

# Crystal Engineering

# Crystal Structures and Phase Sequences of Metallocenium Salts with Fluorinated Anions: Effects of Molecular Size and Symmetry on Phase Transitions to Ionic Plastic Crystals

Tomoyuki Mochida,<sup>\*[a]</sup> Yusuke Funasako,<sup>[b]</sup> Mai Ishida,<sup>[a]</sup> Shingo Saruta,<sup>[c]</sup> Takashi Kosone,<sup>[c]</sup> and Takafumi Kitazawa<sup>[c, d]</sup>

**Abstract:** Sandwich compounds often exhibit various phase transitions, including those to plastic phases. To elucidate the general features of the phase transitions in metallocenium salts, the thermal properties and crystal structures of  $[Fe(C_5Me_5)_2]X$  ([1]X),  $[Co(C_5Me_5)_2]X$  ([2]X), and  $[Fe(C_5Me_4H)_2]X$  ([3]X) have been investigated, where the counter anions (X) are  $Tf_2N$  (=(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>), OTf (=CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), PF<sub>6</sub>, and BF<sub>4</sub>. The  $Tf_2N$  salts commonly undergo phase transitions from an ordered phase at low temperatures to an anion-disordered

## phase, followed by a plastic phase and finally melt at high temperatures. All these salts exhibit a phase transition to a plastic phase, and the transition temperature generally decreases with decreasing cation size and increasing anion size. The crystal structures of these salts comprise an alternating arrangement of cations and anions. About half of these salts exhibit phase transitions at low temperatures, which are mostly correlated with the order–disorder of the anion.

# Introduction

Organic ionic plastic crystals containing alkylammonium, alkylphosphonium, and other onium cations, have recently attracted much attention because they are useful as solid state electrolytes owing to their high ionic conductivity.<sup>[1]</sup> Many studies have been conducted on molecular motion, phase transitions, and electrochemical properties of ionic plastic crystals.<sup>[1,2]</sup> Plastic phases are often exhibited by solids containing globular molecules, in which the molecules exhibit orientational or rotational disorder.<sup>[3]</sup> Plastic crystals generally display a small entropy of fusion as a consequence of the disorder ( $\Delta S <$ 20 JK<sup>-1</sup>mol<sup>-1</sup>), and they often have highly symmetric crystal lattices such as cubic or hexagonal. Such materials often mani-

[a] Prof. Dr. T. Mochida, M. Ishida Department of Chemistry, Faculty of Science Kobe University, Rokkodai, Nada, Hyogo 657-8501 (Japan) E-mail: tmochida@platinum.kobe-u.ac.jp
[b] Dr. Y. Funasako

- Department of Applied Chemistry, Faculty of Engineering Tokyo University of Science, Yamaguchi Sanyo-Onoda, Yamaguchi, 756-0884 (Japan)
- [c] S. Saruta, Dr. T. Kosone, Prof. Dr. T. Kitazawa Department of Chemistry, Faculty of Science Toho University, Miyama, Funabashi, Chiba 274-8510 (Japan)
- [d] Prof. Dr. T. Kitazawa Research Center for Materials with Integrated Properties Faculty of Science, Toho University Miyama, Funabashi, Chiba 274-8510 (Japan)

Chem. Eur. J. 2016, 22, 1-9

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201603170.

fest phase transitions from an ordered crystalline phase to increasingly disordered structures with increasing temperatures.

Furthermore, the phase transitions in organometallic compounds have attracted attention for many years from the aspects of crystal engineering and molecular motion in the solid state.<sup>[4]</sup> For example, [FeCp<sub>2</sub>]PF<sub>6</sub> (Cp = C<sub>5</sub>H<sub>5</sub>) exhibits two phase transitions at 213 and 347 K, and the highest-temperature phase is a plastic phase.<sup>[5]</sup> [CoCp<sub>2</sub>]PF<sub>6</sub> has a similar phase sequence.<sup>[6]</sup> [Fe(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>]BF<sub>4</sub> exhibits a plastic phase above 409 K.<sup>[7]</sup> Metallocenium salts often exhibit plastic phases at high temperatures owing to the globular shape of the cation. Molecular motion and phase transitions in various metallocenium salts have been investigated by means of calorimetry, solid state NMR spectroscopy, X-ray crystallography, and Mossbauer spectroscopy.<sup>[4–8]</sup>

Based on this background, we considered that systematic exploration of organometallic ionic plastic crystals would expand the possibilities of ionic plastic crystals. To date, many studies have been conducted on the phase transitions of metallocenium salts with various anions,<sup>[4–8]</sup> including our previous studies on  $[CoCp_2][(SO_2C_nF_{2n+1})_2N]^{[9]}$  and  $[Fe(C_5Me_4R)_2]X$  ( $X = C_nF_{2n+1}CO_2^-$ ,  $C_nF_{2n+1}SO_3^-$ ).<sup>[10]</sup> However, no systematic studies have been conducted on the size and shape of the constituent ions. Therefore, in this study, we investigate the phase transitions in  $[Fe(C_5Me_5)_2]X$  ([1]X),  $[Co(C_5Me_5)_2]X$  ([2]X), and  $[Fe(C_5Me_4H)_2]X$  ([3]X), where the counter anions ( $X^-$ ) are Tf<sub>2</sub>N<sup>-</sup> (= (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>), OTf<sup>-</sup> (= CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), PF<sub>6</sub><sup>-</sup>, and BF<sub>4</sub><sup>-</sup> (Figure 1). The phase transitions and crystal structures of [1]OTf and [2]OTf were previously reported.<sup>[10]</sup> The crystal structures of [1]PF<sub>6</sub>–[3]PF<sub>6</sub><sup>-</sup>[11-13] and [3]BF<sub>4</sub><sup>[7]</sup> are known.

These are not the final page numbers! **77** 

Wiley Online Library



Figure 1. a) Metallocenium cations, and b) fluorinated anions used in this study. The volume of each ion is also shown.

