Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Charge Transport Properties and Crystal Structure of Partially Oxidized One- Dimensional $[CrPcF(BF_4)x]_n$ Macrocycles

M. Futamata [a]
[a] Government Industrial Research Institute Osaka, Midorigaoka 1, Ikeda, Osaka, 563
Version of record first published: 24 Sep 2006.

To cite this article: M. Futamata (1991): Charge Transport Properties and Crystal Structure of Partially Oxidized One- Dimensional $[CrPcF(BF_4)x]_n$ Macrocycles, Molecular Crystals and Liquid Crystals, 197:1, 109-120

To link to this article: http://dx.doi.org/10.1080/00268949108029706

Mol. Cryst. Liq. Cryst., 1991, Vol. 197, pp. 109–120
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Charge Transport Properties and Crystal Structure of Partially Oxidized One-Dimensional $[CrPcF(BF_4)_x]_n$ Macrocycles

M. FUTAMATA

Government Industrial Research Institute Osaka, Midorigaoka 1, Ikeda, Osaka 563

(Received August 27, 1990; in final form November 1, 1990)

Fluorine-bridged metallophthalocyanines and partially oxidized $[MPcF(BF_4)_x]_n$ polymers (M = Cr or Fe) were prepared. Static magnetic susceptibility of the doped compounds reveals a temperature dependent Curie component and a temperature independent Pauli-like contribution. The magnitude of the latter is linearly proportional to oxidation levels associated with the increment of the phthalocyanine (Pc) cation radical. An X-ray powder diffraction study of $[CrPcF(BF_4)_x]_n$ revealed that the doping process is inhomogeneous and the CrPc unit stacks perpendicular to the molecular plane. The unit cell parameters of $[CrPcF(BF_4)_{0.80}]_n$ are a = 18.90 Å, c = 3.688 Å with space group P4/n, Z = 2. The Pc separations along and perpendicular to the polymer chain vary by only several percent after BF_4^- doping. The eclipsed stacking of the Pc molecule persists in $[CrPcF(BF_4)_{0.80}]_n$. In spite of longer inter-ring distances, the doped polymer reveals extremely high electrical conductivity of 5.6×10^{-4} S cm^{-1} which can be related to the face-to-face, eclipsed ring stacking. The polymerization of CrPc by fluorine diminishes the crystal structure change after doping while showing excellent charge transport properties.

Keywords: conductivity, one-dimensional, fluorine-bridged metallophthalocyanine, susceptibility

INTRODUCTION

Intense scientific research has been devoted to the area of low-dimensional electrically conductive materials for the past ten years. A great deal of excitement has been generated by the synthesis and properties of unusual substances with metal-like properties[1] or superconductivity.[22,37,38] Development of new conducting compounds continues to be sparked by the numerous new potential applications in solid-state devices. In particular, because of their chemical, thermal stability and ready availability, much interest has been focused on metallophthalocyanines (MPc, Figure 1) as low-dimensional electrical conductors,[1-6,10,20-24,33,34] electrochromic displays,[9,28] and catalysts for O_2 reduction.[29,30] Various MPc compounds are also well known as promising cathode materials for lithium secondary batteries.[7,8] These functions are due to the accessible redox states of the MPc molecules. However, several problems exist associated with MPc crystals, such as substantial structure

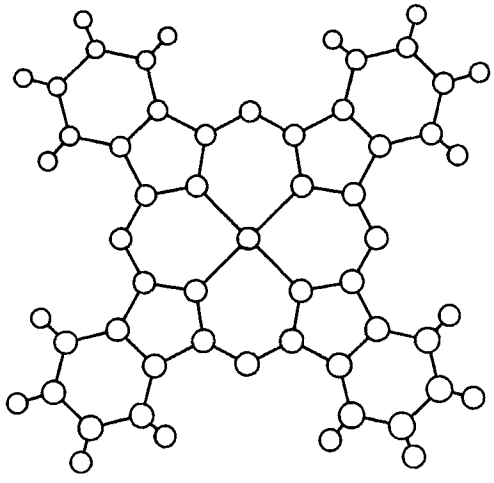

FIGURE 1 Molecular structure of metallophthalocyanine (MPc).

change from slipped to perpendicular stackings,[1,36] and high solubility in the reduced and oxidized states.[12]

Recently, some of the Pc complexes have been modified in an attempt to control the molecular stacking. Several polymers covalently linked forming O—M—O chains have been prepared and partially oxidized by Marks et al.[5,18,19,24] To control the crystal architecture, I have also studied fluorine-bridged one-dimensional polymers of $[MPcF]_n$, where M = Ga, Cr or Fe.[13,14,32] In the preceding contributions, the charge transport properties and crystal structure of the co-facially joined $[FePcF]_n$, $[FePcFI_x]_n$[13,14] and $[GaPcF(BF_4)_x]_n$[32] were discussed. In the present paper, attention was focused on the crystal structure, electronic, magnetic and charge transport properties of $[CrPcF]_n$ after $NOBF_4$ oxidation.

