic semiconductors, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic solar cells (OSCs) or emerging printed microelectronic circuits require stable p- and n-type organic semiconductors with excellent electrical and optoelectronic properties. Additionally, it is desired that these organic semiconductors are easily synthesized and stable during the whole life-time. These are thoughtful requirements and all have been achieved but not simultaneously in one organic semiconductor. The highest mobility in organic semiconductors has been achieved in small molecules like the p-type rubrene¹. However, rubrene for mass applications is too expensive due to multi-steps synthesis and additionally easily oxidizes². In contrast, very stable organic semiconductors, like metal phthalocyanines have at least one order of magnitude of lower mobility. To get n-type phthalocyanines, fluorinated phthalocyanines need to be synthesized but the electron mobility in fluorinated phthalocyanines decrease even more. The desirable organic semiconductor with high mobility, low fabrication cost and good air stability is still a big challenge.

A sizeable number of p-type organic semiconductors with mobility larger than 1 cm² V⁻¹ s⁻¹ have been discovered³. However, n-type channel candidates have been limited to C₆₀ and its derivatives⁴, TCNQ and its derivatives⁵, perylene derivatives⁶ and halogenated metal phthalocyanines⁷. Furthermore, only in a few complex molecular structures, the electron mobility is greater than 1 cm² V⁻¹ s⁻¹⁸. For many devices, the mobility of both holes and electrons should be in the same range.

Most high-performance organic semiconductors have complex molecular structures and are synthesized by complicated and expensive processes. Phthalocyanines are the exceptions. They have already been produced in substantial amounts and are used as stable dyes in different branches of industry. However, the charge carrier mobility measured in thin films of metal phthalocyanines is, in general, one or a few orders of magnitude lower than the highest reported value measured for metal phthalocyanine single crystals²². For example, the hole mobility of thin films of copper phthalocyanine (CuPc) is in the range of 10⁻² cm² V⁻¹ s⁻¹, but that of a single crystal can reach even 1 cm² V⁻¹ s⁻¹. The complementary halogenated copper phthalocyanine has an electron mobility in the range of 10⁻² cm² V⁻¹ s⁻¹ when measured on thin films²³. Therefore, it is very interesting to
explore the intrinsic mobility of metal phthalocyanines to determine whether a stable device with hole and electron mobilities in the range of 1 cm² V⁻¹ s⁻¹ can be fabricated.

In our studies, copper hexadecafluorophthalocyanine (F₁₆CuPc), cobalt hexadecafluorophthalocyanine (F₁₆CoPc) and zinc hexadecafluorophthalocyanine (F₁₆ZnPc) were selected. For the evaluation of close to intrinsic transport properties, high-quality centimeter-sized single crystals of F₁₆CuPc, F₁₆CoPc and F₁₆ZnPc have been grown. The reported crystal data for F₁₆CuPc from different research groups are different²⁵–²⁸. Moreover, in the fluorinated metal phthalocyanines, it is not known if the different central metal atoms affect the intermolecular interaction. New crystal structures of F₁₆CuPc, F₁₆CoPc and F₁₆ZnPc have been determined. Organic single-crystal field-effect transistors have been fabricated and the effect of the central metal atom on their charge transport properties has been explored. The observed mobilities in fluorinated metal phthalocyanines with different central metal have been explained using theoretical calculation.

Results

Single-crystal growth and structure analysis. The three powders were purchased from Sigma-Aldrich Corporation and purified two times by sublimation in high vacuum. Large-sized single crystals of F₁₆CuPc, F₁₆CoPc and F₁₆ZnPc were obtained by physical vapor transport methods²⁹. The crystal growth was carried out under argon gas flow with pressure in the range of ~1 Torr. The optical
images of single crystals of F16CuPc, F16CoPc and F16ZnPc are shown in Fig. 1. The three violet single crystals displayed millimeter-sized square columns. The length of some crystals is greater than 1 centimeter.

