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Reversible iodine absorption by alkali-TCNQ salts with associated changes in physical properties

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Alkali metal salts of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) reversibly absorb iodine forming the ternary salts $M(\text{TCNQ})\text{I}$ ($M = \text{Li}, \text{Na}, \text{K}$) and $M_2(\text{TCNQ})_3\text{I}_2$ ($M = \text{Rb}$). The ternary salts are also obtained by solid-state reactions of TCNQ with alkali iodides. These salts are paramagnetic and have high electrical conductivities, $\sim 10^{-1} \text{ S cm}^{-1}$ for compacted pellets, whereas the alkali metal salts of TCNQ are diamagnetic insulators. The ternary salts further absorb iodine to give over-doped salts $M(\text{TCNQ})\text{I}_n$ ($n \sim 6$, $M = \text{Na}, \text{K}$), which gradually release iodine to give $M(\text{TCNQ})\text{I}$. In contrast, the solid-state reaction of F_4TCNQ and sodium iodide produces $\text{Na}(\text{F}_4\text{TCNQ})$, which does not exhibit iodine absorption.

Introduction

Reversible absorption-desorption phenomena by host-guest compounds such as coordination polymers and caged compounds have attracted considerable attention in the last few decades [1]. Several examples of iodine absorption by solids have recently been reported, which are useful materials for iodine storage and to study polyiodide species. It has been found that a metal-organic framework having a three-dimensional structure with flexible pores shows reversible iodine absorption accompanied by changes of its magnetic properties [2]. Iodine absorption of nonporous organic salts of alkylammonium [3] and pyridinium iodides [4] has recently been reported, which is accompanied by the formation of polyiodide species (I_n^- ; $n \geq 3$). Iodine is conventionally used as a dopant for organic conductors and polymers to improve their electrical conductivities owing to its oxidizing ability [5]. We have previously investigated the physical properties of charge-transfer (CT) salts [6]. CT salts show various electronic phenomena such as electrical conduction, magnetism, and phase transitions [7]. The introduction of reversible iodine storage properties into CT salts is interesting, which would lead to the control of the physical properties through the changes of redox states and crystal structures. It has been reported that a few CT complexes including fullerene absorb iodine from the vapor phase [8].

In this paper, we show that simple alkali metal salts of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) reversibly absorb iodine. The alkali-TCNQ salts are well-known CT salts with insulating properties [9]. As related materials, several iodine-containing ternary salts such as $NHMe_3(TCNQ)I$ have been reported, which are electrical conductors [10–12]. These salts are synthesized by the reaction of TCNQ and alkylammonium iodides, whereas the reaction of TCNQ with alkali metal iodides in organic solvents only produces alkali-TCNQ. We also investigated the solid-state reaction of TCNQ and alkali iodides, since solid-state reactions by co-grinding the solid reactants are useful synthetic techniques [13,14].

Experimental

Materials

TCNQ and 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane (F₄TCNQ) were purchased from TCI. TCNQ was recrystallized from acetonitrile prior to use. Alkali iodides (MI) were purchased from Aldrich (M = Li, Rb, and Cs), Kanto Chemical (M = Na), and Nacalai Tesque (M = K) and used without further purification. M(TCNQ) (M = Li, Na, and K) and Na(F₄TCNQ) were prepared according to methods described in the literature [9a].

Methods

X-ray diffraction (XRD) data for the powder samples were recorded on a Rigaku SmartLab diffractometer using CuK α radiation. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet Avatar 360 FTIR spectrometer using KBr plates. Magnetic measurements were carried out using a Quantum Design MPMS-XL7 SQUID susceptometer under an applied field of 0.1 T. The magnetic susceptibility was estimated by subtracting the Pascal diamagnetic part of the alkali metals, TCNQ, and iodine atoms from the total susceptibility. For conductivity measurements, powder samples were pressed into pellets under a pressure of about 20 MPa using a hydraulic molding press. The conductivities were measured by a two-probe method using carbon paste electrodes. Thermogravimetric (TG) analyses were performed at a heating rate of 1 K min⁻¹ in a nitrogen atmosphere using a Rigaku TG 8120 thermal analyzer. Raman spectra were obtained using a Renishaw inVia Reflex spectrometer at 150 K and 100 K. A 488 nm laser was used as the excitation light with the laser power set at 28.6 μ W. UV-vis-NIR spectra were recorded on a JASCO V-570 UV-VIS/NIR spectrometer using KBr plates.

Solid-state reactions

Solid-state reactions were performed by grinding equimolar mixtures of TCNQ and the alkali iodides. A small amount of acetonitrile was added to the mixture prior to grinding to accelerate the reactions [14]. The grinding experiments were carried out either by simple hand grinding with an agate and mortar (~10 min) or by mechanical grinding using a Fritsch P-7 planetary ball mill with the aid of zirconia beads (750 rpm, 30 min). The reactions with lithium iodide were carried out in a glove box under a nitrogen atmosphere because of the hygroscopic nature of lithium iodide.