In Figure 1, the volume of each ion is shown; they decrease in the order  $[Fe(C_5Me_5)_2]^+$   $([1]^+) > [Co(C_5Me_5)_2]^+$  $([2]^+) >$  $[Fe(C_5Me_4H)_2]^+$  ([3]<sup>+</sup>) for the cation and  $Tf_2N^- > OTf^- > PF_6^- >$ BF<sub>4</sub><sup>-</sup> for the anion. This variation allows a systematic investigation of the effects of molecular size and shape on the phase transitions. Cation [2]<sup>+</sup> is a diamagnetic 18-electron species; hence, its volume is smaller than [1]<sup>+</sup>, which is a paramagnetic 17-electron species. The Tf<sub>2</sub>N anion has often been used as a component of ionic liquids, the melting points of which are below 100 °C.<sup>[14]</sup> We previously found that alkylmetallocenium salts with Tf<sub>2</sub>N gave ionic liquids.<sup>[15]</sup> Therefore, an investigation of the phase transitions in these salts bridges the gap in the understanding of organometallic ionic plastic crystals and ionic liquids. Plastic phases have also been found in onium salts with the  $Tf_2N$  anion.<sup>[2a-c]</sup>

In this study, we discuss the phase sequences of these salts, mainly focusing on the  $Tf_2N$  salts, and then discuss their crystal structures and structural changes at low temperatures. It should be noted that a room-temperature organometallic ionic plastic crystal has been found using this approach.

## **Results and Discussion**

#### General features of phase sequences

Investigation by differential scanning calorimetry (DSC) revealed that all the salts exhibit one or more phase transitions in the solid state. The phase sequences for [1]X–[3]X are shown in Figure 2. The phase transition temperatures and entropies are shown in the this graphic; the data shown for [1]OTf and [2]OTf were reported in our previous study.<sup>[10]</sup> The presence of plastic phases in [3]PF<sub>6</sub> and [3]BF<sub>4</sub> has been reported in previous studies.<sup>[7,8]</sup> General features of the phase sequence observed in these salts are summarized as follows. 1) Most salts exhibit two phase transitions in the solid state. 2) The highest-temperature solid phase is a plastic phase in all the salts, and the phase transition temperatures to the plastic phase are correlated with the cation/anion radius ratio. 3) About half of these salts exhibit phase transitions at low temperatures, which are mostly correlated with the order–dis-

order of the anions, as discussed later. 4)  $Tf_2N$  salts exhibit melting, whereas other salts decompose without melting at high temperatures. Detailed discussions on each of the salts are given in the following sections.

#### Phase transitions in Tf<sub>2</sub>N salts

The Tf<sub>2</sub>N salts commonly exhibit two phase transitions in the solid state and melt at high temperatures (Figure 2a). As an example, the DSC trace of [3]Tf<sub>2</sub>N is shown in Figure 3. During the heating process, this salt exhibits phase transitions at  $T_{C1} =$ 189.0 K  $(\Delta S = 1.7 \text{ JK}^{-1} \text{ mol}^{-1})$ and *T*<sub>C2</sub> = 318.6 K  $(\Delta S =$ 54.2  $JK^{-1}mol^{-1}$ ) and melts at  $T_{\rm m} = 496.2 \, {\rm K}$  $(\Delta S_{\rm m} =$ 21.2 JK<sup>-1</sup> mol<sup>-1</sup>).

The phase transitions at low temperatures ( $T_{C1}$ ) in these salts, which accompany small transition entropies ( $\Delta S = 1.0$ – 2.5 JK<sup>-1</sup> mol<sup>-1</sup>), are correlated with the order–disorder of the anion (see below). The transition entropies are smaller than those expected for the ordering of the two-fold disorder ( $\Delta S =$  $R \ln 2 = 5.76$  JK<sup>-1</sup> mol<sup>-1</sup>), which is probably compensated by the difference in lattice entropies. The phase transitions at high temperatures ( $T_{C2}$ ) accompanying large transition entropies ( $\Delta S = 42-54$  JK<sup>-1</sup> mol<sup>-1</sup>) are transitions to plastic phases. Loss of birefringence was observed above  $T_{C2}$  by using polarized microscopy, which indicated that the salts have a cubic or other high-symmetry crystal lattice. In [**3**]Tf<sub>2</sub>N the melting entropy is smaller than the transition entropy to the plastic phase, as often observed in plastic crystals.

The melting points of  $[1]Tf_2N-[3]Tf_2N$  were 586, 558, and 496 K, respectively, which decreased with decreasing cation size. This tendency is characteristic of molecular crystals, indicating that intermolecular interactions, rather than electrostatic interactions, determine the melting points. Consistently, the melting points of  $[MCp_2]Tf_2N$  containing smaller cations are even lower than those observed here ( $T_m$ =409 K for M=Fe, 439 K for M=Co).<sup>[9, 15a]</sup> The comparatively lower melting point of [**3**]Tf<sub>2</sub>N than [**1**]Tf<sub>2</sub>N and [**2**]Tf<sub>2</sub>N may be in part due to the lower symmetry of the cation. The appearance of melting only in Tf<sub>2</sub>N salts can probably be ascribed to the larger size and flexibility of the anion compared with other anions.