EXPERIMENTAL

$[CrPcF(BF_4)_x]_n$ was prepared as described in the preceding contribution.[32] Partial oxidation of the $[CrPcF]_n$ polymers was accomplished by $NOBF_4$ without cleavage of Cr-F backbone. The $[CrPcF(BF_4)_x]_n$ materials produced are stored in a glove box to prevent decomposition. $[FePcF]_n$ was prepared as described in the preceding contributions.[11,13] In contrast to the cases of $[CrPcF]_n$ and $[GaPcF]_n$, destruction of the Fe—F bonds upon $NOBF_4$ doping was evidenced from IR transmission spectroscopy. Thus, the electrochemical oxidation of $[FePcF]_n$ was performed under controlled potential. Without cleavage of the Fe—F bond, the $[FePcF(BF_4)_x]_n$ compounds were actually obtained on a platinum anode at +1.0 V (vs. Ag/AgCl) in a 0.1 mol/l n-Bu_4NBF_4/acetonitrile solution.[14] The $[FePcF(BF_4)_x]_n$ materials prepared revealed an increase in electrical conductivity by as much as 3 orders of magnitude (Table V). Since the compounds showed extreme inhomogeneity, the chemically oxidized $[CrPcF(BF_4)_x]_n$ polymers were used to analyze the structure and charge transport properties.

The transmission optical spectra in the UV and visible regions were measured on a sample of $[CrPcF(BF_4)_x]_n$ powder with a JASCO Model Ubest-50 spectrometer between 300 and 900 nm. Static magnetic susceptibility of the doped polymers was measured from 77 and 295 K using a Shimadzu MB-3 type magnetic balance. The instrument calibration and diamagnetic correction for BF_4^- were undertaken using conventional procedures. The Curie component was analyzed in a χ vs 1/T relation. The direct current four probe van der Pauw technique[15] was used to measure the electrical conductivity of the polymers between 120 and 295 K. The samples were examined as pressed pellets with graphite paste contacts.

X-ray powder data were taken between 2 θ = 3 to 60° using Cu-K_α radiation for powder samples under a slow flow of dry nitrogen to prevent decomposition. The unit cell parameters of the doped $[CrPcF(BF_4)_{0.80}]_n$ crystal are a = 18.90 Å, c = 3.688 Å with space group P4/n, Z = 2. The density of the doped compounds was estimated from the bulk density of the pressed pellets.

CRYSTAL STRUCTURE OF $[CrPcF(BF_4)_x]_n$

As evidenced by X-ray powder diffractometry, only slight structure changes occurred upon incremental doping with BF_4^- (Figure 2). The starting phase is di-

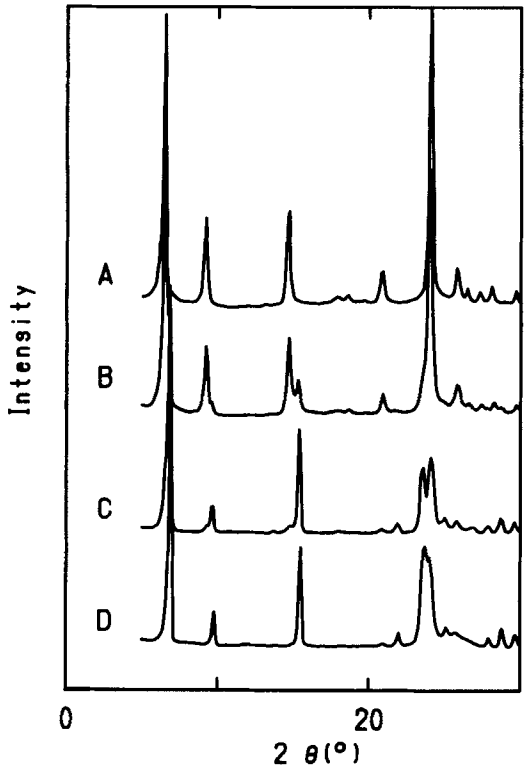

FIGURE 2 Powder X-ray diffraction patterns of $[CrPcF(BF_4)_x]_n$ with progressive doping of BF_4^-. (A) x = 0.80; (B) x = 0.30; (C) x = 0.046; (D) x = 0.00.

