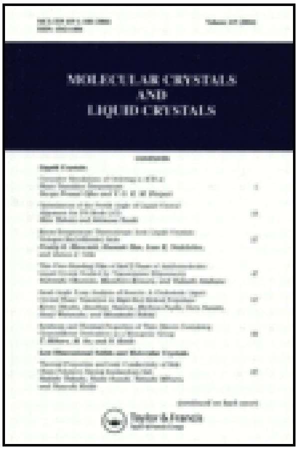


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Development of New Organic Metals and Superconductors from a Non-Ttf Donor System

Jun-Ichi Yamada [a] , Maki Watanabe [a] , Takashi Toita [a] , Hiroki Akutsu [a] , Shin'ichi Nakatsuji [a] , Hiroyuki Nishikawa [b] , Isao Ikemoto [b] & Koichi Kikuchi [b]

[a] Department of Material Science, Faculty of Science, Himeji Institute of Technology, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo, 678-1297, Japan

[b] Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan

Version of record first published: 18 Oct 2010

To cite this article: Jun-Ichi Yamada, Maki Watanabe, Takashi Toita, Hiroki Akutsu, Shin'ichi Nakatsuji, Hiroyuki Nishikawa, Isao Ikemoto & Koichi Kikuchi (2002): Development of New Organic Metals and Superconductors from a Non-Ttf Donor System, Molecular Crystals and Liquid Crystals, 390:1, 121-130

To link to this article: http://dx.doi.org/10.1080/15421400390193512

Mol. Cryst. Liq. Cryst., Vol. 390, pp. 121–130
Copyright © 2003 Taylor & Francis
1542-1406/03 $12.00 + .00
DOI: 10.1080/15421400390193512

DEVELOPMENT OF NEW ORGANIC METALS AND SUPERCONDUCTORS FROM A NON-TTF DONOR SYSTEM

Jun-Ichi Yamada, Maki Watanabe, Takashi Toita,
Hiroki Akutsu, and Shin'ichi Nakatsuji
Department of Material Science, Faculty of Science,
Himeji Institute of Technology, 3-2-1 Kouto, Kamigori-cho,
Ako-gun, Hyogo 678-1297, Japan

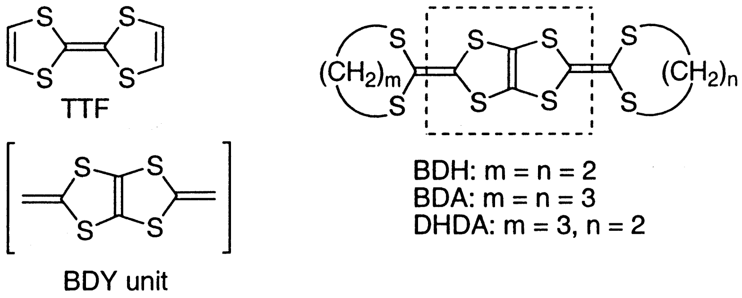
Hiroyuki Nishikawa, Isao Ikemoto, and Koichi Kikuchi
Department of Chemistry, Graduate School of Science,
Tokyo Metropolitan University, Hachioji,
Tokyo 192-0397, Japan

The study of three kinds of non-tetrathiafulvalene (TTF) donors, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA), 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH), and 2-(1,3-dithiolan-2-ylidene)-5-(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (DHDA), which contain the bis-fused 1,3-dithiole-2-ylidene unit instead of the TTF unit as a π-electron system, has been undertaken to develop new molecular-based organic superconductors, magnetic conductors, and organic metals. The BDA donor produces the superconducting SbF_6, AsF_6, and PF_6 salts. The κ-$(BDH)_2FeCl_4$ salt is a paramagnetic organic metal stable down to 1.5 K, whereas β-$(BDA)_2FeCl_4$ exhibits metallic conducting behavior with a sharp metal-to-insulator (MI) transition ($T_{MI} = 113\,K$), and antiferromagnetic ordering with a Néel temperature of near 8.5 K. Several salts of DHDA, a hybrid of BDA and BDH, are found to be metallic.

