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Checkerboard-Type Charge-Ordered State of a Pressure-Induced Superconductor, β-(*meso*-DMBEDT-TTF)$_2$PF$_6$

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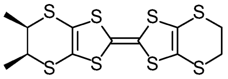
The charge-ordered (CO) state is gaining attention as one of the electronic states induced by an intermolecular Coulomb repulsion energy (V) in a strongly correlated system, which attracts experimental[1] and theoretical[2] interests. The characteristic feature of this system is a competition between two different states, which affords a variety of phenomena. In the case of organic materials, several hot topics have emerged: competition between the metallic and CO states induced by electric field,[1a] laser excitation,[1b,c] and external pressure,[1d,e] and the huge nonlinear responses to external stimuli.[1a,b] Recently, the CO states of two pressure-induced organic superconductors, α-(BEDT-TTF)$_2$I$_3$[1d] and (DODHT)$_2$X,[1e] were suggested by ^{13}C NMR,[1f] ESR,[1g] SQUID,[1g] and Raman spectroscopy[1h] measurements, but there has been no report on the direct structural observation of the CO state. In this communication, we report the first observation of a "checkerboard" pattern derived from a pressure-induced superconductor, β-(*meso*-DMBEDT-TTF)$_2$PF$_6$, by X-ray analysis at low temperature.



meso-DMBEDT-TTF

Our recent report has demonstrated that an attachment of two methyl groups to a BEDT-TTF molecule succeeded in introducing moderate negative chemical pressure and dimerization to afford a new superconductor, β-(*meso*-DMBEDT-TTF)$_2$PF$_6$, with $T_c = 4.3$ K (onset) under 4.0 kbar.[3] At ambient pressure, the salt undergoes a metal−insulator (M−I) transition at 90 K with a small anomaly around 220 K. In this study, the structural change around the M−I transition temperature was investigated by X-ray measurement using an imaging plate detector. By lowering the temperature, the superstructure reflections (h, k/2, l/2) suddenly appear around 90 K (Figure 1), and the lattice parameters also deviate from 90 K. These temperature dependences suggest that the M−I transition occurs with a structural change.

To obtain further information, X-ray diffraction data at 11.5 K were collected by synchrotron radiation.[4] It was determined that the low-temperature structure is $2c_p \times (-b_p + c_p) \times a_p$ with the space group of $P\bar{1}$, where a_p, b_p, and c_p represent the room-temperature triclinic unit cell (Figure 2A). The molecules A and B, making a pair with the strongest donor−donor interaction termed "dimer",[3] are crystallographically independent (Figure 2B) as the inversion center within the dimer has disappeared. Consequently, the volume of the unit cell is twice that at room temperature. According to a report on ET salts, it is possible to estimate the charge distribution by the parameter δ, which means the difference in length between the single and double bonds in the TTF skeleton.[5] We have adopted this method for this salt, and the δ values of the two donors have proved to be 0.73 for molecule A and 0.79 for molecule B. From the equation for charge Q, the estimated ionicity of 0.88+ for charge-rich (molecule A) is evidently larger than that of 0.45+ for the charge-poor (molecule B) site. In fact, the TTF skeleton of molecule A is almost a plane, whereas that of molecule B is slightly bending. The calculated tilting angles between the two 1,3-dithiole rings are 0.5 (molecule A) and 3.9° (molecule B), respectively. The charge distribution is also distinguished by the energy level of HOMO. From the calculation using the atomic coordinate[6] at 11.5 K, the HOMO energy of the charge-rich site is higher than that of the charge-poor site. A similar split of HOMO energy is observed in the CO state of (BEDT-TTF)$_3$(MnCl$_4$)$_2$, where the 4− charge from the two MnCl$_4^{2-}$ is in proportion to one 2+ (rich) and two 1+ (poor) charges of the donor molecules.[7] The calculation proved that the HOMO energy of the 2+ site is higher than that of the 1+ site. The results are consistent with the fact that the HOMO level becomes higher as the charge is injected due to the on-site Coulomb repulsion. In consequence, the charge distribution is illustrated by a checkerboard mapping consisting of charge-rich (molecule A, red) and -poor (molecule B, blue) sites