Crystal growth of M(TCNQ)I

Black powder of K(TCNQ)I obtained by solid-state reactions were immersed in small amounts of methanol and left in air at ambient temperature. After a few days of slow evaporation of the solvent, growth of black prismatic crystals was observed. Very fine crystals of M(TCNQ)I (M = Na, Rb) were obtained similarly. XRD data for the single crystals of K(TCNQ)I were collected at ambient temperature and 173 K on a Bruker SMART APEX II Ultra CCD diffractometer, using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Structure determination was unsatisfactory owing to superlattice reflections, which likely originated from an incommensurate iodine arrangement. The unit cell dimensions determined by ignoring the superlattice reflection were $a = 7.62(9) \text{ \AA}$, $b = 9.66(1) \text{ \AA}$, $c = 10.13(1) \text{ \AA}$, $\alpha = 79.14(2)^\circ$, $\beta = 81.06(2)^\circ$, $\gamma = 82.22(2)^\circ$, and $V = 719.47(2) \text{ \AA}^3$, where the superlattice reflections were observed along the a^* -axis. In a tentative analysis based on this unit cell, the TCNQ molecule was found by the direct method, whereas no iodine atoms could be located and no further structure refinement was possible.

Results and discussion

Solid-state reactions of TCNQ with alkali iodides

Co-grinding of TCNQ and the alkali iodides (MI) was found to quantitatively produce new iodine-containing ternary CT salts following the reaction schemes: $\text{TCNQ} + \text{MI} \rightarrow \text{M}(\text{TCNQ})\text{I}$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) and $3\text{TCNQ} + 2\text{MI} \rightarrow \text{M}_2(\text{TCNQ})_3\text{I}_2$ ($\text{M} = \text{Rb and Cs}$). The powder XRD patterns of the reaction products are shown in Fig. 1. For $\text{M} = \text{Rb and Cs}$, the mixing ratio of $\text{MI}:\text{TCNQ} = 2:3$ produced single components, whereas the XRD peaks of unreacted alkali iodides were observed for a mixing ratio of 1:1. It is known that the reaction of TCNQ and RbI in solution produces a mixture of $\text{Rb}(\text{TCNQ})$ and $\text{Rb}_2(\text{TCNQ})_3$ [15], whereas solid-state reaction enabled selective preparation of the 2:3 salt. This result probably occurred due to mechanochemical effects [13,14], which often give peculiar reaction conditions. In the solid-state reactions, elemental iodine was not produced, as shown by XRD, and extraction of the products with hexane, which indicates that the reaction is stoichiometric. These results indicate that not only the alkali-TCNQ salts but also the iodine-containing salts are stable in the solid state, allowing the change of the valence state of TCNQ (*vide infra*). The solid-state reactions were accelerated by the presence of water. The reactions for the hygroscopic alkali iodides (LiI and NaI) were immediate by hand grinding, which is presumably due to absorbed water. The less hygroscopic alkali iodide (KI, RbI, and CsI) required the ball milling technique and these reactions were accelerated by the addition of a small amount of water.

Crystal growth of $\text{K}(\text{TCNQ})\text{I}$ occurred from the powder immersed in methanol. Similar crystal growth phenomena from powders have been reported for pyridinium iodides [4]. Attempts to determine the crystal structure were unsuccessful because of superstructures probably originating from an incommensurate one-dimensional iodine arrangement. Tentative analysis ignoring the superlattice suggested the presence of a regular stacking of TCNQ, which surrounded one-dimensional channels of iodine atoms. The structure, resembling that

of $\text{NHMe}_3(\text{TCNQ})\text{I}$ [10a], was consistent with the high electrical conductivity of $\text{M}(\text{TCNQ})\text{I}$ (*vide infra*).

For comparison, we investigated the reactivity of F_4TCNQ , which is a stronger electron acceptor than TCNQ. In contrast to the case of TCNQ, co-grinding of F_4TCNQ and NaI produced a mixture of $\text{Na}(\text{F}_4\text{TCNQ})$ and iodine, with no ternary salt of iodine produced.

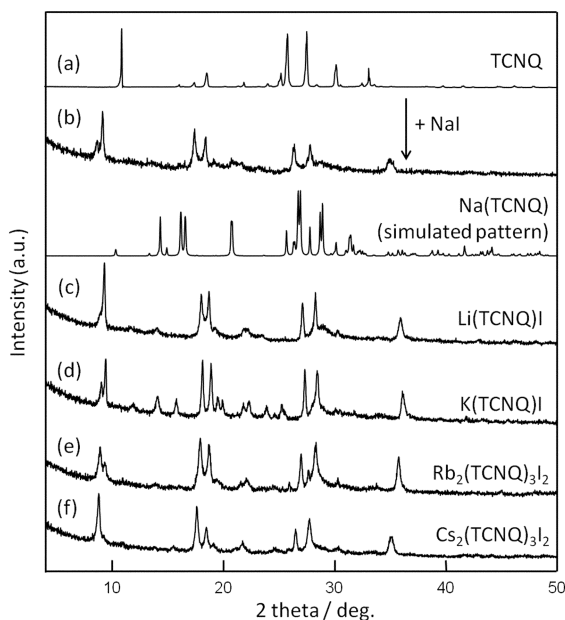


Fig. 1. Powder XRD patterns of (a) TCNQ, and the products obtained by the solid-state reactions of TCNQ with (b) NaI, (c) LiI, (d) KI, (e) RbI, and (f) CsI. The mixing ratios of alkali iodide:TCNQ were 1:1 for $\text{M} = \text{Li}, \text{Na}, \text{and K}$, and 2:3 for $\text{M} = \text{Rb}$ and Cs .