minished while, simultaneously, a new phase is created as the BF_4^- dopant increased. At the doping level of x = 0.80, the starting phase is no longer clear. Furthermore, the observed powder diffraction patterns at the intermediate levels ($0 < x < 0.80$) could be reproduced by the superposition of patterns for the x = 0 and x = 0.80 phases. It appears that the doping process is mostly inhomogeneous. Therefore, the dopant is not uniformly distributed throughout the lattice and a wide range of stoichiometries are formed. The slight angle shift in the diffraction peaks after doping corresponds to the imperceptible but detectable change in the unit cell parameters. These results are quite in accordance with those of the isostructural $[GaPcF(BF_4)_x]_n$ crystals.[32]

First, the space group and unit cell parameters for the $[CrPcF(BF_4)_{0.80}]_n$ crystal were determined with the computer program CELL series developed by Takaki et al.[16,17,25,26] Diffraction lines of $[CrPcF(BF_4)_{0.80}]_n$ can be straightforwardly indexed in the tetragonal crystal system as shown in Table I. By comparing the intensity profiles, the $[CrPcF(BF_4)_{0.80}]_n$ crystal is essentially isostructural with NiPcI[1] and

TABLE I

Crystal Parameters for $[CrPcF]_n$* and $[CrPcF(BF_4)_{0.80}]_n$

Compound	$[CrPcF]_n$	$[CrPcF(BF_4)_{0.80}]_n$
Formula	$C_{32}H_{16}N_8FCr$	$C_{32}H_{16}N_8FCr(BF_4)_{0.80}$
fw	583.53	652.97
a, Å	3.770	3.688
b, Å	12.601	18.90
c, Å	12.793	18.90
α, °	90.271	90.00
β, °	96.42	90.00
γ, °	91.28	90.00
V, Å^3	603.8	1316.7
Z	1	2
$d_{calc.}$ g/cm^3	1.60	1.64
$d_{obs.}$ g/cm^3	1.49	1.53
space group	$P\bar{1}$	P4/n

* Assumed to be isostructural with $[GaPcF]_n$.[11,27]

TABLE II

Inter-ring spacings of metallophthalocyanines

Species	Inter-ring spacing[a] (Å)	Inter-chain distances[b] (Å)	Staggering angle (°)
$[CrPcF]_n$	3.745	12.60, 12.71	0
$[CrPcF(BF_4)_{0.80}]_n$	3.688	13.36	0
$[GaPcF]_n$	3.846	12.60, 12.71	0
$[GaPcF(BF_4)_{0.87}]_n$	3.730	13.36	0
$[SiPcO(BF_4)_{0.36}]_n$*	3.29	13.70	40
NiPcI**	3.244	13.94	39.5

* From Reference 19.
** From Reference 1.
[a] Along the Pc chain.
[b] Perpendicular to the chain.

$[SiPcO(BF_4)_{0.36n}]$.[19] The major differences are the inter-ring spacings, interchain distances and staggering angle of the neighboring rings (Table II). As regards the structure analysis for the $[CrPcF(BF_4)_{0.80}]_n$, it is of prime importance to note the slight crystal changes after doping. Actually, the inter-ring distances along and perpendicular to the CrPc chain vary by only several percent after the BF_4^- addition as shown in Table II.

Next, hypothetical structures associated with the BF_4^- sites were considered for $[CrPcF(BF_4)_{0.80}]_n$ by comparing the observed and calculated X-ray diffraction profiles. In the models, BF_4^- ions are arranged at the (0.5, 0, 0.5) or (0.25, 0.25, 0.5), etc. positions, while the planar phthalocyanine rings are similarly stacked in a co-facial assembly (Figure 3). The Pc ring orientation around the c-axis was also optimized. The conventional values[1] were assumed for the bond lengths and angles in the Pc and BF_4^- being not so sensitive to the diffraction profile of the doped polymers. The model in which the BF_4^- ions are centered at (0.25, 0.25, 0.50) gave a satisfactory result when the trans-coordination bond between chromium and nitrogen is arranged exactly parallel to the a-axis ($\delta = 0°$, Figure 4A, C). Here, the four fluorine atoms of BF_4^- are distributed to eight equivalent sites around a