Keywords: non-TTF donors; organic superconductors; magnetic conductors; organic metals; crystal structures

INTRODUCTION

Tetrathiafulvalene (TTF) and its derivatives have been central to the development of new organic metals and superconductors [1]. Meanwhile, the construction of a new class of π-electron donors, which contains no TTF unit, yet produces organic metal and superconductors, remained as a challenging issue in this field. Our approach to this issue has been initiated by the design and synthesis of a bis-fused dihydro-TTF molecule, 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP or, simply, BDH), and we found that this donor yields metallic charge-transfer (CT) salts stable down to low temperatures regardless of the counteranions used [2]. This finding indicates that the bis-fused 1,3-dithiole-2-ylidene (BDY) unit, which is incorporated into the BDH-TTP molecule as a π-electron system, is a promising candidate for the post-TTF unit. From this viewpoint we have undertaken extensive studies on the synthesis of BDY donors and subsequent preparation of their CT materials. In this paper, we summarize recent investigations of (i) the development of new organic superconductors composed of 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP or BDA), (ii) the Fe-containing BDH and BDA salts, and (iii) an unsymmetrical BDY donor 2-(1,3-dithiolan-2-ylidene)-5-(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (DHDA-TTP or DHDA), which is a hybrid of BDH and BDA.



STRUCTURE 1

THE BDA-BASED SUPERCONDUCTORS

All the hitherto-known π-donors, which form organic superconductors and directly contribute to the superconductivity, were limited to tetrachalcogenafulvalene (TCF) derivatives [3]. Our recent finding of the superconductivity in β-$(BDA)_2X$ ($X = SbF_6$, AsF_6, and PF_6) means we have been able to break into this limited set of donor components [4]. It should be noted that these superconductors have high superconducting transition temperatures (T_c, see Table 1) and loose donor packing motifs. On the other hand, the temperature dependence of resistivities for the I_3, BF_4, and ClO_4 salts of BDA exhibited semiconductive behavior.

TABLE 1 Onset Temperatures of Superconducting Transitions in β-$(BDA)_2$

X	Magnetic T_c (K)	Resistive T_c (K)
SbF_6	6.9	7.5
AsF_6	5.9	5.8
PF_6	5.9	†

†Not determined due to the fragile nature of this crystal, see ref. [4].

DEVELOPMENT OF NEW MOLECULAR MAGNETIC CONDUCTORS

Recent studies on the development of molecular magnetic conductors by combining organic π-donors and inorganic magnetic anions have resulted in a new class of CT salts with multifunctional properties such as antiferro- and ferro-magnetic organic metals [5,6], and antiferro-magnetic organic metals exhibiting superconductivity [7]. However, these CT salts, where magnetic order and metallic conductivity can coexist, are derived from TCF donors. Therefore, the successful formation of metallic or superconducting CT salts consisting of non-TCF donors and magnetic anions would extend the scope of this class of CT salts, and, consequently, could lead to new multiproperty molecular materials. We thus focused on the Fe-containing BDH and BAD salts.

Electrocrystallization of BDH with Et_4FeCl_4 in 5% EtOH/PhCl by the controlled-current method [8] gave κ-$(BDH)_2FeCl_4$. On the other hand, electrocrystallization of BDA under the same conditions afforded two types of crystals, whose preliminary X-ray analyses revealed that one crystal has the β-type structure [designated as β-$(BDA)_2FeCl_4$] and the other is solvated with the composition $(BDA)_3FeCl_4(PhCl)$.