Iodine absorption of $\text{M}(\text{TCNQ})$ by solid-state reactions

Co-grinding of $\text{M}(\text{TCNQ})$ powder ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and a stoichiometric amount of solid iodine gave a black powder of the iodine-containing ternary salt $\text{M}(\text{TCNQ})\text{I}$, which was confirmed by changes of the powder XRD patterns (Fig. 2 and Fig. S1). Washing of the ternary salts with ethanol or annealing at $100\text{ }^\circ\text{C}$ for 30 min caused desorption of iodine, returning the powder to the bluish-purple powders of $\text{M}(\text{TCNQ})$. Thus, $\text{M}(\text{TCNQ})$ reversibly absorbs iodine. The efficiency of the iodine absorption depended on the metal species. For M

= Li and Na, complete iodine absorption was obtained by simple hand grinding, whereas mechanical milling was required for M = K. Moreover, dry grinding of M(TCNQ) (M = Na and K) and an excess of iodine produced over-doped salts M(TCNQ) I_n ($n \sim 6$, *vide infra*), accompanying drastic changes of the XRD patterns (Fig. 2).

Rb₂(TCNQ)₃ also absorbed iodine but more severe conditions were needed than for M(TCNQ) (M = Li, Na, K). Ball milling of Rb₂(TCNQ)₃ and iodine caused an increase of the XRD peaks of Rb₂(TCNQ)₃I₂, although the reaction was slow and incomplete after 30 minutes. Annealing Rb₂(TCNQ)₃I₂ from the solid-state reaction at 120 °C for 3 h produced Rb₂(TCNQ)₃. On the other hand, Cs₂(TCNQ)₃I₂ decomposed by annealing, after which only the XRD peaks of CsI were observed.

To investigate the iodine absorption properties of the corresponding F₄TCNQ salts, Na(F₄TCNQ) was ground with iodine. No reaction occurred, which was confirmed by XRD and IR measurements. In the TCNQ salts, iodine absorption accompanies the valence change of TCNQ. Therefore, the lack of reaction can be partly attributed to the strong tendency of F₄TCNQ to form the monoanion [7a]. This comparison also suggests that matching of the redox potentials of TCNQ⁻¹ and I_n⁻ is important for iodine absorption. Indeed, the redox potentials of TCNQ⁰/TCNQ⁻¹ and triiodide/iodide are very close, which are +0.37 V and +0.35 V (vs. NHE), respectively [16,17].

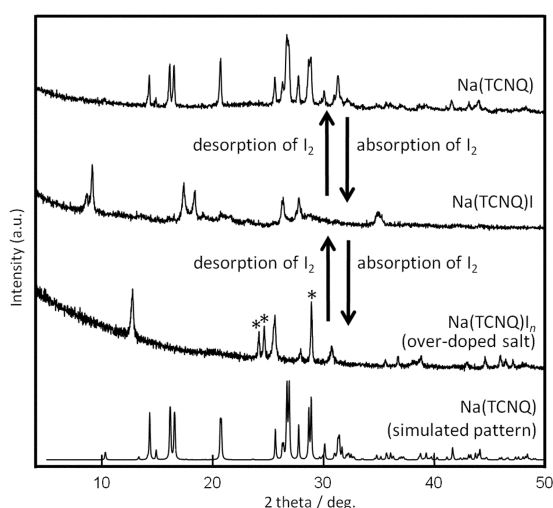


Fig. 2. Changes of the XRD patterns of Na(TCNQ) caused by reversible iodine absorption. The asterisks indicate diffraction peaks of excess iodine.

Iodine absorption of M(TCNQ) from the gas and liquid phases

Iodine absorption of M(TCNQ) also occurred from the gas phase and from solutions of iodine, although much less efficiently than for the solid-state reaction. When the powder of Na(TCNQ) was allowed to stand in iodine vapor for three weeks at ambient temperature, the bluish-purple powder turned black and gave an XRD pattern corresponding to neither of that of Na(TCNQ) or Na(TCNQ)I (Fig. 3b). The product was an over-doped salt with an approximate composition of Na(TCNQ)I_n ($n \sim 6$, *vide infra*). The salt was unstable and excess iodine was released to give M(TCNQ)I by standing in air at room temperature for two weeks or washing with hexane, which was confirmed by XRD measurements (Fig. 3c). When the powder of Na(TCNQ)I was again exposed to iodine vapor, the over-doped salt was recovered (Fig. 3b). Similarly, purple needle-like crystals of K(TCNQ) reacted with iodine vapor to give black fine powder of an over-doped salt (Fig. S2, supporting information) with an approximate composition of K(TCNQ)I_n ($n \sim 6$). Iodine absorption of M(TCNQ) (M = K, Na) also occurred from a solution of iodine. When M(TCNQ) powder, which is insoluble in hexane, was dispersed in a hexane solution of iodine and stirred for 48 h it gave the over-doped salt.

