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Reversible iodine absorption of nonporous coordination polymer Cu(TCNQ)[†]

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Polycrystalline powders of Cu(TCNQ) (TCNQ = 7,7′,8,8′-tetracyanoquinodimethane) absorb iodine to form Cu(TCNQ)I_4 upon solid grinding with iodine or immersion in a hexane solution of iodine. Of the two polymorphs of Cu(TCNQ), phase II Cu(TCNQ) exhibits a much slower iodine-absorption rate than that of phase I Cu(TCNQ) in the liquid-phase reaction, whereas the solid grinding reaction results in efficient absorption for both phases. The valence state of the iodine-containing salt is $[Cu^+I^-(TCNQ^0)](I_2)_{1.5}$, where the copper ion is coordinated with an iodide anion and neutral TCNQ. The salt is a semiconductor ($\sigma_{RT} = 3 \times 10^{-3}$ S cm^{-1}, compaction pellet) with an electrical conductivity one order lower than that of Cu(TCNQ). The salt releases iodine by annealing to regenerate the original phases of Cu(TCNQ) via an intermediate Cu(TCNQ)I state. A solid-state reaction of TCNQ, CuI, and iodine also produces the iodine-containing salt. The iodine absorption–desorption mechanism of Cu(TCNQ) differs from that of alkali-TCNQ salts that we reported previously.

Introduction

Over the last few decades, reversible absorption–desorption of small molecules by coordination polymers and caged compounds has attracted considerable attention.[1] Several porous coordination polymers absorb iodine.[2] Compounds that exhibit reversible iodine-absorption properties are useful for iodine storage. Organic donor compounds and polymers also absorb iodine;[3] this reaction is often used to increase their electrical conductivity. As part of our investigations into solid-state reactions,[4] we reported that powders of alkali-TCNQ salts [M(TCNQ), M = Na, K] reversibly absorb iodine to form M(TCNQ)I, even though they are nonporous materials.[5] Iodine absorption by such simple charge-transfer salts is uncommon and interesting from the perspective of controlling their electronic properties. Their simple composition and easy preparation may be advantageous for practical applications.

In this paper, we report the iodine-absorption properties of Cu(TCNQ) (Fig. 1). Cu(TCNQ) is a nonporous coordination polymer composed of Cu^I and a TCNQ anion. It is a semiconductor, and devices based on its electronic characteristics have been investigated;[6] hence, the ability to control its physical properties is useful. Cu(TCNQ) has two polymorphs: Phase I and phase II. The latter is thermodynamically more stable.[7] In the current study, the iodine-absorption properties of the two phases are investigated, and the solid-state reaction and liquid-phase reaction are compared. The mechanism of iodine absorption–desorption is discussed in comparison with that of alkali-TCNQ compounds.

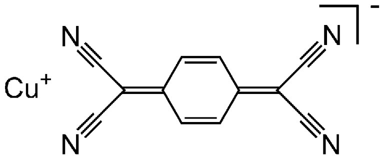

Fig. 1 Structural formula of Cu(TCNQ).

Results and Discussion

Iodine absorption of Cu(TCNQ) by a solid-state reaction

The iodine absorption-desorption properties of Cu(TCNQ) (Phase I and Phase II) found in the present study are summarized in Fig. 2. Solid-state grinding of a dark-blue powder of Cu(TCNQ) and I_2 in a molar ratio of 1:2 produced a black powder of Cu(TCNQ)I_4 within 30 min. The solid-state reaction was efficient for both phases I and II. The use of excess iodine left unreacted iodine in the resultant powder. The iodine-containing salts obtained from the two polymorphs exhibited almost the same amorphous X-ray diffraction (XRD) patterns with several weak peaks (phase I: Fig. 3a, phase II: Fig. 3b). However, their IR spectra were slightly different, indicating the differences in their local structures.