Figures 1 and 2 show the crystal structures of κ-$(BDH)_2FeCl_4$ and β-$(BDH)_2FeCl_4$, respectively. In the donor layer of κ-$(BDH)_2FeCl_4$, the large intermolecular overlap integrals ($p1$ and $p2$ in Figure 1b) are calculated, not only within a pair of donor molecules but also between pairs which suggest a two-dimensional (2D) electronic structure; the same can be said for κ-$(BDH)_2PF_6$ that retains the metallic conductivity down to ca. 2 K [2]. The crystal structure of β-$(BDA)_2FeCl_4$ consists of one $FeCl_4^-$ anion and two crystallographically independent BDA molecules. In the donor layer of this salt, only one S···S contact shorter than the sum of van der Waals radii (3.70 Å) exists within the donor stack, whereas several short intermolecular S···S contacts are observed between the donor stacks (Figure 2b). These S···S contacts, however, do not always reflect the magnitude of the intermolecular overlap integrals calculated on the donor layer in this salt (Figure 2b) [9]. It is noteworthy that the largest overlap

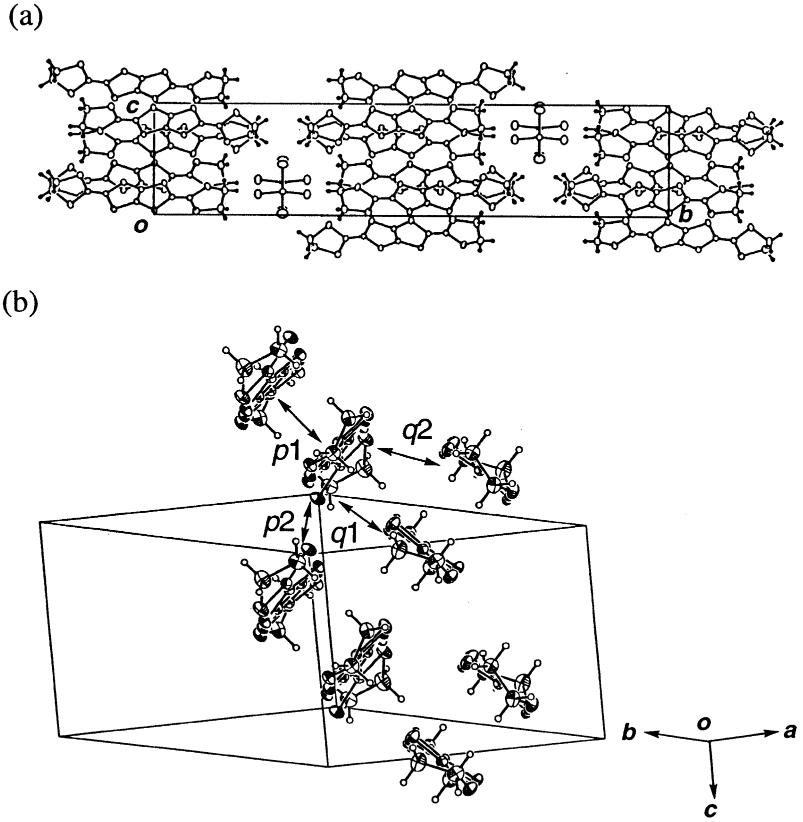


FIGURE 1 (a) Crystal structure of κ-(BDH)$_2$FeCl$_4$ viewed along the a axis. (b) Donor arrangement. The values of the intermolecular overlap integrals $p1$, $p2$, $q1$, and $q2$ are 19.3, 15.7, 6.36, and -6.79×10^{-3}, respectively.

integral (14.4×10^{-3}) is almost equal to those found in the superconducting BDA salts [4], suggesting that the BDA molecules in this salt are also packed loosely.

As expected from the crystal structure of κ-(BDH)$_2$FeCl$_4$ with 2D character, this salt exhibited a high room-temperature conductivity ($\sigma_{\mathrm{rt}} = 39\,\mathrm{S\,cm^{-1}}$) and metallic conducting behavior down to 1.5 K (Figure 3a). Figure 3b shows the temperature dependence of its magnetic susceptibility measured by a SQUID magnetometer from 300 to 2 K. The susceptibility can be well fitted to the Curie-Weiss law, and the values of the Curie and Weiss constants (C and θ) are 4.25 emu K mol^{-1} and 0.041 K, respectively. The fitted Curie constant is close to the value of 4.38 emu K mol^{-1}