The single crystal structures of the three similar molecules were determined by single crystal X-ray diffraction. F16CuPc was of the P1 space group with \(a = 4.8529(7)\) Å, \(b = 10.2721(14)\) Å, \(c = 28.391(4)\) Å, \(\alpha = 86.614(9)\), \(\beta = 87.879(8)\), \(\gamma = 81.701(8)\); F16CoPc was of the P1 space group with \(a = 4.7963(7)\) Å, \(b = 10.1976(14)\) Å, \(c = 28.092(4)\) Å, \(\alpha = 86.590(9)\), \(\beta = 88.100(8)\), \(\gamma = 81.743(8)\); and F16ZnPc was of the P1 space group with \(a = 4.8266(7)\) Å, \(b = 10.1610(14)\) Å, \(c = 27.977(4)\) Å, \(\alpha = 86.186(9)\), \(\beta = 87.482(8)\), \(\gamma = 80.664(8)\). (See the SI, Fig. S1–S3, molecular packing of F16CuPc, F16CoPc and F16ZnPc.) The structures of F16CoPc and F16ZnPc were previously not known.

**Single-crystal growth direction determination.** Transmission electron microscopy (TEM) was used to find the crystal growth direction along the columns (Fig. 2a, 2c, 2e). Selected area electron diffraction (SAED) showed that the preferred crystal growth direction of F16CuPc (Fig. 2a–2b), F16CoPc (Fig. 2c–2d) and F16ZnPc (Fig. 2e–2f) was [100]. In the [100] direction, the metal hexadecafluorophthalocyanines form a stack where the metal atoms are at the shortest distances. The crystal direction of [100] is actually the shortest axis of the metal hexadecafluorophthalocyanines, which is also the densest packing of the molecules (Fig. 1e–g).

**Single-crystal field-effect transistors.** The charge transport behavior along the [100] direction of individual crystals of F16CuPc, F16CoPc and F16ZnPc were studied. Micrometer-thin ribbon-like single crystals were used for field-effect transistor measurements. Asymmetrical electrodes (Au and Ag) were used\(^ {30} \), and all transistors were fabricated and characterized in air under ambient conditions. All transistors showed n-type characteristics, and the mobilities of many devices were larger than 0.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\). Typical output and transfer characteristics of F16ZnPc single-crystal FETs are shown in Fig. 3. Some nonlinearity has been found in the output curve of the transistor which may be caused by the contact and access resistances\(^ {31–33} \). Although the molecular structures of F16MePcs crystals along their [100] direction via density functional theory (DFT), where the electrons transfer integrals have obtained electron transfer integrals by calculating the band method\(^ {38} \) or "energy splitting in dimer" method. In this work, we have obtained electron transfer integrals by calculating the band structures of F16MePcs crystals along their [100] direction via density functional theory (DFT), where the electrons transfer integrals \(t_\text{s}\) between the F16MePcs dimers are taken as 1/4 of the LUMO bandwidth along this direction. We have not displayed the crystal structure for each F16MePc due to their high structural similarity, but a representative structure can be found in Fig. 4(a) and (b). To address the effects of electron-phonon interactions, the polaron binding energy, which is equal to half of the reorganization energy \(\lambda\), is defined as:\(^ {37} \)

\[
E_{\text{pol}} = \sum_j M_j\alpha_j^2 \Delta Q_j^2
\]

(1)

Here, \(\Delta Q_j^2\) represents the normal mode displacement along \(Q_j\) between the equilibrium geometries of neutral and charged (for instance, negatively charged) molecules. The calculated values of polaron binding energies and Huang-Rhys factors are given in method\(^ {18} \) or "energy splitting in dimer" method. In this work, we have obtained electron transfer integrals by calculating the band structures of F16MePcs crystals along their [100] direction via density functional theory (DFT), where the electrons transfer integrals \(t_\text{s}\) between the F16MePcs dimers are taken as 1/4 of the LUMO bandwidth along this direction. We have not displayed the crystal structure for each F16MePc due to their high structural similarity, but a representative structure can be found in Fig. 4(a) and (b). To address the effects of electron-phonon interactions, the polaron binding energy, which is equal to half of the reorganization energy \(\lambda\), is defined as:\(^ {37} \)

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**Discussion**

Some previous reports indicate that the device mobility will increase with decreasing intermolecular spacing distance\(^ {14} \). Very dense molecular packing is helpful for charge transport. In metal phthalocyanines, the dimensions of the central metal atoms determine the intermolecular spacing distance\(^ {25} \). Lower intermolecular spacing distance will result in higher device mobility\(^ {35,36} \). Our experimental results have confirmed this viewpoint. Theoretical calculations were applied to study this structure-property relationship, especially for the function of the metal atoms in metal hexadecafluorophthalocyanines.