Heating the iodine-containing salts generated from phase I and phase II Cu(TCNQ) at 200 °C for 1.5 h under vacuum led to the desorption of iodine to regenerate the corresponding phase of Cu(TCNQ), as seen in the XRD patterns (Fig. 3). This was also confirmed by the recovery of the IR spectrum of each phase. The recovery of the original phases is ascribed to differences in the local structures of Cu(TCNQ)I_4 derived from each polymorph. However, the weaker XRD peak intensities suggest that the product also contain amorphous Cu(TCNQ). In the XRD patterns, peaks corresponding to CuI were also observed. The amount of CuI in the sample from phase I was about 3%, as determined by X-ray fluorescence analysis. Repeating the absorption–desorption procedure resulted in a slight increase in the CuI peak intensities and decrease of the crystallinity of the regenerated Cu(TCNQ) (Fig. S1). Interestingly, phase II Cu(TCNQ) was gradually converted to phase I Cu(TCNQ) by repeating the procedure. Conversion from phase I to phase II occurs in solution,[7] whereas the solid-state reaction caused the reverse conversion.

Figure 4 shows the TG traces of Cu(TCNQ)I_4 prepared from phase I Cu(TCNQ). The trace exhibits a two-step weight loss; the losses in the first step (60–120 °C; 49.4%) and second step (120–230 °C; 15.3%) correspond to the desorption of three and one iodine atoms, respectively. This result indicates that Cu(TCNQ)I is a stable intermediate state (Fig. 2). The TG trace of Cu(TCNQ)I_4 prepared from phase II Cu(TCNQ) exhibited the same total weight loss (65.1%; Fig. S2, ESI†), but with a smaller weight loss in the second step, which is likely due to the microscopic inhomogeneity of the product. Desorption of iodine also occurred upon immersion of Cu(TCNQ)I_4 from Phase I and Phase II Cu(TCNQ) in hexane, producing Cu(TCNQ)I in 40 days.

The iodine-absorption process was investigated by stepwise addition of iodine with grinding. The peaks of Cu(TCNQ) disappeared in the XRD patterns of Cu(TCNQ)I_n (n = 1–2) (phase I: Fig. 5, phase II: Fig. S3, ESI†). The TG curve of Cu(TCNQ)I_2 prepared from phase I Cu(TCNQ) displays a clear two-step iodine desorption via a Cu(TCNQ)I intermediate state (Fig. S4a, ESI†) and indicates the formation of [CuI(TCNQ)]$(I_2)_{0.5}$. In contrast, the TG curve of Cu(TCNQ)I_2 prepared from phase II Cu(TCNQ) displays a continuous loss of iodine, which indicates that the product is inhomogeneous (Fig. S4b, ESI†). This is probably because phase II Cu(TCNQ) is less reactive because it is more thermodynamically stable than phase I.

In Figs. 5 and S3, it is noteworthy that peaks corresponding to CuI were very evident in the XRD patterns of Cu(TCNQ)$_n$ (n = 1 and 2) and were barely evident in the XRD pattern of the sample with n = 4. We found that grinding of CuI, TCNQ, and I_2 produces Cu(TCNQ)I_4. This reaction is probably responsible for the disappearance of CuI during the absorption process and requires iodine as no reaction occurred by grinding only CuI and TCNQ. This contrasts with the results of the reaction of alkali iodides, which produces M(TCNQ)I by grinding with TCNQ.[5] Annealing of Cu(TCNQ)I_4 obtained by the grinding reaction produced Cu(TCNQ) with the XRD pattern of phase II.

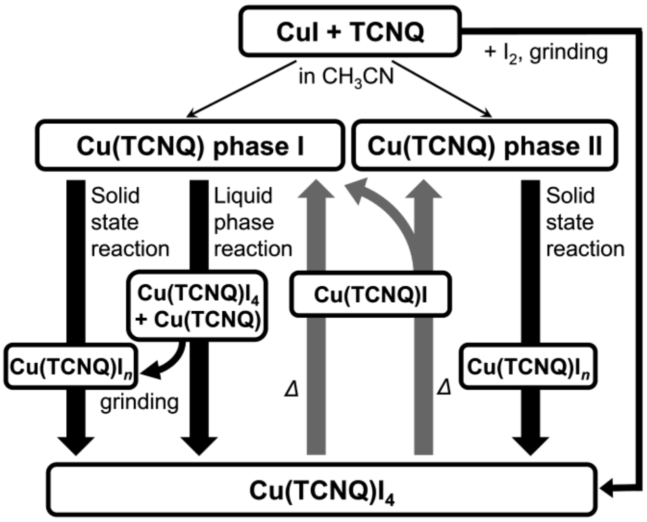

Fig. 2 General reaction scheme.