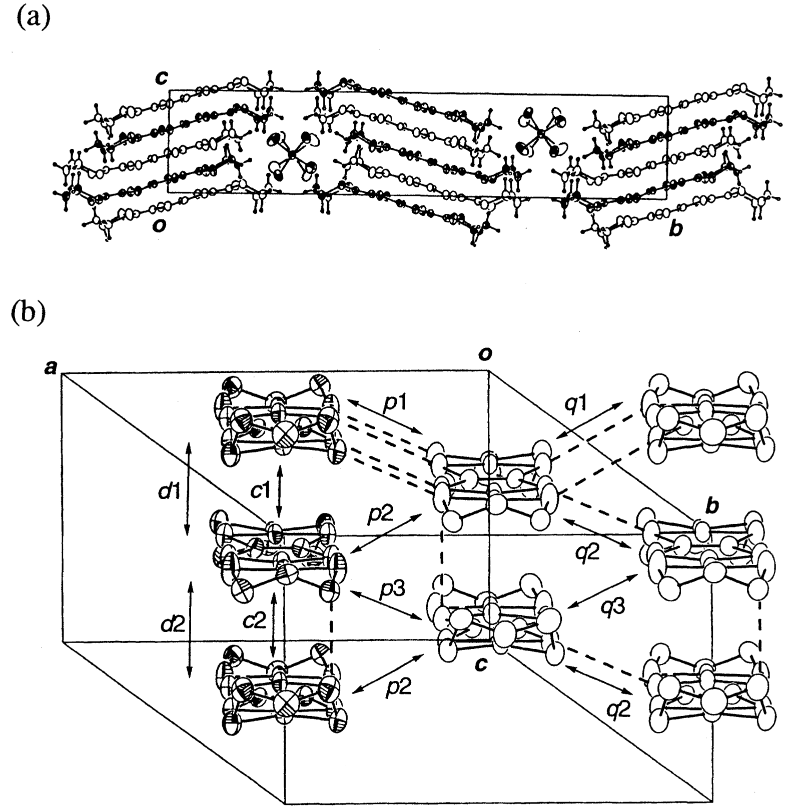


FIGURE 2 (a) Crystal structure of β-$(BDA)_2FeCl_4$ viewed along the *a* axis; open circles indicates the back molecules. (b) Donor arrangement. Interplanar distances of the donor stack are 3.56 (*d*1) and 3.89 (*d*2) Å. Intermolecular S···S contacts (<3.70 Å) are drawn by broken lines. The values of the intermolecular overlap integrals *c*1, *c*2, *p*1, *p*2, *p*3, *q*1, *q*2, and *q*3 are 14.4, 13.5, 1.88, −7.34, 3.44, 6.99,−5.62, and 5.49×10^{-3}, respectively.

calculated for the high-spin Fe^{3+} ion ($S = 5/2$, $g = 2.0$), so that the included Fe in the anion certainly dominates the measured magnetization.

The resistivity of β-$(BDA)_2FeCl_4$ salt as a function of temperature revealed that this salt ($\sigma_{rt} = 9.4\,S\,cm^{-1}$) is metallic from room temperature to 113 K, at which temperature it undergoes a sharp metal-to-insulator (MI) transition (Figure 4a). Although the reason of this MI transition is not clear, the charge separation between two independent donors in the column may be considered as its reason. The susceptibility of this salt obeys the Curie-Weiss law from 300 to 40 K ($C = 4.48$ emu K mol^{-1} and $\theta = -15.1$ K, Figure 4b). Below 40 K, the susceptibility increased to a