The charge transport in organic semiconductors is governed by electronic coupling and electron-phonon interactions, where the latter plays a more profound role in determining charge transport properties. The major transport mechanism can be described by polaron and disorder models\(^ {35} \). A simple yet widely applied way to evaluate the electronic coupling between neighboring molecules in organic semiconductors is referred to as the energy level-splitting method\(^ {18} \) or "energy splitting in dimer" method. In this work, we have obtained electron transfer integrals by calculating the band structures of F16MePcs crystals along their [100] direction via density functional theory (DFT), where the electrons transfer integrals \(t_\text{s}\) between the F16MePcs dimers are taken as 1/4 of the LUMO bandwidth along this direction. We have not displayed the crystal structure for each F16MePc due to their high structural similarity, but a representative structure can be found in Fig. 4(a) and (b). To address the effects of electron-phonon interactions, the polaron binding energy, which is equal to half of the reorganization energy \(\lambda\), is defined as:\(^ {37} \)

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**Figure 3** | (a) Schematic diagram of F16ZnPc single-crystal device. (b) Output and (c) transfer curve of F16ZnPc individual single-crystal field-effect transistor. The inset in 3b presents the device structure.
Table 1. It has been suggested that the reorganization energy of F$_{16}$ZnPc is dominated by phonon modes at approximately 1400 cm$^{-1}$ \(^{39}\). In a recent DFT work \(^{40}\) on F$_{16}$MePcs, they have found the phonon modes at approximately 1400 cm$^{-1}$ for the F$_{16}$MePcs in this work are almost identical. To determine the largest components of different normal modes towards polaron binding energies, we have calculated both electron-phonon coupling strengths and polaron binding energies for all F$_{16}$MePcs by adopting the same methods to calculate both quantities \(^{37}\). Detailed results of the electron-phonon coupling calculations can be found in the supporting information. Four groups of vibrational frequencies of the F$_{16}$MePcs investigated are found to contribute most to the polaron binding energy. Mobility calculations were performed with the aid of a temperature-dependent canonical transformation of the Holstein Hamiltonian by incorporating all physical parameters into the model \(^{41-45}\). The calculated mobilities at room temperature $T = 298$ K and the measured mobilities are also given in Table 1. It is shown in Table 1 that the calculated mobilities are in good accord with the experiments in terms of trends and orders of magnitude. The overall polaron binding energy and the Huang-Rhys factor indicate that F$_{16}$CoPc has the strongest electron-phonon coupling strength, although it also has the highest calculated $t_e$. Stronger electron-phonon coupling directly contributes to a reduction in its mobility due to an increase in electron-phonon scattering. F$_{16}$CuPc has slightly smaller $S$ compared to F$_{16}$CoPc, but it has a much smaller $t_e$. Therefore, it is not surprising that F$_{16}$CuPc has the lowest mobility among these F$_{16}$MePcs. Owing to its relatively smaller $S$ and its higher electron transfer integral, F$_{16}$ZnPc is the best compound in

![Figure 4](https://www.nature.com/scientificreports)

(a) Crystal structure of F$_{16}$MePcs in the [010] direction, (b) molecule packing along the [100] direction, and (c) electronic band structure of F$_{16}$MePcs along the [100] direction; Fermi surfaces are indicated as dashed lines.