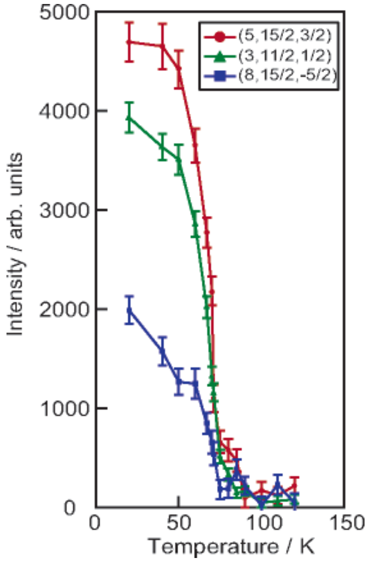


Figure 1. Temperature dependences of the superlattice intensities at (5, 15/2, 3/2), (3, 11/2, 1/2), and (8, 15/2, −5/2).

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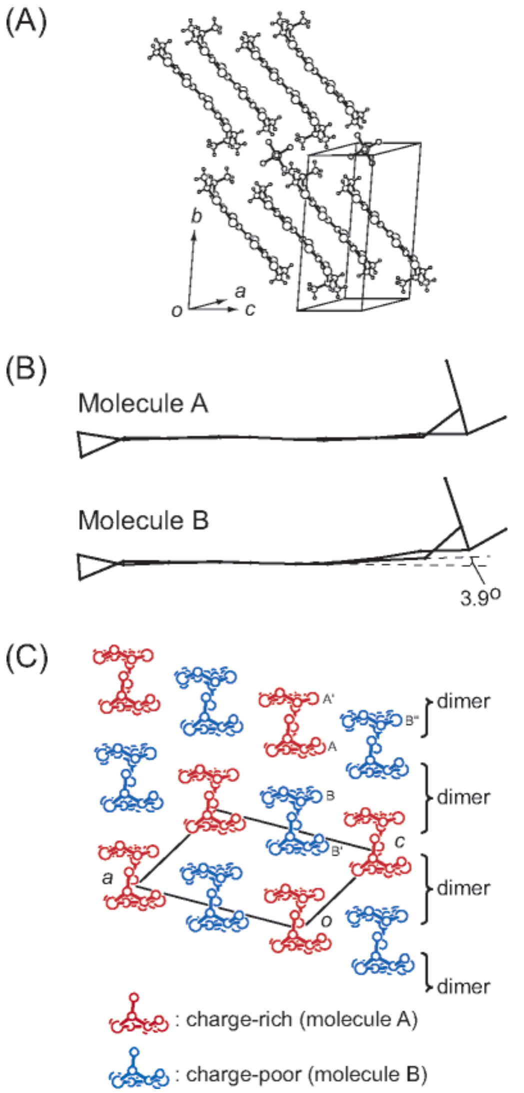

Figure 2. (A) Crystal structure and (B) donor molecules of β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ (hydrogen atoms are omitted for the sake of clarity). (C) A mapping of charge ordering by the charge-rich (red) and -poor (blue) sites.

Table 1. Donor−Donor Distances[a,b]

intradimer	A−B (rich-poor)	3.8 Å
interdimer	A−A′ (rich-rich)	5.3 Å
	B−B′ (poor-poor)	5.5 Å
intercolumn	A−B″ (rich-poor)	6.5 Å

[a] Defined as the distances between the center of gravity of the BEDT-TTF moiety. [b] The numbers of donor molecules follow that in Figure 2C.

(Figure 2C). In the column structure, the charge-rich (r) and -poor (p) molecules are arranged not as rprprprp, but as rrpprrpp. This arrangement is not related to the location of the counteranion, PF$_6^-$. For the purpose of considering the periods of r and p, the donor−donor distances are summarized in Table 1. On the supposition that V is determined by the donor−donor distance based on the point-charge model, the charge distribution should be rp in the nearest intradimer pair, due to the electron−electron repulsion. Along this line, the distribution should be rp in the second-nearest interdimer pair, whereas the result proved to be rr or pp. It must be recalled that the donor−donor distance of the nearest intercolumn pair is 6.5 Å, farther than the two intracolumn pairs. The charge modulation of the interdimer pair is a key to the rrpprrpp period, in other words, a key to the checkerboard CO state. The elaborate model gives an explanation by including the electron−phonon interaction[2a] and the intermolecular electron−electron Coulomb interaction, based not only on the intermolecular distance R but also on the effective molecular size L.[2b] In this system, the latter intermolecular Coulomb repulsion energy (V) causes the charge ordering to produce the flat charge-rich and the bent charge-poor molecules. The motion of charged molecules leads to lattice instability and influences the CO state in organic crystals. Consequently, flexibility of molecules to couple strongly to a lattice with an electronic state is a specific feature of organic materials.