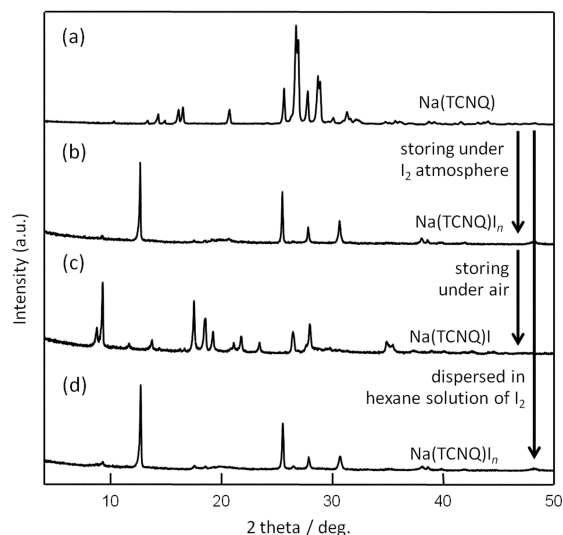


Fig. 3. Powder XRD patterns of (a) Na(TCNQ) prepared by a solution reaction, (b) Na(TCNQ)I_n ($n \sim 6$) obtained by placing Na(TCNQ) in an iodine atmosphere for three weeks, (c) Na(TCNQ)I obtained by standing the over-doped salt in air for two weeks, and (d) Na(TCNQ)I_n ($n \sim 6$) obtained by stirring a dispersion of Na(TCNQ) in a hexane solution of iodine for two days.

Raman spectra of the ternary salts

The valence state of the ternary salts was investigated by Raman spectroscopy. The result suggests that the valence state of M(TCNQ)I is $M^+(\text{TCNQ}^{-2/3})(\text{I}_3^-)_{1/3}$, which is analogous with the ternary salts with ammonium cations such as $(\text{NHMe}_3^+)(\text{TCNQ}^{-2/3})(\text{I}_3^-)_{1/3}$ [10]. It is known that the Raman C=C stretching band of neutral TCNQ appears at about 1454 cm^{-1} , whereas that for the TCNQ^{-1} anion is about 1395 cm^{-1} [18]. In the spectrum of Na(TCNQ)I at 150 K (Fig. 4a), the C=C stretching band was observed at 1406 cm^{-1} , suggesting the presence of $\text{TCNQ}^{-0.7-0.8}$. In addition, the progressive bands of the triiodide anion [10e] were observed at 113 cm^{-1} (s), 223 cm^{-1} (m), and 333 cm^{-1} (w). This is in agreement with the anticipated valence state, although there could be a slight deviation. After desorption of iodine by

annealing, the C=C stretching band was observed at 1391 cm^{-1} , supporting the formation of $\text{Na}^+\text{TCNQ}^{-1}$ (Fig. 4b). The IR spectra of the ternary salts showed an intense broad absorption band extending over the whole IR range, which suggests electrical conductivity of the salts. Because of this band, the characteristic $\text{C}\equiv\text{N}$ stretching band of TCNQ was not observed. After annealing, the broad band disappeared and the stretching bands of TCNQ^- in $\text{M}(\text{TCNQ})$ are observed (Fig. S3, supporting information).

The Raman spectrum of the over-doped Na salt showed C=C stretching bands at 1391 cm^{-1} and 1406 cm^{-1} (Fig. 4c), indicating the coexistence of TCNQ^{-1} and $\text{TCNQ}^{-0.8}$. This result indicates that the average charge distribution in the over-doped salt is $\text{M}^+(\text{TCNQ})^{-0.9}(\text{I}_n)^{-0.1}$. Hence, the negative charge on TCNQ is larger than that in $\text{Na}(\text{TCNQ})\text{I}$. Although the crystal structure is unknown, it is likely that the over-doped salt includes polyiodide species I_n^- ($n > 3$), causing a decrease of the average negative charge density per iodine atom to balance the charge. Several extremely iodine-rich salts that include multiple iodide species have been reported, such as a ferrocenium salt $[\text{Fe}(\text{C}_5\text{H}_5)]_3\text{I}_{29}$ [19]. It is likely that the present over-doped TCNQ salts contain similar polyiodide species.

The UV-vis-NIR spectrum of $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$ showed absorption bands at 366 nm and 573 nm, which can be attributed to the absorption of the TCNQ anion radical [20] (Fig. S4, supporting information). However, in the Raman spectrum the C=C stretching band was observed at 1455 cm^{-1} , which corresponds to neutral TCNQ. It is likely that $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$ contains a TCNQ trimer, in which TCNQ^- is sandwiched between two neutral molecules of TCNQ. In this case, only the Raman bands of the neutral TCNQ can be seen, because those of the central anion are symmetry forbidden. TCNQ trimers are often seen in the salts of TCNQ [21], and a similar phenomenon in the Raman spectrum has been reported for a salt containing F_1TCNQ trimers [22]. After iodine desorption by annealing, the C=C stretching bands were observed at 1389 cm^{-1} and 1442 cm^{-1} . These correspond to the C=C stretching

bands of TCNQ anion and neutral TCNQ, which is consistent with the formation of $\text{Rb}_2(\text{TCNQ})_3$ [15]. No stretching bands characteristic of neutral I_2 ($\sim 200 \text{ cm}^{-1}$) [23] were observed in all of these iodine-containing salts.

