

Temperature Dependence of Carrier Mobility on Non-Peripherally Octahexyl-Substituted Copper Phthalocyanine

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Abstract

Charge carrier mobility of a solution-processable low-molecular-weight organic semiconductor material, 1,4,8,11,15,18,22,25-octahexylphthalocyanine copper complex (C6PcCu), was investigated by using time-of-flight (TOF) technique. The anomalous temperature dependence of carrier mobility was discussed from the viewpoint of the molecular packing structure, which was clarified by single-crystal X-ray structure analysis.

1. Introduction

Low-molecular-weight organic semiconductors have attracted much attention for their application to optoelectronic devices, such as organic solar cells [1, 2]. In the low-molecular-weight organic semiconductors, phthalocyanine possesses high stability and electrical properties, but exhibits low solubility [3, 4]. By introducing alkyl-chains at the non-peripheral positions of phthalocyanine, the liquid crystalline (LC) properties as well as high solubility in typical organic solvents appeared [5, 6]. Particularly, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂) has attracted considerable attention, because of the high hole mobility exceeding 1 cm²/Vs in the crystal phase, which was evaluated by time-of-flight (TOF) method [6]. The overlap of π electron orbitals with the adjacent molecules, which is determined by the molecular packing structure, tends to be strongly related with the charge carrier mobility of organic materials [7].

The analogue molecules, such as a metal complex of C6PcH₂, are also expected to possess excellent carrier transport properties like conventional non-substituted metallophthalocyanines, such as copper phthalocyanine [1, 8]. However, the effect of center metal for carrier transport properties is not still understood clearly. In this study, the carrier mobility of 1,4,8,11,15,18,22,25-octahexylphthalocyanine copper complex (C6PcCu) was measured by TOF technique, and the temperature dependence was investigated. The mechanism of the carrier transport was discussed by taking the molecular packing structure of C6PcCu, which was clarified by single-crystal X-ray structure analysis, into consideration.

2. Experimental

Molecular structures of C6PcH₂ and C6PcCu are shown in Fig. 1. The thermal phase transition behavior of C6PcCu was observed by DSC (TA Instruments Q2000) at a scanning rate of 1 °C/min and a polarizing optical microscope (POM,

Nikon ECLIPSE E600 POL) equipped with a hot stage (Linkam LTS-350).

A sandwich cell, which consisted of two indium-tin-oxide (ITO)-coated glass plates and a 12- μ m-thick spacer of polyethylene terephthalate film, was prepared for the TOF measurement. C6PcCu was heated to a temperature in the isotropic phase, for injecting into the cell by a capillary action. The sample was irradiated with a Q-switched Nd:YAG pulsed laser (wavelength: 355 nm, pulse width: 1 ns) in a vacuum, and the generated transient current was detected by an oscilloscope (Teledyne LeCroy HDO4054).

The single crystal of C6PcCu was grown in the saturated solution by the recrystallization method in slow cooling process. The diffraction data of the single crystal was collected at 213 K using synchrotron radiation ($\lambda=0.8000$ Å) in the BL38B1 beamline at SPring-8 with the approval of JASRI (2016B1746). The cell refinement was carried out with HKL2000 software. The crystallographic calculation was performed with the Crystal Structure 4.2. The crystal structure was solved by direct methods (SHELXT), and refined by the full-matrix least-squares method (SHELXL version 2014/7).

The temperature dependence of the lattice parameters in the single crystal was observed by using a curved imaging plate (RIGAKU R-Axis RAPID 191 R) with Cu K α radiation.

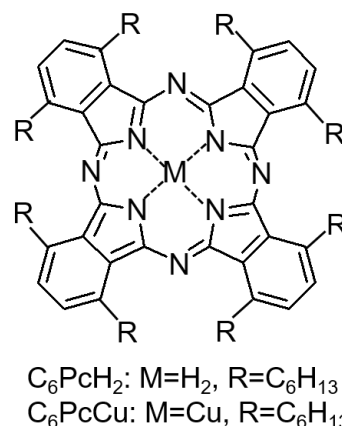


Fig. 1 Molecular structures of C6PcH₂ and C6PcCu.