| Name       | $t_e$ (meV) | $E_{pol}$ (meV) | $S$  | $\mu_{\text{max\,theory}}$ (cm$^2$V$^{-1}$s$^{-1}$) | $\mu_{\text{max\,experiment}}$ (cm$^2$V$^{-1}$s$^{-1}$) | $a$ (Å)  | $D$ (Å)  |
|------------|------------|----------------|------|-----------------------------------------------|--------------------------------------------------|---------|---------|
| F$_{16}$ZnPc | 33.3       | 79.53          | 0.779| 9.6                                           | 1.1                                              | 3.194   | 4.8266  |
| F$_{16}$CoPc | 50.5       | 80.86          | 0.798| 8.6                                           | 0.8                                              | 3.2304  | 4.7963  |
| F$_{16}$CuPc | 24.0       | 79.27          | 0.785| 8.3                                           | 0.6                                              | 3.2486  | 4.8529  |
terms of mobility. The electronic band structures of these F16MePcs, shown in Fig. 4(c), suggest that all LUMO bands maintain simple 1D feature. From this perspective, we may suspect that the electron transport in these F16MePcs is of 1D character due to close packing of the F16MePc molecules along the [100] direction, as shown in Fig. 4(b). The inter-molecular distances in different crystals are measured as: dF16CoPc = 3.194 Å, dF16CuPc = 3.2304 Å and dF16ZnPc = 3.2486 Å (Fig. 1c–g), where Co and Cu complexes with non-zero magnetic moments have comparable intermolecular distances that are larger than that of the Zn complex. Interestingly, we can also observe a trend of increasing mobility with decreasing inter-molecular distances in F16MePcs, as indicated in Table 1. Similar behavior was also observed in metallo-porphyrins (E-OEPs)\(^{38}\). Unlike those found in E-OEPs, F16MePc with Zn as the center ion has smallest inter-molecular distance. It is worth noting that electron transfer integrals are found to be correlated to either center-metal ion distances or the a-axis length, as also shown in Table 1, although the opposite situation was claimed for E-OEPs.\(^{39}\) Further comparison of the inter-molecular distances suggests that F16CoPc should have less π-π overlap compared to F16ZnPc due to larger inter-molecular distances. DFT population analyses of all F16CoPc and F16CuPc complexes (See Table S1 in SI for details) reveal interesting roles for d-orbitals in Co and Cu complexes. In F16CoPc, a super-exchange mechanism may be responsible for its higher electron transfer integral in addition to conventional contributions from intermolecular π-π overlap.\(^{40}\) Meanwhile, F16CuPc has a much smaller electron transfer integral due to the lack of a super-exchange mechanism and weaker π-π interactions.

Conclusions
In conclusion, high-quality, large-size organic single crystals of F16CuPc, F16CoPc and F16ZnPc were obtained by physical vapor transport. Single crystal structures were determined. Organic single-crystal field-effect transistors have been fabricated to study the effects of the central metal atom on their charge transport properties. The crystal field-effect transistors have been fabricated to study the effects of the central metal atom on their charge transport properties. The substrate was thermally grown on a heavily-doped n-type silicon wafer, which was used as a gate electrode. The substrate was first immersed in a boiled mixed solution (sulfuric acid (98%): hydroperoxide = 3:1) for half an hour to clean the surface. It was then cleaned sequentially with deionized water, hot acetone and isopropanol. The solution was heated to 80°C for an ultrasonic cleaner for approximately 15 min to remove the remaining water. The substrate was finally dried under a stream of N₂, Octadecyltrichlorosilane (OTS) modification was carried out for approximately 2 h by the vapor-deposition method. Then, the substrate was rinsed with n-hexane, chloroform and IPA in an ultrasonic cleaner. Finally, the substrate was dried in N₂ ambient before use.

Mobility calculations. Mobility for the organic crystals along any transfer path was determined by the diffusion coefficient of polarons formed by electrons and phonons through the Einstein relationship as follows: \(\mu = e\beta\delta D\), where \(\beta\) is the charge of an electron, \(\delta = 1/k_BT\) and \(k_B\) is the Boltzmann constant. Only local electron-phonon coupling was considered, as both Huang-Rhys factors and transfer integrals suggest that the polarons should be well localized on single lattice sites.\(^{42}\) Mobility contributions from both band-like and hopping transport were simultaneously considered in this model. Other model parameters include a finite phonon bandwidth of \(\Delta = 0.1\varepsilon_0\). A constant scattering rate of \(\Gamma = 1 \times 10^3 \varepsilon_0\) was also considered to account for the effects of impurities on band-like mobilities.