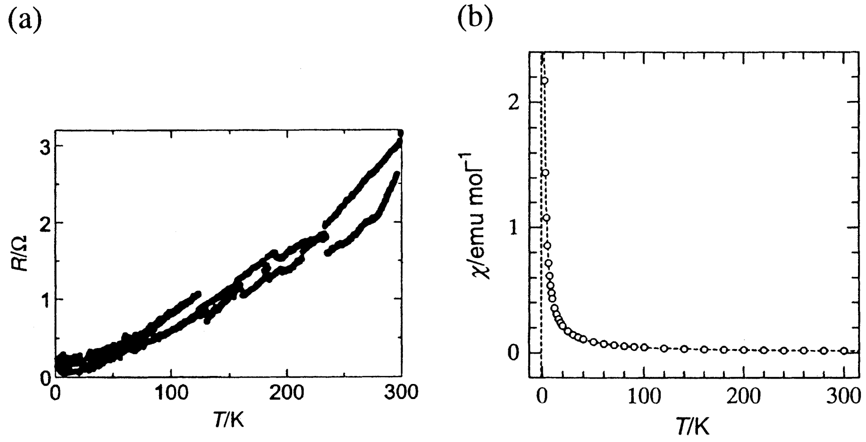


FIGURE 3 (a) Electrical conducting behavior of κ-$(BDH)_2FeCl_4$. (b) Magnetic behavior of κ-$(BDH)_2FeCl_4$. The dashed line is a Curie-Weiss fit.

maximum near 8.5 K, after which it decreased rapidly. As shown in the inset of Figure 4b, the susceptibilities, which were measured under the magnetic field applied along the directions approximately parallel to the crystallographic *a, b,* and *c* axes, were anisotropic below near 8.5 K, indicating antiferromagnetic ordering with a Néel temperature (T_N) of near 8.5 K.

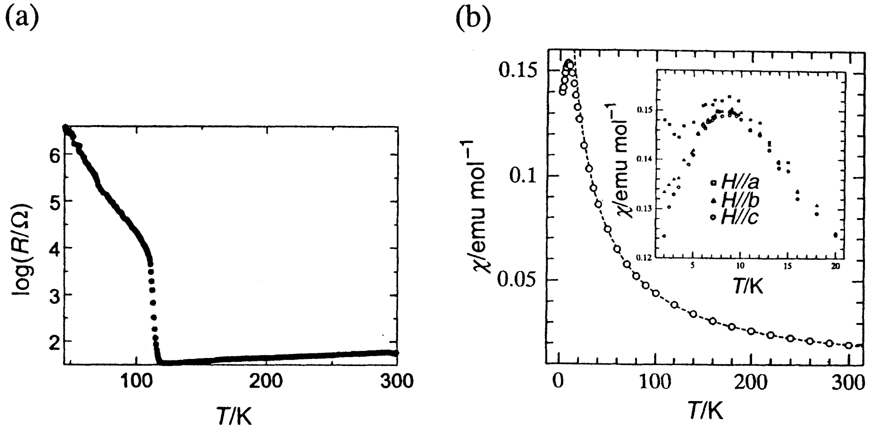


FIGURE 4 (a) Electrical conducting behavior of β-$(BDA)_2FeCl_4$. (b) Magnetic behavior of β-$(BDA)_2FeCl_4$. The dashed line is a Curie-Weiss fit. The inset shows the magnetic anisotropy in magnetic fields approximately parallel to the *a, b,* and *c* axes (*H*//*a*, *H*//*b*, and *H*//*c*).

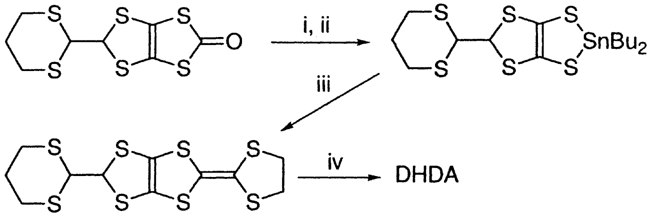
Below T_N, the easy spin axis seems to lie close to the interstacking *c*-direction of the donor molecules. So, considering that the shortest Fe $\cdots$ Fe distance between the most adjacent anions along the *c* axis [7.731(4) Å] is longer than 6 Å, the donor molecules could mediate the observed antiferromagnetic order between the Fe^{3+} ions [10].

On the other hand, the solvated $(BDA)_3FeCl_4(PhCl)$ salt was a semiconductor with a thermal activation energy of 0.11 eV ($\sigma_{rt} = 2.0 \times 10^{-2}\,S\,cm^{-1}$) and exhibited Curie-Weiss behavior from 300 to 2 K. The fitted C and θ are 4.42 emu K mol^{-1} and -0.35 K, respectively. This negative θ suggests very weak antiferromagnetic interaction between the Fe moments.