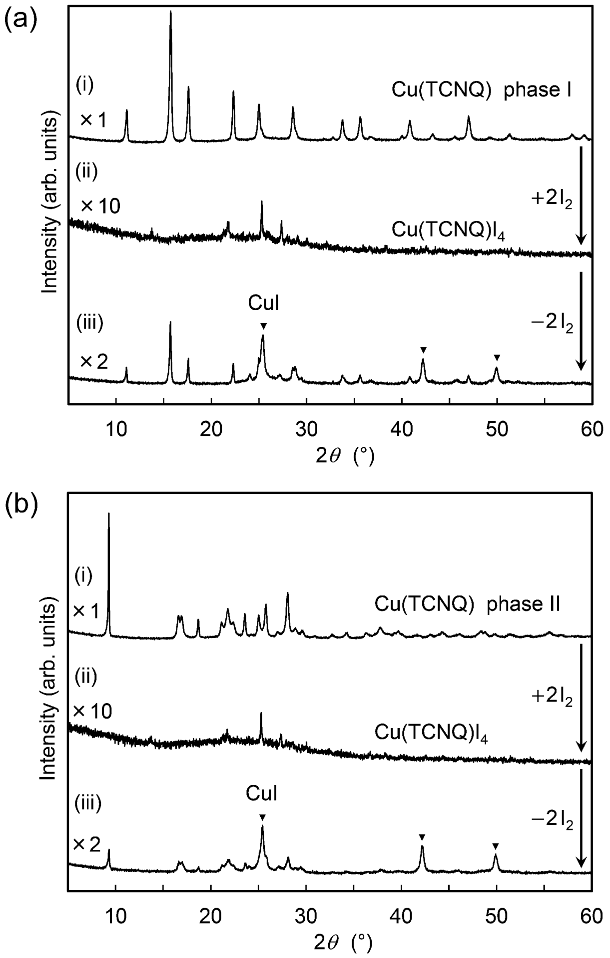

Fig. 3 Powder X-ray diffraction patterns of (a) phase I Cu(TCNQ) and (b) phase II Cu(TCNQ) (i) before iodine absorption, (ii) after iodine absorption by a solid-state reaction, and (iii) after

desorption of iodine by annealing. Triangles indicate the peaks for CuI.

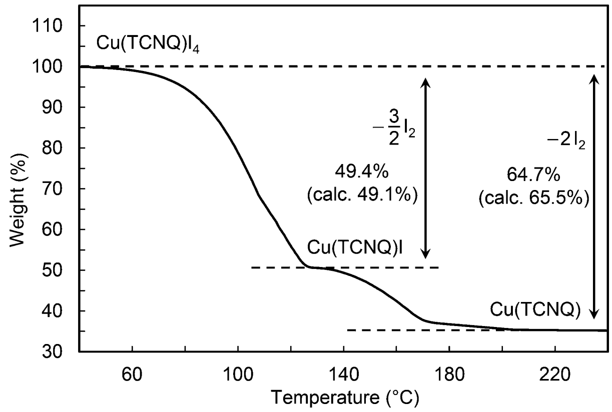

Fig. 4 Thermogravimetric traces of Cu(TCNQ)I_4 prepared by solid-state reactions of phase I Cu(TCNQ).

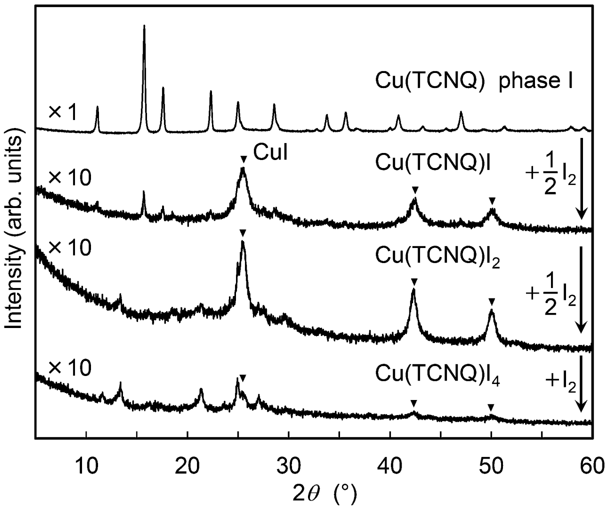

Fig. 5 Powder X-ray diffraction patterns of Cu(TCNQ)I_n (n = 1, 2, and 4) obtained by stepwise solid-state reactions of phase I Cu(TCNQ). Triangles indicate peaks for CuI.