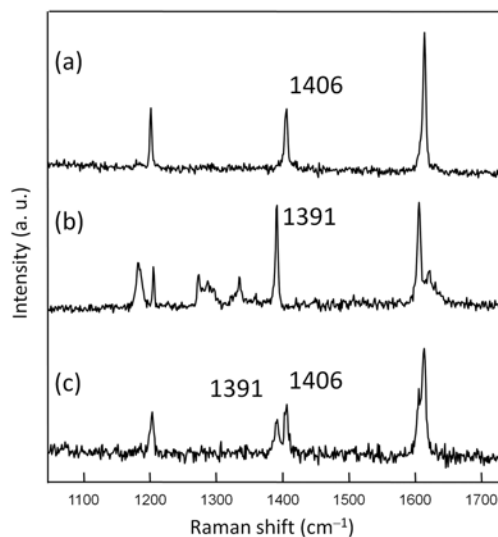


Fig. 4. Raman spectra of (a) $\text{Na}(\text{TCNQ})$, (b) $\text{Na}(\text{TCNQ})\text{I}$ obtained after iodine desorption, and (c) the over-doped Na salts. All spectra were recorded at 150 K.

TG analysis of the ternary salts

The thermal desorption of iodine from the ternary salts was investigated by TG analysis. Figure 5 shows the TG traces for $\text{M}(\text{TCNQ})\text{I}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$. $\text{M}(\text{TCNQ})\text{I}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) showed weight loss between $60 \text{ }^\circ\text{C}$ and $120 \text{ }^\circ\text{C}$, while for $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$ the weight loss occurred at temperatures about $20 \text{ }^\circ\text{C}$ higher. The weight loss ratios were 41%, 35%, 35%, and 26% for the salts with $\text{M} = \text{Li}, \text{Na}, \text{K}$, and Rb , respectively. These ratios are in good agreement with the values calculated from the compositions of 37%, 36%, 34%, and 24%. The over-doped Na and K salts showed higher weight loss ratios of 67–77%, from which the compositions of $\text{M}(\text{TCNQ})\text{I}_n$ ($n \sim 6$) can be estimated. Accurate determination of the iodine content was not possible because these salts easily lost iodine.

In contrast to the present ternary salts, $(\text{NHMe}_3)(\text{TCNQ})\text{I}$ is more thermally stable and shows no iodine desorption, with no weight loss up to about 400 K and only decomposition of the salt above 400 K [10e].

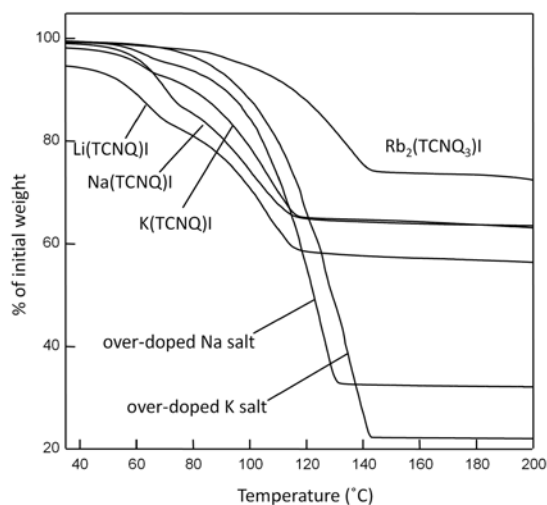


Fig. 5. TG traces of $\text{M}(\text{TCNQ})\text{I}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$), $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$, and the over-doped salts ($\text{M} = \text{Na}, \text{K}$).

Changes in electronic properties

The temperature dependence of the electrical resistivities of $\text{M}(\text{TCNQ})\text{I}$ ($\text{M} = \text{Na}, \text{K}$) were measured for compacted pellets and are shown in Fig. 6a. These salts have conductivities of the order $10^{-1} \text{ S cm}^{-1}$ at room temperature, indicating that they have metallic conduction properties, which is supported by the appearance of broad IR absorption bands. $\text{M}(\text{TCNQ})$ salts are insulators with very low conductivities ($\sim 10^{-5} \text{ S cm}^{-1}$) [9], hence iodine absorption greatly increases the conductivity. The resistivities of the ternary salts rapidly increase below about 100 K, where they become insulators. This behavior resembles that of the iodine-containing ternary salts of TCNQ with ammonium cations, which exhibit metal-insulator transitions at low temperatures [10c–f]. The increase of resistivities is more gradual in the present salts, probably because the samples were in the form of compacted

pellets.