These salts exhibit two-step phase transitions from an ordered phase at low temperatures to a partially disordered phase and then to a plastic phase at high temperatures. It can be noted that such successive phase sequences have also been found in organic ionic plastic crystals.<sup>[1,2]</sup>

#### Phase transitions in OTf, PF<sub>6</sub> and BF<sub>4</sub> salts

Most salts with OTf, PF<sub>6</sub> and BF<sub>4</sub> anions exhibit phase transitions in addition to those to plastic phases (Figure 2b–d). Among the OTf salts, [1]OTf exhibits a phase transition at low temperature ( $\Delta S = 4.9 \text{ J K}^{-1} \text{ mol}^{-1}$ ), which accompanies intramolecular conformational change of the cation, as previously reported.<sup>[10]</sup> Among the PF<sub>6</sub> salts, [1]PF<sub>6</sub> and [2]PF<sub>6</sub> exhibit phase transitions above room temperature ( $\Delta S = 11-12 \text{ J K}^{-1} \text{ mol}^{-1}$ ), though the characters of the transitions are unknown. The salt [3]PF<sub>6</sub> exhibits a phase transition at low temperature ( $\Delta S =$ 

2

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



European Journal Full Paper



Figure 2. Phase sequences of [Fe(C<sub>5</sub>Me<sub>3</sub>)<sub>2</sub>]X ([1]X), [Co(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]X ([2]X), and [Fe(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>]X ([3]X). a) Tf<sub>2</sub>N salts, b) OTf salts, c) PF<sub>6</sub> salts, and d) BF<sub>4</sub> salts. The phase transition temperatures and entropies are shown above and below each bar chart, respectively. The space groups are also shown in the charts, of which those indicated by an asterisk were taken from the literature.<sup>[7,10-13]</sup> The phase diagram shown for [3]BF<sub>4</sub>, which has two polymorphs, is that of the more stable form.<sup>[7]</sup>



Figure 3. DSC trace of [Fe(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>]Tf<sub>2</sub>N ([3]Tf<sub>2</sub>N). An enlarged view is also shown for the low-temperature region.

3.4  $JK^{-1}$  mol<sup>-1</sup>), which is correlated with the order-disorder of the anion, as shown later. Among the BF<sub>4</sub> salts, [1]BF<sub>4</sub> exhibits successive transitions at low temperature  $(\Delta S_{total} =$ 3.2  $JK^{-1}mol^{-1}$ ), which is also correlated with the order–disorder of the anion (see below). Despite being isomorphous with [1]BF<sub>4</sub>, [2]BF<sub>4</sub> does not exhibit a phase transition below room temperature until 100 K. This salt exhibits phase transitions only above room temperature.

#### Phase transition to plastic phases

The phase transition temperatures to plastic phases in [1]X-[3]X are plotted in Figure 4. As shown, the transition temperatures tend to decrease with decreasing cation size  $([1]^+ > [2]^+)$ >[**3**]<sup>+</sup>) and increasing anion size (BF<sub>4</sub><sup>-</sup> < PF<sub>6</sub><sup>-</sup> < OTf<sup>-</sup> < Tf<sub>2</sub>N<sup>-</sup>). This trend is understood in terms of the reduction of the volume difference between the cation and anion, which likely facilitates molecular rotation and decreases the transition temperature. Compared with the overall trend, the higher transition temperatures for the Tf<sub>2</sub>N salts are probably related to the unsymmetrical shape of the anion. Although the plastic phases in metallocenium salts reported to date occur at high temperatures, it can be noted that [3]OTf exhibits the plastic phase at room temperature above 16.5 °C.

Regarding the sum of the phase transition entropies in the solid state, the value for [2]X is slightly smaller than that for [1]X, whereas that for [3]X is larger than both of them owing to the lower symmetry of the cation (e.g., [1]Tf<sub>2</sub>N: 47.9 J K<sup>-1</sup> mol<sup>-1</sup>, [**2**]Tf<sub>2</sub>N: 44.3 J K<sup>-1</sup> mol<sup>-1</sup>, [**3**]Tf<sub>2</sub>N: 55.9 JK<sup>-1</sup> mol<sup>-1</sup>), although the BF<sub>4</sub> salts deviate from this tendency. The transition entropies for the Tf<sub>2</sub>N salts are larger than those for other salts, which seems consistent with the lower symmetry and greater conformational freedom of the anion (e.g., [1]Tf<sub>2</sub>N: 47.9 JK<sup>-1</sup> mol<sup>-1</sup>, [1]X (X = OTf, PF<sub>6</sub>, BF<sub>4</sub>): 35.4–37.5 J K<sup>-1</sup> mol<sup>-1</sup>).

The structure of the plastic phase in [3]OTf was investigated by powder X-ray diffraction at room temperature (Figure 5). This salt was found to have a NaCl-type cubic lattice with a lat-

Chem. Eur. J. 2016, 22, 1-9 www.chemeurj.org These are not the final page numbers! 77

3





**Figure 4.** Phase transition temperatures to plastic phases in  $[Fe(C_5Me_5)_2]X$ ([1]X, **\blacksquare**),  $[Co(C_5Me_5)_2]X$  ([**2**]X,  $\Box$ ), and  $[Fe(C_5Me_4H)_2]X$  ([**3**]X, **\bullet**), where  $X = Tf_2N$ , OTf, PF<sub>6</sub>, and BF<sub>4</sub>, respectively.

tice constant of 13.00 Å. The interionic distance is 6.50 Å, which is in agreement with the sum of the ionic radii estimated by DFT calculations (6.95 Å). The radii of the ions were tentatively calculated by assuming spheres having the same volume as the ions. The radius ratio ( $r_{anion}/r_{cation}$ ) for this salt was 0.65. Therefore, the structure is in accord with the radius ratio rule in ionic crystals, which predicts that the radius ratio range of a NaCl-type structure is 0.41–0.73.<sup>[17]</sup> We also measured the magnetic susceptibility of [**3**]OTf; this salt was a paramagnetic ionic crystal ( $\chi T$ =0.76 emu K<sup>-1</sup> mol<sup>-1</sup>, at 300 K). Cations [1]<sup>+</sup> and [**3**]<sup>+</sup> are paramagnetic, and hence their salts are paramagnetic crystals. Recently, an example of a paramagnetic ionic plastic crystal, [choline][FeCl<sub>4</sub>], has been reported.<sup>[16]</sup> These materials may lead to novel electromagnetic phenomena.



