Available online at www.sciencedirect.com

SCIENCE DIRECT

ELSEVIER

Synthetic Metals 153 (2005) 385–388

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Changes of physical properties of anion radical salts having low melting points in the TCNQ system

K. Nishimura [a],* and G. Saito [a]

[a] *Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan*

Abstract

The anion radical salts in the TCNQ system with 1-ethyl-3-methylimidazolium (EMI) and 1-butyl-3-methylimidazolium (BMI) were prepared. The 1:1 salts of EMI-TCNQ (**1**) and BMI-TCNQ (**3**) melted at 145 and 155 °C, respectively, and were stable even in the liquid state. The conductivity of **1** increased by four orders of magnitude at melting owing to the carrier generation by the dissociation of TCNQ dimers and decreased by three orders of magnitude at freezing.

Keywords: TCNQ, alkyl-imidazolium cations, ionic liquid, anion radical salt, conductivity in the liquid state.

---

1. Introduction

Anion radical salts in a TCNQ system are well known as highly electronic-conductive materials in the partial CT state and exhibit characteristic physical phenomena in a low-dimensional system [1,2]. The studies of molecular conductors including TCNQ salts have mainly been carried out in the solid state rather than in the liquid state. Preparing molecular conductors with low melting point is one possible method to develop molecular conductors in the liquid state. In general, asymmetric cations, such as quinolinium derivatives, give TCNQ anion radical salts with relatively low melting points. One example is (*N*-*n*-butyl-isoquinolinium)($TCNQ^{0.5-}$)$_2$, which is known as an organic semiconducting condenser (OSCON) exhibiting an excellent frequency dependence of impedance, melts at 215 °C [3]. So far reported, a quadrinary mixed crystal consisting of *N*-*n*-propyl-isoquinolinium, *N*-methyl-isoquinolinium, TCNQ and methyl-TCNQ (MeTCNQ) claimed to be a molecular conductor with the lowest melting point (80°C) [4]. The averaged charge in this compound is –0.5 and its electronic conductivity at room temperature (RT) is 5×10^{-5} Scm^{-1}, which is quite a low value for partially charged TCNQ radical salts. The temperature dependence of its conductivity is semiconductive with an activation energy (E_a) of 0.14 and 0.11 eV in the solid and liquid states, respectively, and the conductivity increases by twice the magnitude when the compound melts. The irreversible transition to the amorphous phase by melting is found based on the change of the IR spectra of this quadrinary mixed crystal [5]. Another example is (C_7TET-TTF)(TCNQ) (C_7TET-TTF = bis(*n*-heptylthio)ethylenedithiotetrathiafulvalene), which is a neutral charge transfer (CT) compound with alternating stacks, melts at 55 °C, which is quite low melting point compared to those of other CT compounds. While the conductivity of crystalline state is in the order of 10^{-10} Scm^{-1}, that of the molten state at 60 °C is 10^{-4} Scm^{-1}, where the extreme increase in conductivity by melting is observed [6].

As for asymmetric cations, alkylimidazolium cations have been well and widely studied in the ionic liquids. Among them, 1-ethyl-3-methyl-imidazolium (EMI) and 1-butyl-3-methylimidazolium (BMI) cations are the most popular ones [7,8]. In these ionic liquid salts of EMI and BMI, inorganic closed-shell anions are usually used as counter anions. The replacement of inorganic anions with TCNQ radical anions is expected to give conducting materials with low melting points and with both ionic and electronic conductivities in the liquid state simultaneously. So far, the preparation of alkylimidazolium-TCNQ (alkyl = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl) salts with 1:1 and 2:3 stoichiometries were reported [9]. The electronic condutivities at RT were 10^{-7}~10^{-9} and 10^{0}~10^{-4} Scm^{-1} for 1:1 and 2:3 salts, respectively, and the melting points were in the range of 124-177 °C for 1:1 salts (the melting points

---

* Corresponding author. Tel: +81-75-753-4037; fax: +81-75-753-4000; E-mail: nishimura@kuchem.kyoto-u.ac.jp

doi:10.1016/j.synthmet.2005.07.312

of 2:3 salts were not reported). For the 1:1 EMI-TCNQ salt (**1**), crystal structure and magnetic properties were also reported; one-dimensional columns with strongly dimerized TCNQ molecules was formed in the crystal [10]. Here we discuss the thermal, electronic and magnetic properties of the anion radical salts in the TCNQ system with EMI or BMI in the liquid state, of which the conducting behaviour has not been reported yet.

2. Experimental

The 1:1 compound **1** was obtained by the metathesis between EMI chloride and an equivalent amount of $K^+ \cdot TCNQ^-$ in an acetone solution under a nitrogen atmosphere. A substitution of BMI chloride for EMI chloride afforded **3** in the same method. The 1:2 compound **2** was obtained by the metathesis of an equivalent amount of EMI chloride, neutral TCNQ and $K^+ \cdot TCNQ^-$ in an acetone solution. Instead of EMI chloride, BMI chloride afforded **4** in the same method. The preparation of substituted TCNQs salts (**5**,**6**) and the mixed crystal with EMI and BMI (**7**) were also obtained by the method mentioned above. The crude products of **1**-**7** were purified by the recrystallization from ethyl acetate. The list of anion radical salts mentioned in this text are listed in Table 1, and their chemical structures are shown in Figure 1.