The temperature dependence of the magnetic susceptibilities of M(TCNQ)I (M = Na, K) is shown in Figure 6b. These salts show paramagnetic behavior with a susceptibility of 10^{-4} emu mol⁻¹ at room temperature, which is a typical value for Pauli paramagnetism of synthetic metals [24]. This is in contrast to M(TCNQ), which are essentially diamagnetic below room temperature [9]. The Curie fractions of M(TCNQ)I (M = Li, Na, K) are estimated to be 1.1%, 1.1%, and 0.74%, respectively. Defects of the solid-state preparations may be responsible for the large Curie fractions. In the salts with M = Na and K, slight decreases of the magnetic moments are observed at around 100 K. This behavior likely corresponds to a metal-insulator transition, as suggested by the decrease of electrical conductivity. Similar magnetic changes associated with metal-insulator transitions have been observed in the ternary salts with ammonium cations [10c–f]. The over-doped salts showed paramagnetic properties with susceptibilities of 3×10^{-4} emu mol⁻¹ (M = Na) and 1.6×10^{-4} emu mol⁻¹ (M = K) at room temperature (Fig. S5, supporting information).

Rb₂(TCNQ)₃I₂ showed paramagnetic behavior with a χT value of 0.129 emu mol⁻¹ K at 297 K (Fig. S6, supporting information). The magnetic moment is smaller than that of the localized spins, which slightly decreases at around 150 K. The electrical conductivity of the compaction pellets of this salt was 5×10^{-3} S cm⁻¹, suggesting semiconducting behavior.

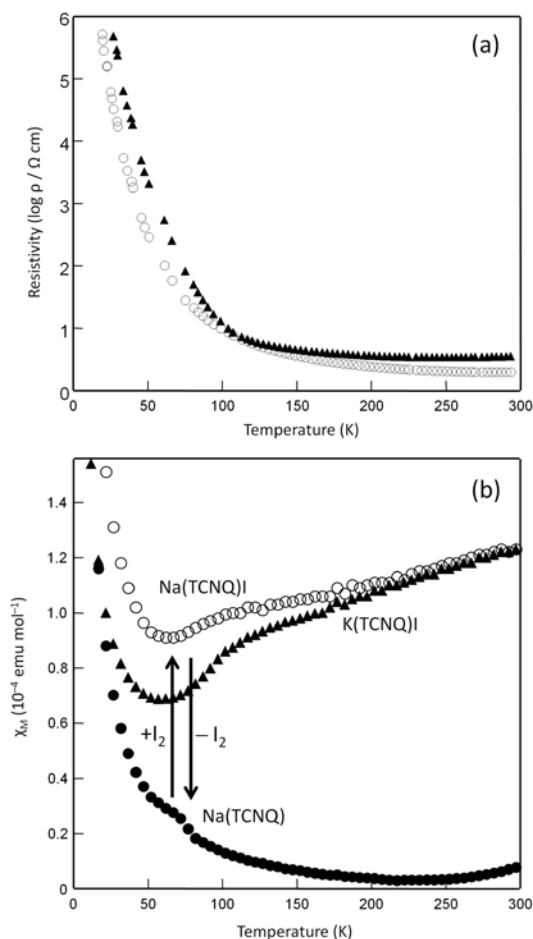


Fig. 6. (a) Temperature dependence of the electrical resistivities of compacted pellets of Na(TCNQ)I (○) and K(TCNQ)I (▲). (b) Temperature dependence of the magnetic susceptibilities of Na(TCNQ)I (○), K(TCNQ)I (▲), and Na(TCNQ) (●).

Conclusions

Despite being nonporous, alkali-TCNQ salts underwent reversible iodine absorption to give iodine-containing ternary salts: $M(\text{TCNQ}) + \text{I}_2 \rightarrow M(\text{TCNQ})\text{I}$ ($M = \text{Li}, \text{Na}, \text{K}$) and $\text{Rb}_2(\text{TCNQ})_3 + \text{I}_2 \rightarrow \text{M}_2(\text{TCNQ})_3\text{I}_2$. Alkali-TCNQ salts reacted with solid, vapor, and solutions of iodine. Excessive iodine absorption occurred to give $M(\text{TCNQ})\text{I}_n$ ($n \sim 6$, $M = \text{Na}$ and K), which gradually released iodine to give $M(\text{TCNQ})\text{I}$. The ternary salts were electrically conductive and paramagnetic, whereas $M(\text{TCNQ})$ salts were diamagnetic insulators. The ternary salts were also prepared by the reaction of TCNQ and alkali metal

iodides by solid-state reactions: $\text{TCNQ} + \text{MI} \rightarrow \text{M}(\text{TCNQ})\text{I}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and $3\text{TCNQ} + 2\text{MI} \rightarrow \text{M}_2(\text{TCNQ})_3\text{I}_2$ ($\text{M} = \text{Rb}, \text{Cs}$). Although $\text{M}(\text{TCNQ})$ salts are typical CT salts, their iodine absorption properties were unknown, probably because solution reactions only give the $\text{M}(\text{TCNQ})$ salts. In iodine absorption by $\text{M}(\text{TCNQ})$ salts, the variable valence state of TCNQ and the matching of its redox potential with that of the iodide play an essential role. Exploration of absorption-desorption phenomena in CT complexes is a promising approach toward novel functionalities of solids.