Figure 5. Powder XRD pattern of [3]OTf at room temperature.

#### General features of crystal structures

The space groups of the room-temperature phase and low-temperature phase of each salt, as determined by single crystal X-ray crystallography, are shown in Figure 2. Crystal structure determination failed for [**3**]OTf, which has a plastic phase at room temperature. Regarding the room temperature struc-

tures, [1]X and [2]X are isomorphous for each anion, whereas [3]X exhibits a different structure.

The crystal structures of the salts commonly comprise an alternating arrangement of cations and anions. In addition, the  $C_5$  axes of the cations are aligned in the same direction in the unit cell in each salt except [1]OTf.<sup>[10]</sup> It is interesting that such a molecular arrangement, which accompanies the uniaxial magnetic anisotropy of the crystal,<sup>[15c]</sup> is commonly found in these salts. Because these salts contain nearly spherical cations, the radius ratio rules for inorganic ionic crystals may hold, not only for the plastic phase, but also for the crystal phase. The rule predicts a coordination number of eight for crystals with  $\rho >$  0.73 and six for those with 0.73  $> \rho >$  0.41, where  $\rho$  is the anion/cation radius ratio.<sup>[17]</sup> In agreement with the rule, it was found that the number of counter ions surrounding an ion is eight for [1]Tf<sub>2</sub>N and [2]Tf<sub>2</sub>N ( $\rho = 0.77$ ) and six for all the OTf,  $PF_{6'}$  and  $BF_4$  salts (0.63 >  $\rho$  > 0.54). The only exception is [3]Tf<sub>2</sub>N  $(\rho = 0.79)$ , the coordination number for which is six, despite the large radius ratio. This is probably because of the unsymmetrical shape of the constituent ions.

Furthermore, low-temperature structure determinations revealed that the low-temperature phase transitions observed in many of the salts accompany the order–disorder of the anion, except for [1]OTf.<sup>[10]</sup> Crystal structures of each salt are discussed in the following sections.

#### Crystal structures of Tf<sub>2</sub>N salts

Crystal structure determination for  $Tf_2N$  salts revealed that [1] $Tf_2N$  and [2] $Tf_2N$  are isomorphous crystals but [3] $Tf_2N$  exhibits a different structure. Each salt exhibits a phase transition at low temperature, as shown above.

The packing diagrams of  $[1]Tf_2N$  ( $T_{C1} = 167.4$  K) at 180 and 100 K are shown in Figure 6a. The cell volume of the low-temperature phase (Z=2) is twice that of the room-temperature phase (Z=1), whereas the space group is  $P\overline{1}$  in both phases. The molecular arrangements particularly, are the same in both phases, where the cations and anions are alternately arranged in the crystal lattice. Each anion is surrounded by eight cations and vice versa, hence forming a highly deformed CsCl-like lattice. The molecular structures of the anion, exhibiting the trans (C2) conformation, are also shown in the figure. In addition to the phase-transition temperature, the central moiety is disordered over two sites with a 0.5 occupancy, and the CF<sub>3</sub> groups exhibit rotational disorder. This type of disorder is often seen in Tf<sub>2</sub>N salts.<sup>[2a]</sup> The anion is ordered in the low-temperature phase, which results in ion pair formation of the anion with one of the two adjacent cations and cell doubling. This type of anion ordering has also been observed in [CoCp<sub>2</sub>][(SO<sub>2</sub>C<sub>n</sub>F<sub>2n+</sub> <sub>1</sub>)<sub>2</sub>N].<sup>[9]</sup> In the room temperature phases of [1]Tf<sub>2</sub>N and [2]Tf<sub>2</sub>N, both the cation and anion are located on inversion centers; hence, the asymmetric unit contains half of the molecules. In the low-temperature phase, however, the inversion centers are removed and the asymmetric unit contains a cation and anion.

The crystal structures of  $[2]Tf_2N$  determined above (297 K) and below (90 K) the low-temperature phase transition ( $T_{C1} =$  176.5 K) are isomorphous with  $[1]Tf_2N$  in the corresponding

Chem. Eur. J. 2016, 22, 1–9 www.chemeurj.org

4

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

**N** These are not the final page numbers!



CHEMISTRY A European Journal Full Paper



**Figure 6.** a) Packing diagrams of  $[Fe(C_5Me_5)_2]Tf_2N$  ([1]Tf\_2N) at 180 K ( $P\bar{1}$ , Z=1) and 100 K ( $P\bar{1}$ , Z=2). ORTEP drawings (50% probability ellipsoids) of the anion at each temperature are shown below, where one of the disordered moieties of the anion is displayed in gray. b) Packing diagrams of  $[Fe(C_5Me_4H)_2]Tf_2N$  ([3]Tf\_2N) at 200 K (Pnma, Z=4) and 90 K ( $P2_12_12_1$ , Z=4). c) Packing diagrams of  $[Fe(C_5Me_5)_2]BF_4$  ([1]BF\_4) at 195 and 90 K. d) Packing diagram of  $[Fe(C_5Me_4H)_2]Tf_2N$  ([3]PF\_6) at 100 K. Only half of the unit-cell content is shown along the *a*-axis. Hydrogen atoms have been omitted for clarity.

5

phases, showing the order–disorder of the anion. The unit-cell volume of [2]Tf<sub>2</sub>N (1282 Å<sup>3</sup> at 90 K) was 2% smaller than that of [1]Tf<sub>2</sub>N (1304 Å<sup>3</sup> at 100 K), a difference that is probably responsible for their different phase-transition temperatures.