DEVELOPMENT OF NEW ORGANIC METALS BASED ON DHDA

As mentioned above, new organic superconductors and molecular magnetic conductors can be obtained from the symmetrical BDY donors BDA and BDH. Our next attention was thus focused on the unsymmetrical BDY donor DHDA, which is a hybrid between BDA and BDH. If metallic and/or superconducting states could occur with the use of this BDY donor, the importance of the BDY donor system as a post-TTF donor family would increase.

The synthesis of DHDA was carried out as shown in Scheme 1, in analogy with the synthetic routes to BAD and BDH [2,4]. The cyclic voltammogram of DHDA showed three pairs of reversible redox waves and one irreversible oxidation wave. Table 2 compares its oxidation potentials with those of BDA and BDH measured under identical conditions. The E_1 and



Reagents and conditions: i, MeMgBr, THF, room temperature (rt), 2 h; ii, Cl_2SnBu_2, THF, –78 °C → 0 °C; iii, ethyl 1,3-dithiolane-2-carboxylate, Me_3Al, CH_2Cl_2, –78 °C → rt, overnight (52% overall yield); iv, DDQ, toluene, reflux, 40 min (85% yield).

SCHEME 1 Synthesis of DHDA.

TABLE 2 Oxidation Potentials of BDY Donors†

Compound	E_1	E_2	E_3	E_4	$\Delta E(E_2 - E_1)$
BDA	0.72	0.90	1.26‡		0.18
DHDA	0.67	0.87	1.35	1.53‡	0.20
BDH	0.56	0.82	1.52‡		0.26

†V vs. saturated calomel electrode (SCE), 0.1 M n-Bu_4NClO_4 in $PhCN/CS_2 = 1/1$, Pt electrode, at room temperature, under nitrogen, scan rate 50 m V s^{-1}.

‡Irreversible wave.

ΔE ($E_2 - E_1$) values of DHDA are midway between the corresponding values of BDA and BDH.

The DHDA donor reacted with 7,7,8,8-tetracyanoquinodimethane-(TCNQ) and its tetrafluoro analogue ($TCNQF_4$) in 1,1,2-trichloroethane (TCE) at room temperature to form CT complexes. However, their room-temperature conductivities were fairly low (see Table 3) and not superior to those of the corresponding complexes of BDA and BDH. Preparation of the DHDA salts listed in Table 3 was carried out in PhCl or TCE by the controlled-current electrocrystallization method [8]. The DHDA salts with the I_3^-, AuI_2^-, and BF_4^- anions exhibited metallic conducting behavior down to 2 K. Among these salts, the AuI_2, salt was found to possess the κ-type donor arrangement by X-ray analysis. On the other hand, the ClO_4^-, PF_6^-, and AsF_6^- salts underwent MI transitions near 80, 30, and 60 K, respectively, whose X-ray analyses revealed that they are all the β-type salts and

TABLE 3 Conducting Behavior of CT Materials Based on DHDA

Acceptor	Solvent	D:A†	$\sigma_{rt}/S\,cm^{-1}$‡
TCNQ	TCE	3:1	$< 10^{-6}$¶
$TCNQF_4$	TCE	3:1	$< 10^{-6}$¶
I_3^-	PhCl	3:1	53(metallic > 2K)
AuI_2^-	TCE	4:1§	7.4(metallic > 2K)
BF_4^-	TCE	2:1	2.3(metallic > 2K)
ClO_4^-	TCE	2:1§	9.1(T_{MI} = ca. 80 K)
PF_6^-	TCE	2:1	8.1(T_{MI} = ca. 30 K)
AsF_6^-	TCE	2:1	39(T_{MI} = ca. 60 K)
SbF_6^-	TCE	2:1§	2.6(E_a = 16 meV)

†Determined by elemental analysis unless otherwise noted.

‡Room-temperature conductivity measured by a four-probe technique for a sngle crystal unless otherwise noted.

¶Measured on a compressed pellet.