Iodine absorption of Cu(TCNQ) by a liquid-phase reaction

Immersion of a polycrystalline powder of phase I Cu(TCNQ) in a hexane solution of iodine produced a black powder of Cu(TCNQ)I_4 within two weeks. In contrast, the iodine-absorption rate of phase II was much slower, reaching only $n \approx 0.7$ after two months; this is ascribed to the higher thermodynamic stability of phase II than phase I. The efficiency of the solid-state reaction for both phases, as described above, is ascribed to the mechanochemical effect.[8]

The powder XRD patterns of phase I Cu(TCNQ) before and after iodine absorption are shown in Fig. 6. The peaks of phase I Cu(TCNQ) disappeared after absorption of iodine and new weak peaks appeared. The product exhibited higher crystallinity than the solid-state reaction product. Heating the iodine-containing salt under vacuum led to desorption of the iodine to regenerate phase I Cu(TCNQ). The weaker XRD peaks suggest that the solid also contains amorphous Cu(TCNQ). In the XRD pattern, peaks corresponding to CuI were also observed after desorption of iodine. The TG curves of $Cu(TCNQ)I_4$ were very similar to those of solid-state reaction products, exhibiting two-step weight losses (total weight loss 65.9 %; Fig. S5, ESI†).

We investigated the iodine-absorption process and found that $Cu(TCNQ)I_4$ was directly produced by the liquid phase reaction without a partially doped intermediate state (Fig. 2). For example, $Cu(TCNQ)I_n$ ($n = 2.1$), which was obtained from a short reaction period, comprises a 1:1 mixture of Cu(TCNQ) and $Cu(TCNQ)I_4$; Cu(TCNQ) was observed by XRD measurements and two-step weight loss of $Cu(TCNQ)I_4$ was observed by TG analysis (Fig. S6, ESI†). This result is in sharp contrast with the solid-state reaction, which produced a partially doped homogeneous product (Fig. 2), as described above. The phase separation in the liquid phase reaction probably occurs because the reaction proceeds from the surface and the formation of defects accelerates absorption. We further investigated the effect of grinding. Ball-milling of $Cu(TCNQ)I_n$ ($n = 2.1$) prepared by the liquid-phase reaction produced a homogeneous solid, i.e., $[CuI(TCNQ)](I_2)_{0.5}$, as confirmed by XRD and TG measurements (Fig. S6, ESI†). This result clearly indicates that grinding induces diffusion and the homogeneous reaction of iodine.

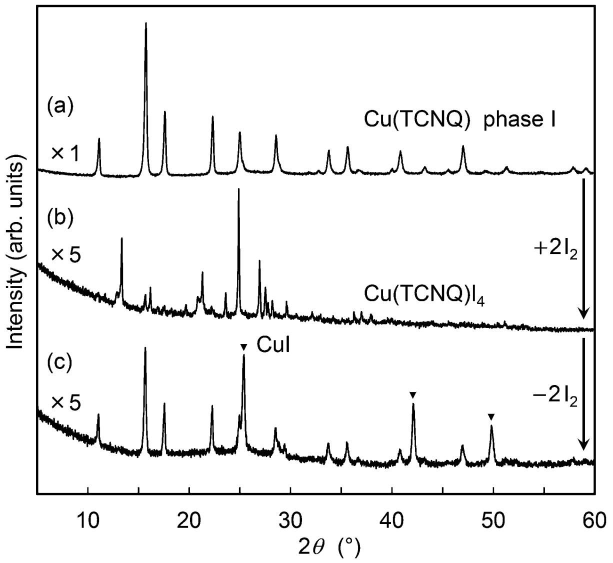

Fig. 6 Powder X-ray diffraction patterns of phase I Cu(TCNQ) and its products: (a) Before iodine absorption, (b) after absorption of iodine by the liquid-phase reaction (immersion in a hexane solution of iodine), and (c) after desorption of iodine by annealing. Triangles indicate peaks for CuI.