The packing diagrams of  $[3]Tf_2N$  ( $T_{C1} = 189.0$  K) at 200 and 90 K are shown in Figure 6b. Each anion is surrounded by six cations and vice versa. The space group changed from orthorhombic Pnma (200 K) to P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (90 K), whereas the molecular arrangements were fundamentally the same in both phases. The phase transition accompanies the order-disorder of the anion, but no cell doubling occurred (Z=4) in contrast to [1]Tf<sub>2</sub>N and [2]Tf<sub>2</sub>N. Both the cation and anion are located on mirror planes in the high-temperature phase, with the asymmetric unit containing half of the molecules, whereas the mirror planes are removed in the low-temperature phase. In both phases, there are short contacts between the ring hydrogen of the cation and the oxygen atom in the anion  $(C_{CD}H \cdots O = 2.46 \text{ Å}$  at 200 K, 2.54 Å at 90 K), which are shorter than the van der Waals distance by about 0.2 Å. Similar intermolecular anion-cation contacts have been observed in the salts of octamethylferrocenium derivatives.<sup>[15c]</sup> We previously reported that a charge-transfer complex of octamethylferrocene with an organic acceptor exhibits a phase transition accompanying an order-disorder of the C<sub>5</sub>Me<sub>4</sub>H ring.<sup>[18]</sup> In the present salt, however, the cation exhibits no disorder in the room-temperature phase, which is probably responsible for its larger transition entropy to the plastic phase, as compared with  $[1]Tf_2N$  and  $[2]Tf_2N$ .

#### Crystal structures of PF<sub>6</sub> and BF<sub>4</sub> salts

The crystal structures of [1]X and [2]X (X = PF<sub>6</sub><sup>[11, 12]</sup> and BF<sub>4</sub>) in the room-temperature phase were found to be almost the same, and exhibited the same space group and similar cell parameters. The differences are that the cell volume of the BF<sub>4</sub> salts are slightly smaller (e.g., V = 1021 Å<sup>3</sup> for [2]BF<sub>4</sub>, V =1065 Å<sup>3</sup> for [2]PF<sub>6</sub> at room temperature) and the anions are disordered in the BF<sub>4</sub> salts. In contrast, the crystal structures of [3]BF<sub>4</sub><sup>[7]</sup> and [3]PF<sub>6</sub><sup>[13]</sup> are different, having a different intramolecular ring conformation of the cation, and the anions are disordered in both salts. In all the PF<sub>6</sub> and BF<sub>4</sub> salts, each cation is surrounded by six anions and vice versa. Low-temperature structure determination revealed that the phase transitions in [1]BF<sub>4</sub> and [3]PF<sub>6</sub> accompany the order–disorder of the anion.

Compound [1]BF<sub>4</sub> exhibits successive phase transitions at low temperatures ( $T_c = 147$ , 166, and 183 K). The packing diagrams of this salt at above and below the transition temperatures are shown in Figure 6c. The space group changes from  $P2_1/c$  (195 K) to C2m (90 K). At 195 K, the asymmetric unit contains half of each of the cation and anion. The cation is located on the mirror plane, and the C<sub>5</sub>Me<sub>5</sub> rings seem to undergo liberation or rotation around the C<sub>5</sub> axis, judging from the elon-

Chem. Eur. J. <b>2016</b> , 22, 1–9	www.chemeurj.org		
These are not the	final page numbers! 77		



gated thermal ellipsoids. The anion, which is also located on the mirror plane, exhibits disorder. At 90 K, however, the mirror planes are removed, and the asymmetric unit contains a pair of cations. The cations in the unit cell, which exhibits a slightly canted orientation to each other, have fairly small thermal ellipsoids and the anions are nearly ordered. The phase transition accompanies cell doubling; hence, the successive phase transition might be due to the formation of a long-range periodic structure related to the ordering of the anion or cation.

The room-temperature structure of [**3**]PF<sub>6</sub> has been reported (space group C2/c, Z=4, V=1967 Å<sup>3</sup>), where the asymmetric unit contains half of each of the cation and anion, exhibiting disorder of the anion.<sup>[13]</sup> The packing diagram of this salt, determined at 100 K, below the phase transition temperature ( $T_c$ =117 K), is shown in Figure 6d. The space group is unchanged, but the cell volume is significantly reduced (V= 1888 Å<sup>3</sup>) and the anions are fully ordered. At 100 K, there are short cation–anion contacts between the ring hydrogen and the F atom ( $C_{ring}H$ ···F=2.46 Å), which are shorter than the van der Waals distance by 0.20 Å. These contacts are absent in the room temperature phase; hence, the formation of the short contacts may be related to the anion ordering.

## Conclusions

The phase behavior of [1]X-[3]X (Tf<sub>2</sub>N, OTf, PF<sub>6</sub>, and BF<sub>4</sub>) has been investigated, and all the salts are found to exhibit phase transitions in the solid state. The phase sequences, generally accompanying stepwise enhancement of disorder or molecular motion, resemble those for typical organic ionic plastic crystals. All the salts exhibit phase transitions to the plastic phase, and the transition temperature is dependent on the cation/anion radius ratio. Only the  $Tf_2N$  salts exhibit melting at high temperatures, and the melting points decrease with decreasing cation size.

The crystal structures of these salts comprise an alternating arrangement of cations and anions, where the coordination numbers depend on the cation/anion radius ratio. Compounds [1]X and [2]X are isomorphous crystals for the same anion. It is intriguing to note that the  $C_5$  axes of the cations are generally aligned in the same direction in the unit cell. Such molecular arrangement accompanies uniaxial magnetic anisotropy of the crystal, which is interesting in terms of magnetic functionality.

This study gives an account of the phase transitions and crystal structures of a series of metallocenium salts. Together with our previous study on related ionic liquids,<sup>[15c]</sup> this study provides information about the boundary between ionic liquids and plastic crystals. Metallocenium salts with a globular molecular shape generally give plastic phases, but the introduction of an alkyl substituent, which lowers the molecular symmetry and increases the conformational freedom of the cation, leads to the loss of the plastic phase and appearance of a liquid phase.