§Determined by X-ray analysis.

isostructural. In contrast to the above-mentioned metallic DHDA salts, the SbF_6 salt was a small gap semiconductor with an activation energy of 16 meV, though its preliminary X-ray analysis indicated the κ-type crystal structure. The detailed crystal structures of the DHDA salts will be reported elsewhere.

CONCLUSION

As a non-TTF donor system, we describe herein the study of BDH, BDH, and DHDA, which contain the BDY unit in common instead of the TTF unit. Although considerable research effort in this field has been applied to the synthesis and study of π-electron donors containing no TTF unit, this work did not develop into the achievement of superconductivity [3]. Therefore, the construction of a new π-donor system comparable to the TTF donor family is subject to the achievement of superconductivity. The occurrence of superconductivity in the BDA salts demonstrates that the BDY donor system meets this qualification. In addition, the production of CT salts, composed of non-TCF donors and magnetic anions, with an enhanced interaction between conduction π-electrons and localized d-spins will be the subject of continued interest. Our effort to synthesize a variety of BDY donors capable of providing CT materials with more interesting and exciting solid-state properties currently continues.

REFERENCES

[1] Proceedings of ICSM '98, Montpellier, *Synth. Met.*, 101–103 (1999); Proceedings of ICSM '00, Gastein, *Synth. Met.*, 119–121 (2001).

[2] Yamada, J., Watanabe, M., Anzai, H., Nishikawa, H., Ikemoto, I., & Kikuchi, K. (1999). *Angew. Chem. Int. Ed.*, *38*, 810.

[3] Ishiguro, T., Yamaji, K., & Saito, G. (1998), *Organic Superconductors*, 2nd ed., Springer, Berlin; Williams, J. M., Ferraro, J. R., Thorn, R. J., Carlson, K. D., Geiser, U., Wang, H. H., Kini, A. M., & Whangbo, M.-H. (1992). *Organic Superconductors* (*Including Fullerenes*) Prentice Hall: Englewood Cliffs.

[4] Yamada, J., Watanabe, M., Akutsu, H., Nakatsuji, S., Nishikawa, H., Ikemoto, I., & Kikuchi, K. (2001). *J. Am. Chem. Soc.*, *123*, 4174.

[5] Enoki, T., Umeyama, T., Miyazaki, A., Nishikawa, H., Ikemoto, I., & Kikuchi, K. (1998). *Phy. Rev. Lett.*, *81*, 3719.

[6] Coronado, E., Galán-Mascarós, J. R., Gómez-Garciá, C. J., & Laukhin, V. (2000). *Nature*, *408*, 447; Nishijo, J., Ogura, E., Yamaura, J., Miyazaki, A., Enoki, T., Tanaka, T., Kuwatani, Y., & Iyoda, M. (2000). *Solid State Commun.*, *116*, 661.

[7] Otsuka, T., Kobayashi, A., Miyamoto, Y., Kiuchi, J., Wada, N., Ojima, E., Fujiwara, H., & Kobayashi, H. (2000). *Chem. Lett.*, 732; Fujiwara, H., Fujiwara, E., Nakazawa, Y., Narymdetov, B. Z., Kato, K., Kobayashi, H., Kobayashi, A., Tokumoto, M., & Cassoux, P. (2001). *J. Am. Chem. Soc.*, *123*, 306.

[8] Anzai, H., Delrieu, J. M., Takasaki, S., Nakatsuji, S., & Yamada, J. (1995). *J. Cryst. Growth*, *154*, 145; Nishikawa, H., Ishikawa, H., Sato, T., Kodama, T., Ikemoto, I., Kikuchi, K., Tanaka, S., Anzai, H., & Yamada, J. (1998). *J. Mater. Chem.*, *8*, 1321.

[9] Mori, T. (1998). *Bull. Chem. Soc. Jpn.*, *71*, 2509.

[10] Tanaka, H., Adachi, T., Ojima, E., Fujiwara, H., Kato, K., Kobayashi, H., Kobayashi, A., & Cassoux, P. (1999). *J. Am. Chem. Soc.*, *121*, 11243.