3. Results and Discussion

The result of the DSC measurement exhibited that the obvious phase transitions of C6PcCu appeared at 240 °C for the

isotropic (Iso)-hexagonal columnar (Col_h), 233 °C for the Col_h-rectangular columnar (Col_r), and 172 °C for the Col_r-Crystal (Cry) in the cooling process.

Figure 2 shows the temperature dependence of carrier mobility of C6PcCu from 245 °C to -50 °C. An anomalous increases of the mobilities of electron and hole were observed at around transition temperatures of Col_h-Col_r and Col_r-Cry. Though C6PcCu also exhibited ambipolar carrier transport properties like C6PcH₂, the mobility of electrons was higher than that of holes in the whole temperature region, which was completely different from the case of C6PcH₂ [6]. It is noted that both of the hole and electron mobilities were gradually enhanced with increasing the temperature in the crystal phase, and exhibited a slight negative temperature dependence in Col_r phase.

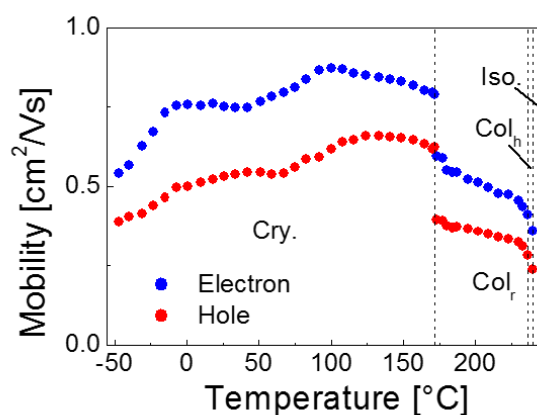


Fig. 2 Temperature dependences of the hole and electron mobilities of C6PcCu.

The crystal structure of C6PcCu single crystal was determined to be the monoclinic structure with space group P2₁/c, $a=28.3638$ Å, $b=9.26350$ Å, $c=53.4694$ Å, $\alpha=90^\circ$, $\beta=92.3965^\circ$, $\gamma=90^\circ$ as shown in Fig. 3. The column axis of C6PcCu was parallel to the b axis. The directions of phthalocyanine core normal vectors alternated every two columns to give a herringbone-like packing structure. The shortest intermolecular distance and the tilt angle of the phthalocyanine core normal vectors were 3.6 Å and 39°, respectively, which were not so different from those of C6PcH₂ [9]. It is noted that the molecular plane of C6PcCu rotated by 14.5° with the adjacent molecules in the same columns unlike the case of C6PcH₂.

In order to explain the temperature dependence of the carrier transport properties for C6PcCu, the further single crystal X-ray structure analysis was carried out at various temperature. The marked change of the lattice parameters depending on the temperature could be observed in the crystal phase, therefore, the carrier transport properties was discussed by taking the lattice parameters including the rotation angle of the molecules into consideration.

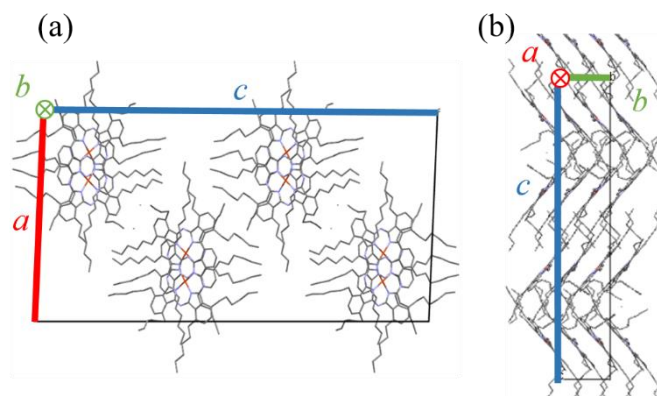


Fig. 3 Molecular packing structure of the single crystal of C6PcCu in the direction of columnar axis (a) and in-plane axis (b).

Acknowledgements

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