This study, focusing on organometallic plastic salts, extends the field of ionic plastic crystals and contributes to the understanding of the effects of shape and size of constituent molecules in ionic plastic crystals. In addition, the systematic investigation leads to the finding of a room temperature organometallic ionic plastic crystal. It should be noted that the salts containing iron atoms are regarded as magnetic plastic crystals. Details of the electronic properties of these salts will be reported in the near future.

	[ <b>1</b> ]Tf <sub>2</sub> N		[ <b>2</b> ]Tf <sub>2</sub> N		[ <b>3</b> ]PF <sub>6</sub>
	100 K	180 K	90 K	297 K	100 K
empirical formula	$C_{22}H_{30}F_6FeNO_4S_2$		C <sub>22</sub> H <sub>30</sub> CoF <sub>6</sub> NO <sub>4</sub> S <sub>2</sub>		$C_{18}H_{26}F_6FeP$
formula weight	606.44		609.52		443.21
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	ΡĪ	ΡĪ	ΡĪ	РĪ	C2/c
a [Å]	9.8444(16)	8.1370(17)	9.8077(11)	8.1408(13)	12.723(9)
b [Å]	11.2361(19)	8.7985(18)	11.1638(13)	8.8562(13)	11.748(8)
c [Å]	12.660(2)	9.854(2)	12.5748(14)	9.9243(15)	12.821(9)
α [°]	85.391(3)	69.048(3)	84.961(2)	69.627(2)	90
β [°]	74.641(2)	88.975(3)	74.289(2)	89.267(3)	99.937(11)
γ [°]	74.912(2)	83.714(3)	75.375(2)	84.306(3)	90
V [ų]	1303.7(4)	654.7(2)	1282.2(3)	667.26(18)	1888(2)
Ζ	2	1	2	1	4
$ ho_{calcd}  [gcm^{-3}]$	1.545	1.538	1.579	1.517	1.560
F(000)	626	313	628	314	916
refins collected	8837	4467	8209	4542	4854
independent reflns	6091	2970	5198	2832	1991
parameters	335	219	335	219	123
R(int)	0.0421	0.0198	0.0188	0.0181	0.0801
$R_{1'}{}^{[a]} R_{w}{}^{[b]} (I > 2\sigma)$	0.0598, 0.0964	0.0470, 0.1107	0.0331, 0.0895	0.0396, 0.1087	0.0833, 0.2202
$R_{1}^{[a]} R_{w}^{[b]}$ (all data)	0.1496, 0.1192	0.0640, 0.1187	0.0351, 0.0916	0.0415, 0.1108	0.1191, 0.2357
GOF	1.033	1.108	1.072	1.059	1.265
$\Delta \rho_{\text{max,min}} [e \text{\AA}^{-3}]$	0.817, -0.970	0.509, -0.297	0.790, -0.650	0.375, -0.411	0.995, -0.941

Chem. Eur. J. **2016**, 22, 1–9

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Table 2. Crystallographic parameters.								
	[ <b>3</b> ]Tf <sub>2</sub> N 90 K	200 K	[1]BF <sub>4</sub> 90 K	195 K	[ <b>2</b> ]BF₄ 297 K			
empirical formula formula weight crystal system space group a [Å] b [Å] c [Å] $\beta$ [°] V [Å <sup>3</sup> ] Z $\rho_{calcd}$ [g cm <sup>-3</sup> ] F(000) refins collected independent refins parameters R(int) $R_{1,}^{(a)} R_w^{(b)}$ ( $l > 2\sigma$ ) $R_{1,}^{(a)} R_w^{(b)}$ (all data) GOF $\Delta \rho_{max, min}$ [e Å <sup>-3</sup> ]	$C_{20}H_{26}F_6FeNO_4S_2$ 578.39 orthorhombic $P_{2,2_12_1}$ 8.8073(9) 12.0045(12) 22.759(2) 90 2406.2(4) 4 1.597 1188 17375 5547 316 0.0590 0.0415, 0.0837 0.0534, 0.0881 1.033 0.556, -0.338	orthorhombic <i>Pnma</i> 23.2063(19) 12.1995(10) 8.8167(7) 90 2496.1(4) 4 1.539 1188 15551 3014 215 0.0809 0.0432, 0.0784 0.0989, 0.0966 1.008 0.315, -0.340	$\begin{array}{c} C_{20}H_{30}BF_4Fe \\ 413.1 \\ monoclinic \\ P2_1/c \\ 8.7716(19) \\ 17.065(4) \\ 14.122(3) \\ 109.806(11) \\ 1988.8(8) \\ 4 \\ 1.380 \\ 868 \\ 11.323 \\ 4559 \\ 255 \\ 0.0290 \\ 0.0407, 0.01020 \\ 0.0631, 0.1149 \\ 1.011 \\ 0.885, -0.632 \end{array}$	monoclinic C2/m 14.1675(10) 8.6843(6) 8.8556(6) 110.6460(10) 1019.57(12) 2 1.346 434 3308 1252 83 0.0208 0.0455, 0.1249 0.0460, 0.1253 1.110 1.053, -0.698	$\begin{array}{c} C_{20}H_{30}BCoF_4\\ 416.18\\ monoclinic\\ C2/m\\ 14.088(12)\\ 8.710(8)\\ 9.009(8)\\ 112.521(14)\\ 1021.2(15)\\ 2\\ 1.354\\ 436\\ 2635\\ 990\\ 83\\ 0.0512\\ 0.0665, 0.1742\\ 0.0665, 0.1742\\ 0.0695, 0.1782\\ 1.100\\ 1.250, -0.547\\ \end{array}$			
[a] $R_1 = \Sigma   F_o  -  F_c   / \Sigma  F_o $ . [b] $R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ .								