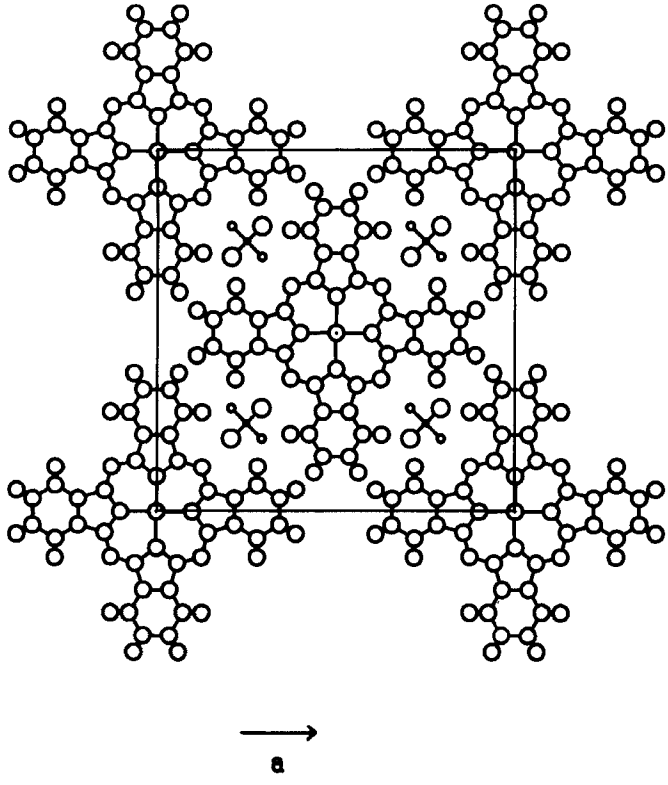

FIGURE 3 Crystal structure models of $[CrPcF(BF_4)_{0.80}]_n$. Model (II) is pictured in which BF_4^- are centered at (0.25, 0.25, 0.50) and equivalent positions. In model (I), BF_4^- are arranged at (0.5, 0, 0.5) whereas CrPc are stacked in the same way as in the model II.

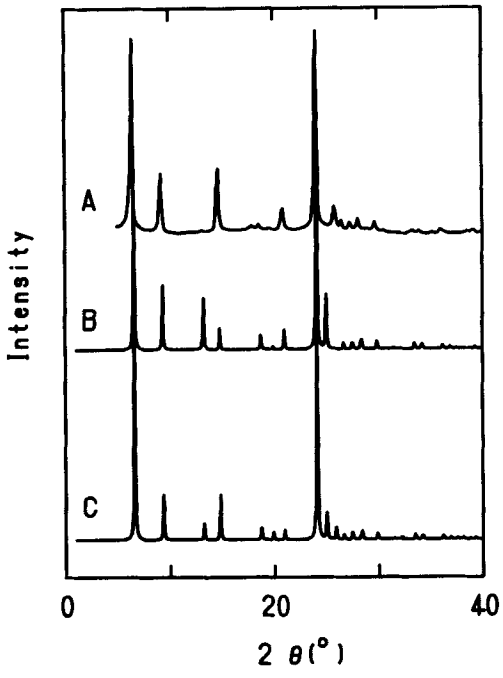

FIGURE 4 Powder X-ray diffraction profiles. (A) Observed, (B) calculated (model I, $\delta = 30.3°$); and (C) calculated (model II, $\delta = 0°$) intensity. Conformation of CrPc are optimized in (B) and (C).

boron atom due to the site symmetry. In this eclipsed model, the nearest interatomic distances between nitrogen and fluorine, and between carbon and fluorine are 2.44 and 2.75 Å. These values are a little shorter than the well-known nonbonded distances (summation of van der Waals radii) of 2.90 and 3.05 Å, respectively. This is probably due to electrostatic interaction between the CrPc and BF_4^- and incomplete occupation 0.40 of BF_4^- sites. All other BF_4^- sites, e.g. (0.5, 0, 0.5), resulted in a poor fit to the observed profiles (Figure 4(B)). By evaluating the intensity profile for various conformations, it was verified that the eclipsed stacking of the neighboring rings along the c-axis is maintained after partial oxidation. The staggered conformation of $\delta_1 = 0$ and $\delta_2 = 22°$ reproduced the observed diffraction profile for $[CrPcF(BF_4)_x]_n$. However, it had to be excluded because of the anomalous nonbonded F—C distance of 1.29 Å.

RESULTS AND DISCUSSION

The $[CrPcF]_n$ materials can be doped by dispersing the polymer and $NOBF_4$ in dichloromethane and stirring for 12 hr under a dried atmosphere at room temperature. The composition of prepared materials was checked by elemental analysis. The isolated stoichiometry never exceeded $x = 0.80$ regardless of reaction time and $NOBF_4$ concentration. This value of $x = 0.80$ is much larger than that of $x = 0.36$ found for $[SiPcO]_n$. It is probably due to the increased inter-ring spacing

for $[CrPcF(BF_4)_{0.80}]_n$ by 0.40 Å as shown in Table II. The $[CrPcF(BF_4)_x]_n$ materials appeared to be stable in dried air at room temperature for extended periods of time. However, BF_4^- was easily washed away by polar solvents. The π-electron oxidation of CrPc macrocycles was clear from the appearance of long wavelength absorption (ca. 720 nm) for $[CrPcF(BF_4)_x]_n$ in the region of the Pc π-π* Q band (HOMO-LUMO) (Figure 5). Such a red shifting of the Q band is known to accompany Pc π-cation radical formation as observed for $[GaPcF(BF_4)_x]_n$[32] (Table III).