In conclusion, we have solved the crystal structure of β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ at 11.5 K by X-ray analysis. The structure reveals that the dimer molecules with equal 0.5+ charges at room temperature have split into crystallographically independent molecules with the rich and poor charges below 90 K, so that the low-temperature insulating phase is a CO state. The pattern of charge distribution is a checkerboard-type, and the first time this type of pattern has been observed in pressure-induced organic superconductors. Further investigations of the checkerboard CO state by several methods are underway.

Supporting Information Available: Experimental data and an X-ray crystallographic file at 11.5 K in CIF format for β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ are available. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Sawano, F.; Terasaki, I.; Mori, H.; Mori, T.; Watanabe, M.; Ikeda, N.; Nogami, Y.; Noda, Y. *Nature* **2005**, *437*, 522−524. (b) Tajima, N.; Fujisawa, J.; Naka, N.; Ishihara, T.; Kato, R.; Nishio, Y.; Kajita, K. *J. Phys. Soc. Jpn.* **2005**, *74*, 511−514. (c) Chollet, M.; Guerin, L.; Uchida, N.; Fukaya, S.; Shimoda, H.; Ishikawa, T.; Matsuda, K.; Hasegawa, T.; Ota, A.; Yamochi, H.; Saito, G.; Tazaki, R.; Adachi, S.; Koshihara, S. *Science* **2005**, *307*, 86−89. (d) Tajima, N.; Ebina-Tajima, A.; Tamura, M.; Nishio, Y.; Kajita, K. *J. Phys. Soc. Jpn.* **2002**, *71*, 1832−1835. (e) Nishikawa, H.; Morimoto, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Yamada, J.-I.; Murata, K. *J. Am. Chem. Soc.* **2002**, *124*, 730−731. (f) Takano, Y.; Hiraki, K.; Yamamoto, H. M.; Nakamura, T.; Takahashi, T. *J. Phys. Chem. Solids* **2001**, *62*, 393−395. (g) Nishikawa, H.; Sato, Y.; Kodama, T.; Kikuchi, K.; Ikemoto, I.; Yamada, J.-I. *J. Phys. IV France* **2004**, *114*, 565−567. (h) Wojciechowski, R.; Yamamoto, K.; Yakushi, K.; Inokuchi, M.; Kawamoto, A. *Phys. Rev. B* **2003**, *67*, 224105.

(2) (a) Clay, R. T.; Mazumdar, S.; Campbell, D. K. *Phys. Rev. B* **2003**, *67*, 11521−11529. (b) Tamura, M.; Kato, R. *J. Phys. Soc. Jpn.* **2004**, *73*, 3108−3110. (c) Seo, H.; Hotta, C.; Fukuyama, H. *Chem. Rev.* **2004**, *104*, 5005−5036.

(3) Kimura, S.; Maejima, T.; Suzuki, H.; Chiba, R.; Mori, H.; Kawamoto, T.; Mori, T.; Moriyama, H.; Nishio, Y.; Kajita, K. *Chem. Commun.* **2004**, 2454−2455.

(4) Crystal data for β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ (11.5 K): $C_{24}H_{24}F_6PS_{16}$; FW 970.38; triclinic; $P\bar{1}$ (No. 2); $a = 13.294(3)$ Å; $b = 16.663(4)$ Å; $c = 9.006(2)$ Å; $\alpha = 97.787(7)°$; $\beta = 111.12(1)°$; $\gamma = 68.101(9)°$; $V = 1726.6(6)$ Å^3; $D_{calc} = 1.866$ g/cm^3; $Z = 2$; $R = 0.088$; $R_w = 0.099$ ($I > 3\sigma(I)$). All atoms were isotropically refined.

(5) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, *86*, 1973−1974.

(6) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627−633.

(7) Mori, T.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 591−593.

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