# **Experimental Section**

### General

DSC measurements were performed by using a Q100 differential scanning calorimeter (TA instruments) in the temperature range of 100–550 K at a heating/cooling rate of 10 K min<sup>-1</sup>; other rates were applied as required. Loss of birefringence of the crystals in the plastic phase was observed using a polarized microscope equipped with a Linkam LTS350 hot stage. The melting points of Tf<sub>2</sub>N salts were visually determined under a microscope. Molecular volumes were estimated based on DFT calculations (B3LYP/LanL2DZ) using Spartan '14 software (Wavefunction Inc.).

### Materials

Chem. Eur. J. 2016, 22, 1-9

 $[Co(C_5Me_5)_2]PF_6$  ([2]PF<sub>6</sub>) was purchased from Sigma–Aldrich and was used after recrystallization from acetonitrile. The preparations of [1]X (X =  $PF_{6'}^{[19]} BF_{4}^{[20]}$ ) and [3]X (X =  $PF_{6'}^{[21]} BF_{4}^{[7]}$ ) can be found in the literature. The general procedure for the preparation of other salts is as follows. A slight excess of an acetonitrile solution of AgX (X^- =  $Tf_2N^{-}$ , <sup>[22]</sup> OTf<sup>-</sup>, PF<sub>6</sub><sup>-</sup>) was added dropwise to an acetonitrile solution of ferrocenes while being stirred. After stirring for 1 h at room temperature, silver precipitates were removed by filtration. The filtrate was evaporated under reduced pressure and dried under vacuum. The obtained powders were dissolved in acetonitrile and filtered. Further, the filtrate was evaporated and dried under vacuum. Single crystals suitable for characterization were obtained by vapor diffusion of diethyl ether into acetonitrile solutions of the salts. [1]Tf<sub>2</sub>N: Yield 88%; elemental analysis calcd (%) for C<sub>22</sub>H<sub>30</sub>F<sub>6</sub>FeNO<sub>4</sub>S<sub>2</sub>: C 43.57, H 4.99, N 2.31; found: C 43.69, H 5.07, N 2.25. [2]Tf<sub>2</sub>N: Yield 88%; elemental analysis calcd (%) for C<sub>22</sub>H<sub>30</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub>Co: C 45.35, H 4.96, N 2.30; found: C 43.34, H 5.00, N 2.28. [3]Tf<sub>2</sub>N: Yield 85%; elemental analysis calcd (%) for C<sub>20</sub>H<sub>26</sub>F<sub>6</sub>FeNO<sub>4</sub>S<sub>2</sub>: C 41.53, H 4.53, N 2.42; found: C 41.61, H 4.60, N 2.36. [3]OTf: Yield 98%; elemental analysis calcd (%) for C<sub>19</sub>H<sub>26</sub>F<sub>3</sub>FeO<sub>3</sub>S: C 51.01, H 5.86; found: C 50.83, H 5.86. [1]BF<sub>4</sub>: Yield 92%; elemental analysis calcd (%) for  $C_{20}H_{30}BF_4Co$ : C 57.72, H 7.27; found: C 57.41, H 7.20.

## X-ray structure analysis

X-ray diffraction data for single crystals of [1]Tf<sub>2</sub>N-[3]Tf<sub>2</sub>N, [1]BF<sub>4</sub>, [2]BF<sub>4</sub>, and [3]PF<sub>6</sub> were collected on a Bruker SMART APEX CCD diffractometer by using Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å). Temperature variation was performed at 1 Kmin<sup>-1</sup>. Crystallographic parameters are listed in Table 1 and Table 2. The structures were solved by the direct methods (SHELXS-97<sup>[23]</sup>). ORTEP-3 for Windows<sup>[24]</sup> and Mercury<sup>[25]</sup> were used for the molecular graphics. The disorder model could not be applied to the methyl groups in [1]BF<sub>4</sub> at 195 K.

CCDC 1062857, 1062858, 1062859, 1062860, 1062861, 1062862, 1062865, 1062866, 1062867 and 1487788 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

# Acknowledgements

This work was financially supported by JSPS KAKENHI (16H04132). We thank T. Tominaga (Kobe University) for help with X-ray crystallography and polarized microscope observation.

Keywords: crystal structures • metallocenes phase transitions · plastic crystals · structure elucidation

These are not the final page numbers! **77** 

www.chemeurj.org

7

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

<sup>[1]</sup> a) D. R. MacFarlane, J. Huang, M. Forsyth, Nature 1999, 402, 792-794; b) J. M. Pringle, Phys. Chem. Chem. Phys. 2013, 15, 1339-1351; c) K. Matsumoto, U. Harinaga, R. Tanaka, A. Koyama, R. Hagiwara, K. Tsunashima, Phys. Chem. Chem. Phys. 2014, 16, 23616-23626; d) Y. Abu-Lebdeh, P.-J. Alarco, M. Armand, Angew. Chem. Int. Ed. 2003, 42, 4499-4501; Angew. Chem. 2003, 115, 4637-4639; e) Z. B. Zhou, H. Matsumoto, Electrochem. Commun. 2007, 9, 1017-1022; f) J. Luo, A. H. Jensen, N. R. Brooks, J. Sniekers, M. Knipper, D. Aili, Q. Li, B. Vanroy, M. Wübbenhorst, F. Yan,



CHEMISTRY A European Journal Full Paper

L. V. Meervelt, Z. Shao, J. Fang, Z.-H. Luo, D. E. De Vos, K. Binnemans, J. Fransaer, *Energy Environ. Sci.* **2015**, *8*, 1276–1291; g) M. Lee, U. H. Choi, S. Wi, C. Slebodnick, R. H. Colby, H. W. Gibson, *J. Mater. Chem.* **2011**, *21*, 12280–12287.