The static magnetic susceptibility of the materials was studied as a function of dopant level and temperature (Figure 6, Table IV). $[CrPcF]_n$ is a novel material in contrast to the $[GaPcF]_n$ polymer, because Cr^{3+} (d^3, S = 3/2) is paramagnetic. A Curie-like susceptibility of the undoped $[CrPcF]_n$ polymer was observed as 59.9×10^{-4} emu mol^{-1} at room temperature. It agrees very closely with the spin-only value (62.5×10^{-4} emu mol^{-1}) for Cr^{3+}(d^3, S = 3/2). Oxidation at Cr^{3+} centers to Cr^{4+} (d^2, S = 2/2) which could cause a diminishing of paramagnetic susceptibility. However, partial oxidation of the Pc ring would leave the Cr^{3+} centers intact and would create π-charge carriers that exhibit Pauli paramagnetism. Thereby, it would give rise to greater than three spins per formula unit. To the first approximation,

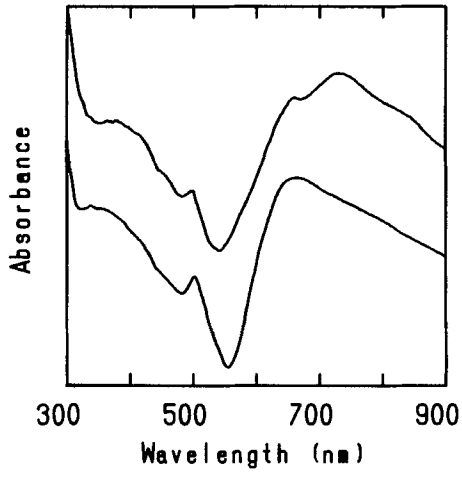

FIGURE 5 UV-vis transmission spectra of polycrystalline samples of $[CrPcF(BF_4)_x]_n$. (A) x = 0.80; (B) x = 0.00.

TABLE III

UV-visible region transmission spectra for $[CrPcF(BF_4)_x]_n$ powder

Species	Absorption wavelength (nm)
$[CrPcF]_n$	350, 500, 662
$[CrPcF(BF_4)_{0.87}]_n$	350, 500, 662, 720
$[GaPcF]_n$*	350, 632
$[GaPcF(BF_4)_{0.87}]_n$*	350, 643, 710

* From Reference 32.

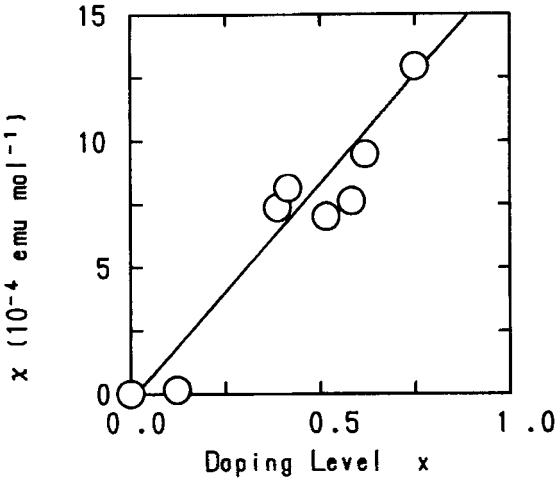

FIGURE 6 Pauli-like susceptibility of $[CrPcF(BF_4)_x]_n$ as a function of doping level at room temperature.

TABLE IV

Pauli-like susceptibility for $[CrPcF(BF_4)_x]_n$

Species	Susceptibility* (10^{-4} emu/mol) Pauliterm 290 K	Overall 290 K	Overall 77 K	Spin density (spins/molecule)
$[CrPcF]_n$	0.00	59.90	97.06	0.00
$[CrPcF(BF_4)_{0.12}]_n$	0.16	60.06	119.4	0.13
$[CrPcF(BF_4)_{0.39}]_n$	7.37	67.27	134.7	0.59
$[CrPcF(BF_4)_{0.42}]_n$	8.14	68.04	157.7	0.65
$[CrPcF(BF_4)_{0.52}]_n$	7.02	66.92	144.7	0.56
$[CrPcF(BF_4)_{0.58}]_n$	7.63	67.53	141.8	0.61
$[CrPcF(BF_4)_{0.62}]_n$	9.48	69.38	145.5	0.76
$[CrPcF(BF_4)_{0.75}]_n$	12.9	72.82	151.9	1.03
$[GaPcF(BF_4)_{0.87}]_n$**	3.73			0.298

* Pauli-like susceptibility for $[CrPcF(BF_4)_x]_n$ are estimated by subtracting Cr^{3+} (d^3, S = 3/2) contribution from overall room temperature susceptibility.