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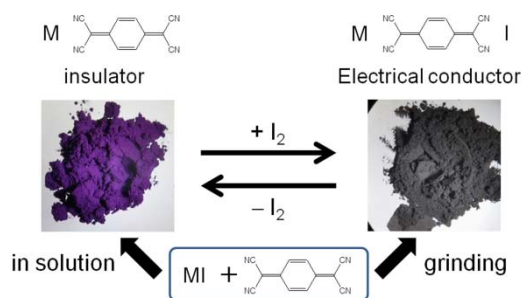
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Table of contents entry



Alkali-TCNQ salts reversibly absorb iodine to form ternary salts $M(TCNQ)I$ and $M(TCNQ)I_n$ ($n \sim 6$).

Supporting Information

Reversible iodine adsorption by alkali-TCNQ salts with associated changes in physical properties

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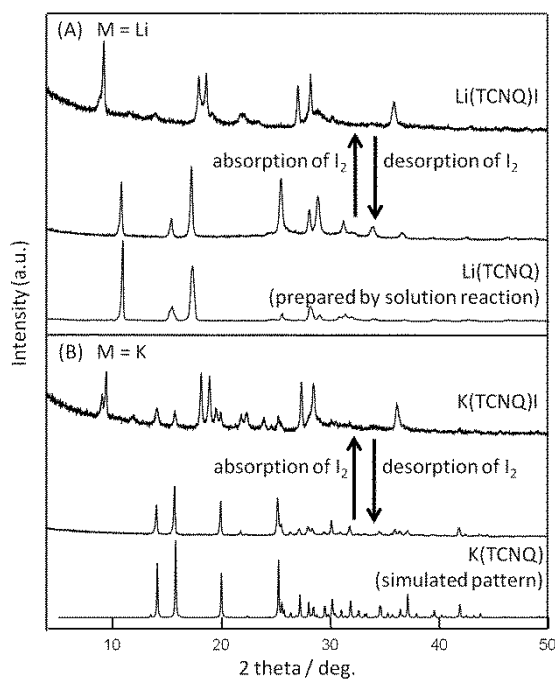


Fig. S1. Changes of the powder XRD patterns of M(TCNQ) caused by reversible iodine adsorption for the salts: (A) Li and (B) K.

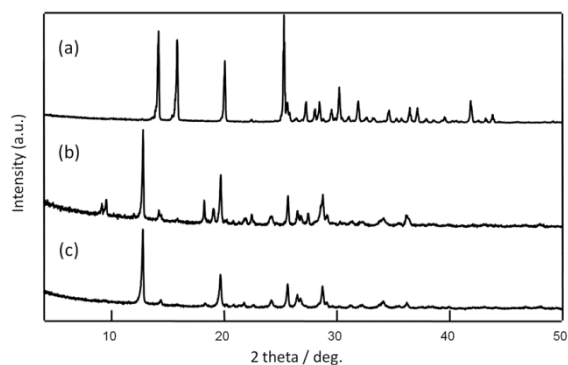


Fig. S2. Powder XRD patterns of (a) K(TCNQ) prepared by solution reactions, (b) an over-doped salt obtained by storing K(TCNQ) in an iodine atmosphere for one month, which contains a small portion of K(TCNQ)I, and (c) the over-doped salt obtained by stirring a dispersion of K(TCNQ) in a hexane solution of iodine for two days.

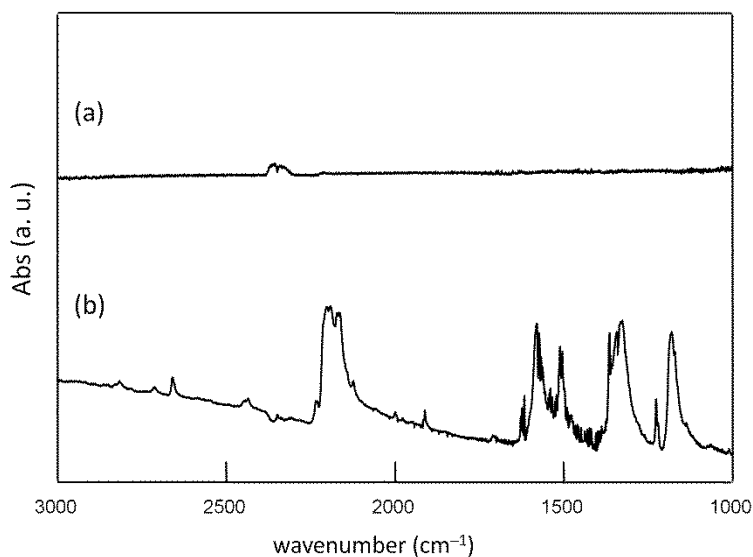


Fig. S3. IR spectra of (a) Na(TCNQ)I prepared by solid-state reactions and (b) Na(TCNQ) obtained by annealing Na(TCNQ)I.