Electronic state of the iodine-containing salt

The valence state of Cu(TCNQ)I$_4$ obtained from the liquid-phase reaction was investigated by Raman spectroscopy. The C=C stretching bands of TCNQ in Cu(TCNQ)I$_4$ were observed at 1451 cm^{-1} (Fig. S7, ESI[†]), which indicates that TCNQ is neutral.[9] Hence the TCNQ^{-1} in Cu(TCNQ) is oxidized upon iodine absorption. The characteristic stretching band of I$_3^-$ was not observed;[10] hence, it is likely that the iodine exists as I$^-$ and/or I$_2$. The results of the Raman and TG measurements suggest that the valence state of Cu(TCNQ)I$_4$ is [Cu$^+$I$^-$(TCNQ^0)](I$_2$)$_{1.5}$. A plausible local structure around the copper ion is schematically shown in Fig. 7: Four neutral TCNQ molecules and one iodide anion coordinate to the copper ion, and this unit forms a network structure via Cu···NC– bonds; the remaining iodine molecules are probably located between the units. The Cu–I bonds likely form because Cu$^+$ and I$^-$ are both soft ions according to the HSAB theory. This structure accounts for the formation of Cu(TCNQ)I during the iodine desorption process. X-Ray photoelectron spectra measurements consistently revealed that Cu(TCNQ)I produced by iodine desorption contains Cu^+ and I^-; the main Cu $2p_{3/2}$ and I $3d_{5/2}$ peaks were observed at 932 and 619 eV, respectively.[7,11]

The valence change in the iodine absorption reaction ($[Cu^+(TCNQ)^-] + 0.5\ I_2 \rightarrow [Cu^+I^-(TCNQ^0)]$) is reasonable in terms of the redox potentials. Oxidation of TCNQ by iodine is possible due to the comparable redox potentials of $TCNQ/TCNQ^-$ (0.22 V,[12a] vs. SCE in CH_3CN) and I_2/I^- (0.22 V[12b]), and the product is further stabilized by the formation of the Cu–I bond. The redox potentials including those of the copper ions (Cu^+/Cu: –0.5 V, Cu^{2+}/Cu^+: 1.05 V[12c,d]) are consistent with the invariant copper valency. The triiodide anion is not formed due to the Cu–I bond formation despite the favorable redox potential (I_2/I_3^-: 0.62 V[12b]).

The proposed structure and valence state are reasonable considering that an analogous CuI complex containing a thiophene-fused DCNQI (3,7-dimethyl-*N*,*N′*-dicyanobenzo[1,2-*b*:4,5-*b′*]dithiophene-4,8-dionediimine, abbreviated as TP-DCNQI) has a valence state of $[Cu^+I^-(\text{TP-DCNQI})^0]$ and contains a Cu–I bond.[13] The electrical conductivity of a compaction pellet of $Cu(TCNQ)I_n$ (n = 3.7, obtained by the liquid phase reaction) was 3.1×10^{-3} S cm^{-1} at room temperature, which is one order lower than that of phase I Cu(TCNQ).[7] The decreased conductivity is consistent with the valence change of TCNQ from anionic to neutral. The conductivity seems to be rather high for a complex with neutral TCNQ, but may be reasonable considering that [CuI(TP-DCNQI)] containing neutral acceptors exhibits a conductivity of 7.6×10^{-3} S cm^{-1} (single crystal).[13] The temperature dependence of the conductivity revealed semiconducting behavior with an activation energy of 0.1 eV (Fig. S8, ESI†); this contrasts with the change in the electrical conductivity of alkali-TCNQ, which increases upon the absorption of iodine.[5] These results demonstrate that the affinity of I^- and Cu^+ is important for the iodine-absorption mechanism of the current salt, in contrast with that of alkali-TCNQ.[5]

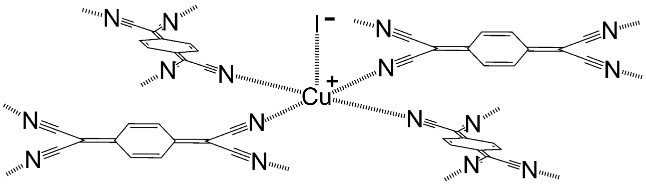

Fig. 7 Schematic illustration of a plausible local structure around the copper ion in Cu(TCNQ)I$_n$.