** From Reference 32.

the room temperature Pauli-like component was estimated by subtracting the Curie-term of Cr^{3+} spins from the overall paramagnetic susceptibility. In fact, the temperature independent Pauli-like contribution, linearly proportional to doping level, was unambiguously observed in addition to the temperature dependent "Curie tailing" of Cr^{3+} spins between 77 and 290 K (Figure 6, Table IV). Furthermore, the observed susceptibility of 72.82×10^{-4} emu mol^{-1} for $[CrPcF(BF_4)_{0.80}]_n$ is evidently larger than the value 59.9×10^{-4} emu mol^{-1} for the undoped state. Thus, additional support was provided for the conclusion that the partial oxidation does not occur at the Cr^{3+} metal sites but at the Pc π-electrons in this material.

The magnetic coupling between spins of Curie-like moment of Cr^{3+} ions and π-spin charge carriers of the Pc rings was not clarified in $[CrPcF(BF_4)_x]_n$. It is because the overall magnetic susceptibility of 72.82×10^{-4} emu mol^{-1} for this compound is in fair agreement with the spin-only value 72.51×10^{-4} emu mol^{-1} for an uncoupled summation of the S = 3/2 (Cr^{3+}) and the S = 1/2 (Pc cation radical). However, it should be noticed that the estimated paramagnetic susceptibility for $[CrPcF(BF_4)_x]_n$ was 2 or 3 times larger than the values for other MPc compounds.[1,18,19,32] A low temperature magnetic susceptibility measurement is necessary to establish the coupling properties in more detail. A study is now being carried out regarding this.

I turn now to the crystal structure of $[CrPcF(BF_4)_x]_n$. Three important structural characteristics of the metallophthalocyanine stack were clarified from the fitting of the theoretical X-ray diffraction profiles. First, the $[CrPcF]_n$ polymer shows a slight change in the crystal architecture after BF_4^- doping (Table I). Second, a slight contraction in the inter-ring distance was observed after partial oxidation in accordance with other phthalocyanines (Table II). Third, an eclipsed face-to-face stacking in the phthalocyanine ring of $[CrPcF]_n$ persists after oxidation.

The relationship between the doping level and electrical conductivity of $[CrPcF(BF_4)_x]_n$ is shown in Figure 7. It reveals a rapid increase in electrical conductivity by as much as 6 orders of magnitude after BF_4^- doping (Table V). Since inhomogeneous doping occurred and the two crystal phases of x = 0 and x = 0.80 coexisted, the simple percolation model was considered. The three-dimensional percolation theory predicts the conductivity dependence shown in Equation 1 for the composition region near the insulator-conductor transition threshold.[31]

$$\sigma = \sigma_o (X - X_c)^s \tag{1}$$

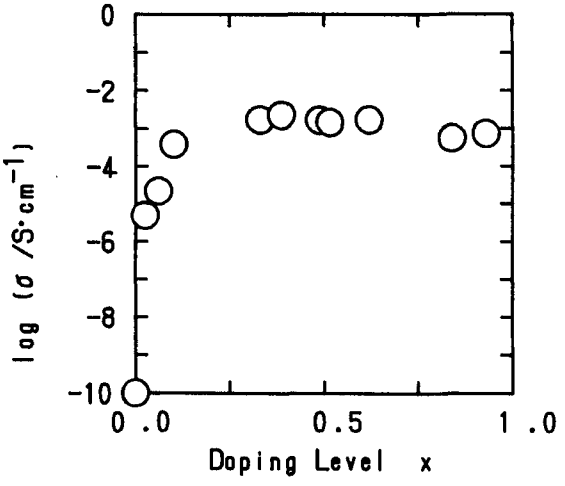

FIGURE 7 Electrical conductivity for polycrystalline samples of $[CrPcF(BF_4)_x]_n$ as a function of doping level.

TABLE V

Electrical conductivity for $[CrPcF(BF_4)_x]_n$

Species	Conductivity (Scm^{-1})	Activation energy (eV)
$[CrPcF]_n$	$< 1.00 \times 10^{-10}$	—
$[CrPcF(BF_4)_{0.025}]_n$	4.8×10^{-6}	0.40
$[CrPcF(BF_4)_{0.10}]_n$	3.9×10^{-4}	0.20
$[CrPcF(BF_4)_{0.31}]_n$	2.3×10^{-3}	0.13
$[CrPcF(BF_4)_{0.49}]_n$	1.7×10^{-3}	0.097
$[CrPcF(BF_4)_{0.80}]_n$	5.6×10^{-4}	0.100
$[FePcF]_n$*	8.0×10^{-8}	0.40
$[FePcF(BF_4)_{0.27}]_n$	2.24×10^{-5}	—
$[FePcF(PF_6)_{0.29}]_n$	8.08×10^{-5}	—
$[GaPcF(BF_4)_{0.87}]_n$**	4.21×10^{-2}	0.082

* From Reference 13.
** From Reference 32.