Methods
Single-crystal growth. A physical vapor transport system with argon flow was used for the purification of source materials and crystal growth. A rotary vacuum pump was used to control the pressure in the quartz tube in the range of ~3 torr. The high-temperature and low-temperature zones were kept at 360°C and 280°C, respectively. All experimental parameters for gas flow and temperature gradient were the same for the above-mentioned three types of crystals. Needle-like crystals that were a centimeter in length were collected for structure determination. If fresh, purified fluorinated metal phthalocyanines were used as the source materials, the single crystals of F16CuPc, F16CoPc and F16ZnPc were repeatedly obtained.

XRD characterization. The X-ray powder diffraction (XRD) data were obtained with a Bruker D8 Advance diffractometer. Single crystal structures were collected using a Bruker SMART APEX II single crystal diffractometer (X-ray radiation, Mo Kα, \(\lambda = 0.71073 \AA\)).

Fabrication of organic single-crystal field-effect transistors. Organic single-crystal field-effect transistors (OFETs) were fabricated on a 600-nm SiO₂ substrate. The substrate was thermally grown on a heavily-doped n-type silicon wafer, which was used as a gate electrode. The substrate was first immersed in a boiled mixed solution (sulfuric acid (98%): hydroperoxide = 3:1) for half an hour to clean the surface. It was then cleaned sequentially with deionized water, hot acetone and isopropanol. The solution was heated to 80°C for an ultrasonic cleaner for approximately 15 min to remove the remaining water. The substrate was finally dried under a stream of N₂, Octadecyltrichlorosilane (OTS) modification was carried out for approximately 2 h by the vapor-deposition method. Then, the substrate was rinsed with n-hexane, chloroform and IPA in an ultrasonic cleaner. Finally, the substrate was dried in N₂ ambient before use.

For preparation of the FET unit cells, we constrained the lattice parameters to experimental values, allowing only relaxation of atom positions. Furthermore, geometry optimization, vibrational frequencies, polaron binding energies, population analysis and molecular orbital analysis were carried out at the level of B3LYP density functional and with hybrid basis sets of 6-31G** for non-metallic elements and SDD effective core potential (ECP) for transition metal atoms using the ORCA 3.0.0 package. Single point energy calculations of F16MePc dimers were also performed using same methods. In the ORCA geometry optimization runs, convergence tolerances were set to smaller than 5 \(\times 10^{-4}\) Ha for energy change, max gradient smaller than 5 \(\times 10^{-3}\) Ha/bohr, root mean square gradient smaller than 1 \(\times 10^{-3}\) Ha/bohr, max displacement smaller than 4 \(\times 10^{-4}\) bohr and root mean square displacement smaller than 2 \(\times 10^{-4}\) bohr. For both ORCA geometry optimization and single point calculations, the convergence criteria were all set to 1 \(\times 10^{-4}\) Ha.

Mobility calculations. Mobility for the organic crystals along any transfer path was determined by the diffusion coefficient of polarons formed by electrons and phonons through the Einstein relationship as follows: \(\mu = e\beta\delta D\), where \(\beta\) is the charge of an electron, \(\delta = 1/k_BT\) and \(k_B\) is the Boltzmann constant. Only local electron-phonon coupling was considered, as both Huang-Rhys factors and transfer integrals suggest that the polarons should be well localized on single lattice sites.\(^{42}\) Mobility contributions from both band-like and hopping transport were simultaneously considered in this model. Other model parameters include a finite phonon bandwidth of \(\Delta = 0.1\varepsilon_0\). A constant scattering rate of \(\Gamma = 1 \times 10^3 \varepsilon_0\) was also considered to account for the effects of impurities on band-like mobilities.

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Author contributions
H.J. and C.K. conceived the experiments. H.J. performed the experiments including single-crystal growth, device fabrication, characterization and data analysis. P.H. performed the TEM characterization. J.Y. and T.B. performed the calculations and simulations. J.Y. prepared Figs 4 and Table 1 and wrote the the part on theoretical calculations and discussions. F.X.W., K.Z.D., N.W. and S.L.F. analyzed the single crystal structures. H.J. and C.K. co-wrote the manuscript. All of the authors reviewed the manuscript, discussed the data and gave profound suggestions.

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