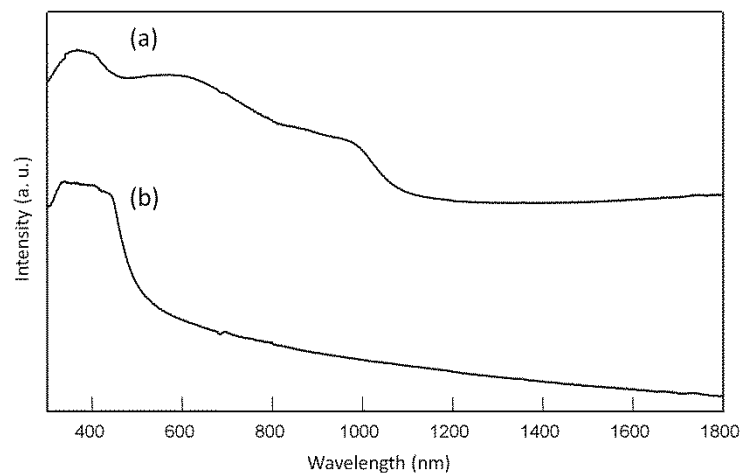


Fig. S4. Solid-state UV-vis-NIR absorption spectra of (a) $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$ prepared by solid-state reaction and (b) TCNQ.

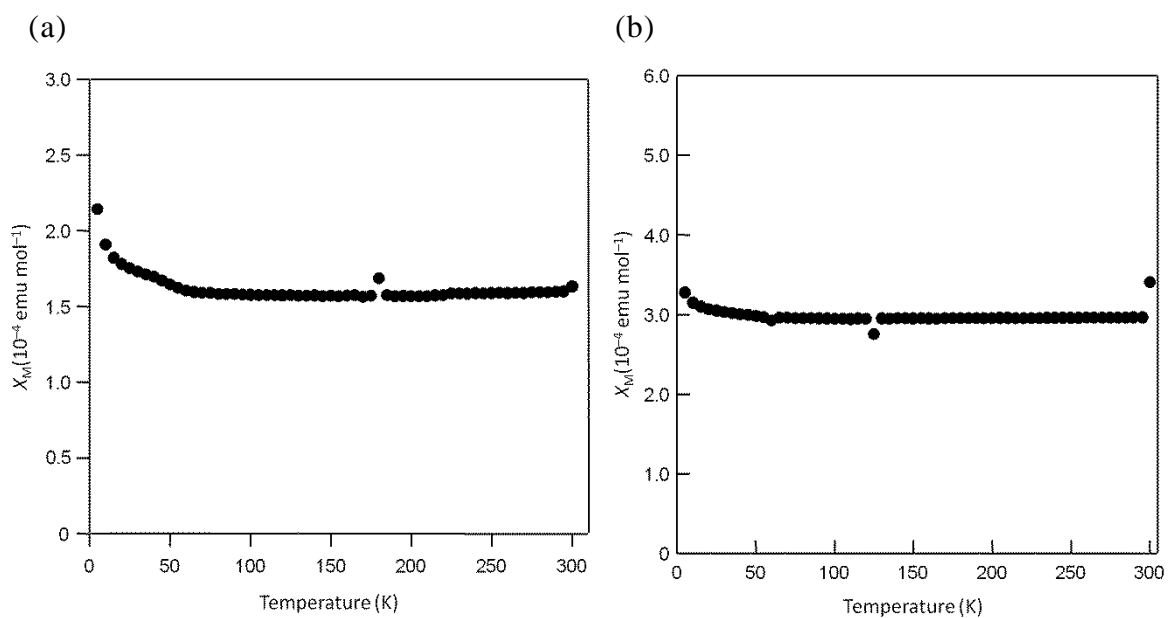


Fig. S5. Temperature dependence of the magnetic susceptibilities of (a) $\text{Na}(\text{TCNQ})\text{I}_{6.0}$ and (b) $\text{K}(\text{TCNQ})\text{I}_{5.8}$ prepared by liquid phase reactions.

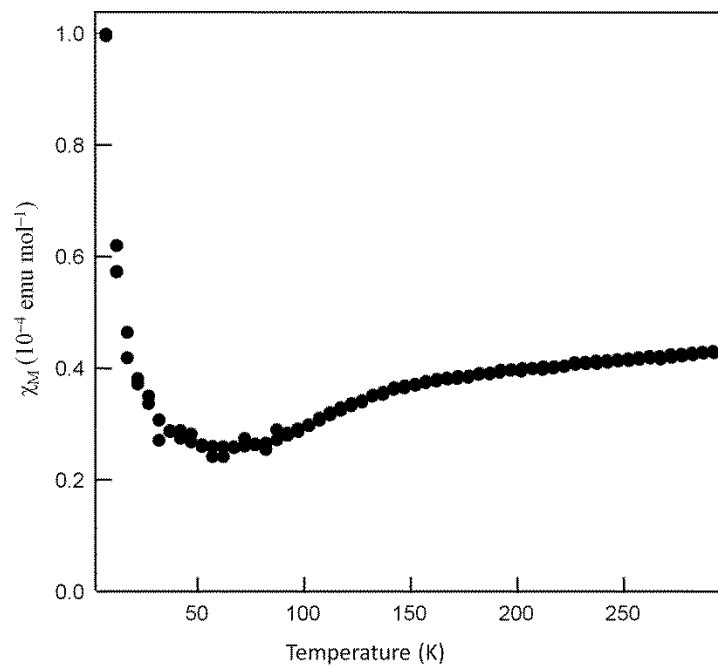


Fig. S6. Temperature dependence of the magnetic susceptibility of $\text{Rb}_2(\text{TCNQ})_3\text{I}_2$ prepared by solid-state reaction.