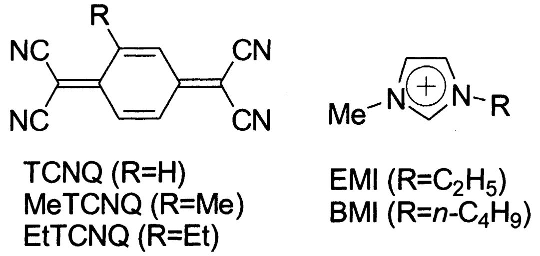

Figure 1 Chemical structures in text.

Table 1. Stoichiometries and melting points of anion radical salts in text.

	cation	anion	stoichiometry	melting point[a]
1	EMI	TCNQ	1:1	144.8
2	EMI	TCNQ	1:2	239.6
3	BMI	TCNQ	1:1	154.7
4	BMI	TCNQ	1:2	199.3
5	EMI	MeTCNQ	1:1	132.4
6	EMI	EtTCNQ	1:1	148.3
7	$EMI_{0.5}BMI_{0.5}$	TCNQ	1:1	151.9

a) Determined by the onset of an endothermic peak.

The differential scanning calorimetry (DSC) measurement was carried out on a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. Dc conductivities in the solid and liquid states were measured based on a standard two- or four-probe technique attaching platinum plates and wires plugged into the compressed sample in a cavity (2×4×4 mm^3) on a Teflon® cell. EPR measurements were performed on a continuous wave X band EPR spectrometer (JEOL JES-TE200) with an Oxford TE_{011} cavity.

3. Results and Discussion

3.1 Melting points and thermal stability

The stoichiometries and melting points are listed in Table 1. The 1:1 salts (**1**,**3**) were stable at around 200 °C under a nitrogen atmosphere even after melting, while the 1:2 salts (**2**,**4**) exhibited higher melting points and broad exothermic peaks just after melting due to decomposition (Figure 2a). Two interpretations of the increased melting points of 1:2 salts are possible. One is that there is a decrease in the ratio of asymmetric EMI/BMI molecules to symmetric planar TCNQ molecules in 1:2 salts compared to that of 1:1 salts. The other is that there is a gain in the stabilization energy due to the formation of a conduction band consisting of partially charged TCNQ molecules. The substitution of MeTCNQ for TCNQ (**5**) led to a decrease in the melting point of 12 °C, while substituting EtTCNQ (**6**)

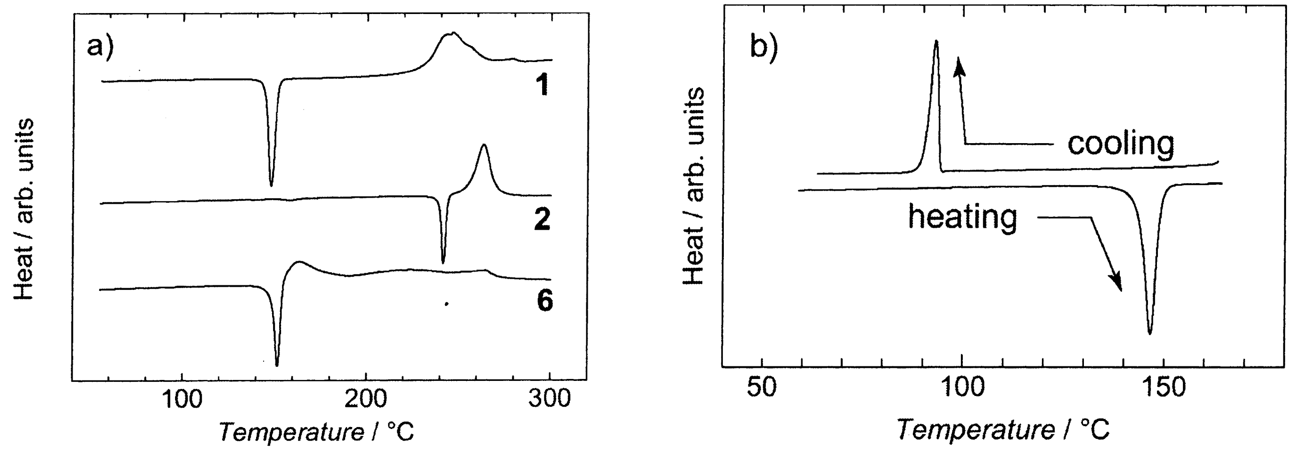

Figure 2 a) The DSC trace of **1**, **2** and **6** for the heating up to 300 °C. b) That of **1** for the heating and cooling cycle up to 165 °C.