- [2] a) W. A. Henderson, M. Herstedt, V. G. Young, Jr., S. Passerini, H. C. De Long, P. C. Trulove, *Inorg. Chem.* 2006, *45*, 1412–1414; b) W. A. Henderson, V. G. Young, Jr., S. Passerini, P. C. Trulove, H. C. De Long, *Chem. Mater.* 2006, *18*, 934–938; c) Y. Lauw, T. Rüther, M. D. Horne, K. S. Wallwork, B. W. Skelton, I. C. Madsen, T. Rodopoulos, *Cryst. Growth Des.* 2012, *12*, 2803–2813; d) T. Hayasaki, S. Hirakawa, H. Honda, *Bull. Chem. Soc. Jpn.* 2013, *86*, 993–1001; e) H. Ishida, T. Iwachido, N. Hayama, R. Ikeda, M. Terashima, D. Nakamura, *Z. Naturforsch. Sect. A* 1989, *44*, 741–746.
- [3] a) J. Timmermans, J. Phys. Chem. Solids 1961, 18, 1–8; b) J. Sherwood, The Plastically Crystalline State: Orientationally Disordered Crystals, Wiley, Chichester, 1979.
- [4] a) D. Braga, F. Grepioni, *Chem. Soc. Rev.* 2000, *29*, 229–238; b) D. Braga,
  F. Grepioni, in *Topics in Organometallic Chemistry* (Eds.: J. M. Brown, P. Hofmann), Springer, Heidelberg, 1999, pp. 47–68; c) D. Braga, M. Curzi,
  S. L. Giaffreda, F. Grepioni, L. Maini, A. Pettersen, M. Polito, in *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Štěpnička), Wiley, Chichester, 2008, Chapter 12.
- [5] R. J. Webb, M. D. Lowery, Y. Shiomi, M. Sorai, R. J. Wittebort, D. N. Hendrickson, *Inorg. Chem.* **1992**, *31*, 5211–5219.
- [6] F. Grepioni, G. Cojazzi, S. M. Draper, N. Scully, D. Braga, *Organometallics* 1998, 17, 296–307.
- [7] H. Schottenberger, K. Wurst, U. J. Griesser, R. K. R. Jetti, G. Laus, R. H. Herber, I. Nowik, J. Am. Chem. Soc. 2005, 127, 6795–6801.
- [8] L. Nowik, R. H. Herber, Inorg. Chim. Acta 2000, 310, 191-195.
- [9] T. Mochida, Y. Funasako, T. Inagaki, M. J. Li, K. Asahara, D. Kuwahara, Chem. Eur. J. 2013, 19, 6257–6264.
- [10] S. Hamada, Y. Funasako, T. Mochida, D. Kuwahara, K. Yoza, J. Organomet. Chem. 2012, 713, 35–41.
- [11] H. Heise, F. H. Köhler, M. Herker, W. Hiller, J. Am. Chem. Soc. 2002, 124, 10823–10832.

- [12] D. Braga, O. Benedi, L. Maini, F. Grepioni, J. Chem. Soc. Dalton Trans. 1999, 2611–2617.
- [13] V. G. Andrianov, Y. T. Struchkov, I. R. Lyatifov, R. B. Materikova, Koord. Khim. 1982, 8, 846–850.
- [14] A. Stark, K. R. Seddon, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 5th ed., **2007**, Vol. 26, pp. 836–919.
- [15] a) T. Inagaki, T. Mochida, M. Takahashi, C. Kanadani, T. Saito, D. Kuwahara, *Chem. Eur. J.* **2012**, *18*, 6795–6804; b) T. Inagaki, T. Mochida, *Chem. Lett.* **2010**, *39*, 572–573; c) Y. Funasako, T. Inagaki, T. Mochida, T. Sakurai, H. Ohta, K. Furukawa, T. Nakamura, *Dalton Trans.* **2013**, *42*, 8317–8327.
- [16] I. de Pedro, A. García-Saiz, J. González, I. Ruiz de Larramendi, T. Rojo, C. A. M. Afonso, S. P. Simeonov, J. C. Waerenborgh, J. A. Blanco, B. Ramajog, J. Rodríguez Fernández, *Phys. Chem. Chem. Phys.* **2013**, *15*, 12724– 12733.
- [17] P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, Shriver and Atkins' Inorganic Chemistry, Oxford University Press, Oxford, 2010.
- [18] Y. Funasako, T. Mochida, K. Yoza, J. Organomet. Chem. 2012, 698, 49-52.
- [19] D. M. Duggan, D. N. Hendrickson, Inorg. Chem. 1975, 14, 955-970.
- [20] J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, A. J. Epstein, J. Am. Chem. Soc. 1987, 109, 769–781.
- [21] A. N. Nesmeyanov, R. B. Materikova, I. R. Lyatifov, T. K. Kurbanov, N. S. Kochetkova, J. Organomet. Chem. 1978, 145, 241–243.
- [22] A. Vij, Y. Y. Zheng, R. L. Kirchmeier, J. M. Shreeve, *Inorg. Chem.* **1994**, *33*, 3281–3288.
- [23] G. M. Sheldrick, Acta Crystallogr. Sect. D 2008, 64, 112-122.
- [24] L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837-838.
- [25] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, J. Appl. Crystallogr. 2008, 41, 466–470.

Received: July 2, 2016 Published online on ■ ■ ■, 0000

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

8



# **FULL PAPER**

**Organometallic ionic plastic crystals**: Metallocenium salts  $[M(C_5Me_5)_2]X$ (M = Fe, Co) and  $[Fe(C_5Me_4H)_2]X$  with fluorinated anions commonly exhibit ionic plastic phases. With increasing temperature, these salts mostly undergo phase transitions from an ordered phase to an anion-disordered phase and then to a plastic phase. The crystal structures and transition temperatures are correlated with the cation/anion radius ratio.



# Crystal Engineering

T. Mochida,\* Y. Funasako, M. Ishida, S. Saruta, T. Kosone, T. Kitazawa

## 

Crystal Structures and Phase Sequences of Metallocenium Salts with Fluorinated Anions: Effects of Molecular Size and Symmetry on Phase Transitions to Ionic Plastic Crystals