Here, X is the volume fraction of conducting species, X_c the percolation threshold below which the conductivity falls rapidly and s the critical index due to dimension. It was found that the σ vs X data for $[CrPcF(BF_4)_x]_n$ could be readily fit to Equation 1 when the parameters are $X_c = 0.05$, $s = 1.80$, and $\sigma_o = 3.00 \times 10^{-3}$ Scm^{-1}. These results are in good agreement with the theoretical values, $X_c = 0.15$, $s = 1.5–1.7$, for the three-dimensional simple percolation model. It was also in ac-

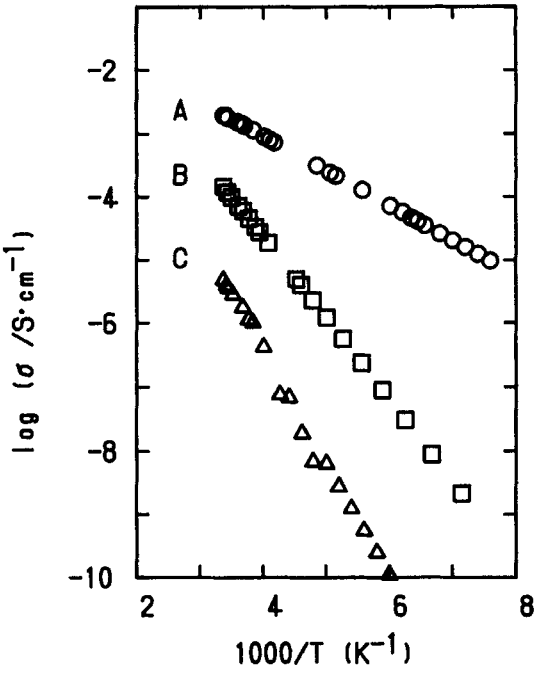

FIGURE 8 Electrical conductivity for polycrystalline samples of $[CrPcF(BF_4)_x]_n$. (A) x = 0.80, (B) x = 0.046, (C) x = 0.025 as a function of temperature.

cordance with the result for the metallophthalocyanine polymers, i.e., $X_c = 0.20$, and $s = 1.52$ for $[GaPcF(BF_4)_x]_n$.[32]

The temperature dependence of the electrical conductivity for $[CrPcF(BF_4)_x]_n$ (Figure 8) is seen to be thermally activated. A single exponential fit is satisfactory over the measured temperature region and doping range. To obtain the evidence of the conducting mechanism, it should be studied in a wider temperature range but beyond the scope of the equipment. The conductivity data for $[MPcF(BF_4)_x]_n$ (M = Cr, Fe and GA) are summarized in Table V. In spite of the longer inter-ring separation of $[CrPcF]_n$ in comparison with other monomer MPc compounds (Table II), BF_4^- doping results in extremely high electrical conductivity. These charge transport properties can be rationalized by the face-to-face, eclipsed Pc stacking in reference to the results of the theoretical band calculation.[35]

CONCLUSION

Crystal structural changes of $[CrPcF]_n$ after BF_4^- doping were well explained by a model in which the BF_4^- ions are arranged at the (0.25, 0.25, 0.50) sites between the polymer chains. The inter-ring distances along and perpendicular to the chains vary by only several percent and face-to-face, eclipsed stacking of the rings are maintained after BF_4^- doping. The structural changes are responsible for the charge transport properties of the doped compounds. The electrical conductivity of the $[CrPcF]_n$ polymer increased by 6 orders of magnitude upon partial oxidation whereas the bridging inter-ring separation increased by about 0.4 Å. The existence of phthalocyanine cation radical species in the doped state was clarified by optical and magnetic properties. Therefore, it was verified that the one-dimensional bridging of the metal by a fluorine atom is a useful technique to reduce the crystal structural change without any deterioration of the unusual properties.

Acknowledgment

The author would like to thank Prof. Y. Takaki (Osaka Kyoiku Univ.) for copying the computer program CELL series and many helpful discussions.

References

1. C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers and T. J. Marks, *J. Am. Chem. Soc.*, **102**, 6702 (1980).
2. K. Yakushi, M. Sakuda, I. Hamada, H. Kuroda, A. Kawamoto, J. Tanaka, T. Sugano and M. Kinoshita, *Synth. Metals*, **19**, 769 (1987).
3. K. Yakushi, H. Yamakado, M. Yoshitake, N. Kosugi, H. Kuroda, A. Kawamoto, J. Tanaka, T. Sugano, M. Kinoshita and S. Hino, *Synth. Metals*, **29**, F95 (1989).
4. S. Hino, K. Matsummoto, H. Yamakado, K. Yakushi and H. Kuroda, *Synth. Metals*, **32**, 301 (1989).
5. G. E. Kellogg, J. G. Gaudiello, J. A. Schulueter, S. M. Tetrick, T. J. Marks, H. O. Marcy, W. J. McCarthy and C. R. Kannewurf, *Synth. Metals*, **29**, F15 (1989).
6. M. Y. Ogawa, S. M. Palmer, K. Lion, G. Quirion, J. A. Thompson, M. Poirier and B. M. Hoffman, *Phys. Rev.*, **B39**, 10682 (1989), and references therein.

7. J. Yamaki and A. Yamaji, *J. Electrochem. Soc.*, **129**, 5 (1982).
8. H. Djellab and F. Dalard, *J. Electroanal. Chem.*, **221**, 105 (1987).
9. G. C. S. Collins and D. J. Schriffrin, *J. Electroanal. Chem.*, **139**, 335 (1982).
10. J. Metz and M. Hanack, *J. Am. Chem. Soc.*, **105**, 828 (1983).
11. J. P. Linsky, T. R. Paul, R. S. Nohr and M. E. Kenney, *Inorg. Chem.*, **19**, 3131 (1980).
12. A. Mclendres and S. Q. Xu, *J. Electrochem. Soc.*, **131**, 466 (1984).
13. M. Futamata, S. Higuchi and S. Takahashi, *Synth. Metals*, **30**, 39 (1989).
14. M. Futamata, S. Higuchi and S. Takahashi, 40th ISE Meeting, Ext. Abst. Vol. I, 466 (1989).
15. L. J. van der Pauw, *Phillip. Tech. Rev.*, **20**, 220 (1955).
16. Y. Takaki, T. Taniguchi, K. Nakata and H. Yamaguchi, *J. Ceram. Soc. Jpn.*, **97**, 763 (1989).
17. T. Yamanaka, *Jpn. J. Crystallogr.*, **22**, 226 (1980).
18. B. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1551 (1983).
19. T. Inabe, J. G. Gaudiello, M. K. Moguel, J. W. Lyding, R. L. Burton, W. J. McCarthy, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, **108**, 7595 (1986).
20. Y. Orihashi, N. Kobayashi, E. Tsuchida, H. Matsuda, H. Nakanishi and M. Kato, *Chem. Lett.*, 1617 (1985).
21. P. Brant, R. S. Nohr, K. J. Wynne and D. C. Weber, *Mol. Cryst. Liq. Cryst.*, **81**, 255 (1982).
22. H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto and J. Tanaka, *Chem. Lett.*, 55 (1988).
23. P. M. Kuznesof, R. S. Nohr, K. J. Wynne and M. E. Kenny, *J. Makromol., Sci.-Chem.*, **A16**, 299 (1981).
24. C. W. Dirk, E. A. Mintz, K. F. Schoch, Jr. and T. J. Marks, *J. Makromol., Sci.-Chem.*, **A16**, 275 (1981).
25. Y. Takaki, T. Taniguchi, H. Yamaguchi and T. Ogura, *J. Ceram. Soc. Jpn.*, **95**, 610 (1987).
26. Y. Takaki, T. Taniguchi, H. Yamaguchi and K. Nakata, *J. Ceram. Soc. Jpn.*, **96**, 13 (1988).
27. R. S. Nohr and K. J. Wynne, *J. Chem. Soc., Chem. Commun.*, 1210 (1981).
28. M. T. Riou and C. Larisse, *J. Electroanal. Chem.*, **249**, 181 (1988).
29. R. Jasinski, *Nature*, **201**, 1212 (1964).
30. J. Zagal, R. Sen and. E. Yeeger, *J. Electroanal. Chem.*, **83**, 207 (1977).
31. S. Kirkpatrick, *Rev. Mod. Phys.*, **45**, 574 (1973).
32. M. Futamata and Y. Takaki, *Synth. Metals*, to be published.
33. G. Meyer, M. Hartmann and D. Wohrle, *Makromol. Chem.*, **176**, 1919 (1975).
34. M. Y. Ogawa, J. Martinsen, S. M. Palmer, J. L. Stanton, J. Tanaka, R. L. Greene, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, **109**, 1115 (1987).
35. M-H. Whangbo and K. R. Stewart, *Isr. J. Chem.*, **23**, 133 (1983).
36. J. M. Robertoson, *J. Chem. Soc.*, 615 (1935).
37. A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 459 (1987).
38. S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott and R. L. Greene, *Phys. Rev. Lett.*, **50**, 270 (1983).