Conclusion

A nonporous coordination polymer, i.e., Cu(TCNQ), absorbs iodine through a solid-state grinding or liquid-phase reaction to produce Cu(TCNQ)I$_4$. Both phases efficiently produced the iodine-containing salt using the solid-state reaction, although the iodine-absorption rate of phase II Cu(TCNQ) was much slower via the liquid-phase reaction. During iodine absorption, the liquid-phase reaction produced mixtures of Cu(TCNQ) and Cu(TCNQ)I$_4$, whereas solid-state grinding produced homogeneous products. Annealing of the salt led to release of iodine to selectively regenerate the original phases of Cu(TCNQ), although the product contains amorphous components.

This study shows that Cu(TCNQ) reversibly absorbs iodine similarly to alkali-TCNQ, but via a different mechanism. The iodine-containing salts produced from alkali-TCNQ are crystalline solids represented as $[M^+(TCNQ^{-2/3})](I_3^-)^{1/3}$, whereas Cu(TCNQ)I$_4$ is represented as $[Cu^+I^-(TCNQ^0)](I_2)_{1.5}$, which contains Cu^+I^-, neutral TCNQ, and iodine that is likely located between the coordination networks. Reflecting the different valence states, the electrical conductivity of alkali-TCNQ increases after iodine absorption, while that of Cu(TCNQ) decreases. In contrast to the iodine absorption of alkali-TCNQ, the affinity of I^- and Cu^+ according to the HSAB theory plays an important role in the iodine absorption of Cu(TCNQ). The iodine absorption–desorption properties shown here can be also used to control the physical properties of Cu(TCNQ).

Acknowledgements

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Experimental

Phase I and phase II Cu(TCNQ) samples were prepared according to the methods described in literature.[7] The XRD data were recorded on a Rigaku SmartLab diffractometer using Cu Kα radiation. The FT-IR spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrometer using KBr plates. Raman spectra were obtained using a Renishaw inVia Reflex spectrometer at room temperature with a 488 nm laser as the excitation light. Thermogravimetric analyses were performed at a heating rate of 1 K min^{-1} under a nitrogen atmosphere using a Rigaku TG 8120 thermal analyzer. Elemental analyses were carried out on a Yanaco MT5 analyzer. The electrical conductivity of the compaction pellets was measured by a four-probe method with carbon paste electrodes using a HUSO HECS-994C multichannel resistivity meter. X-Ray photoelectron spectra were recorded on a PHI X-tool system (ULVAC-PHI) with an Al source. The amount of CuI in the product after iodine desorption was determined by X-ray fluorescence analysis using a Shimadzu EDX-720 energy dispersive X-ray fluorescence spectrometer.

Iodine absorption by solid-state grinding was performed using a Fritsch P-7 planetary ball mill. A mixture of Cu(TCNQ) and I_2 (~0.2 g) was subjected to ball-milling in a zirconia rotor with the aid of zirconia beads (750 rpm, 30–90 min). The solid-state reactions were carried out under solventless conditions, but the addition of a few drops of water was found to accelerate them. Desorption of iodine was carried out by annealing the iodine-containing salts at 200 °C for 1.5 h under vacuum. The liquid-phase reaction was performed by immersing a powder of Cu(TCNQ) (97 mg, 3.6×10^{-4}

mol) in a hexane solution (300 mL) of iodine (830 mg, 3.3×10^{-3} mol) for 1–2 weeks at 12 °C. The products were collected by filtration, washed with hexane, and vacuum dried for 10 min. Anal. Calcd for $C_{12}H_4N_4CuI_4$: C, 18.54; H, 0.52; N, 7.23; Found: C, 18.84; H, 1.17; N, 7.25. The reactions under air produced only heterogeneous mixtures containing hygroscopic materials; this is probably because of the reaction of TCNQ anion with oxygen.[14]

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Supporting Information

Reversible iodine absorption of nonporous coordination polymer Cu(TCNQ)

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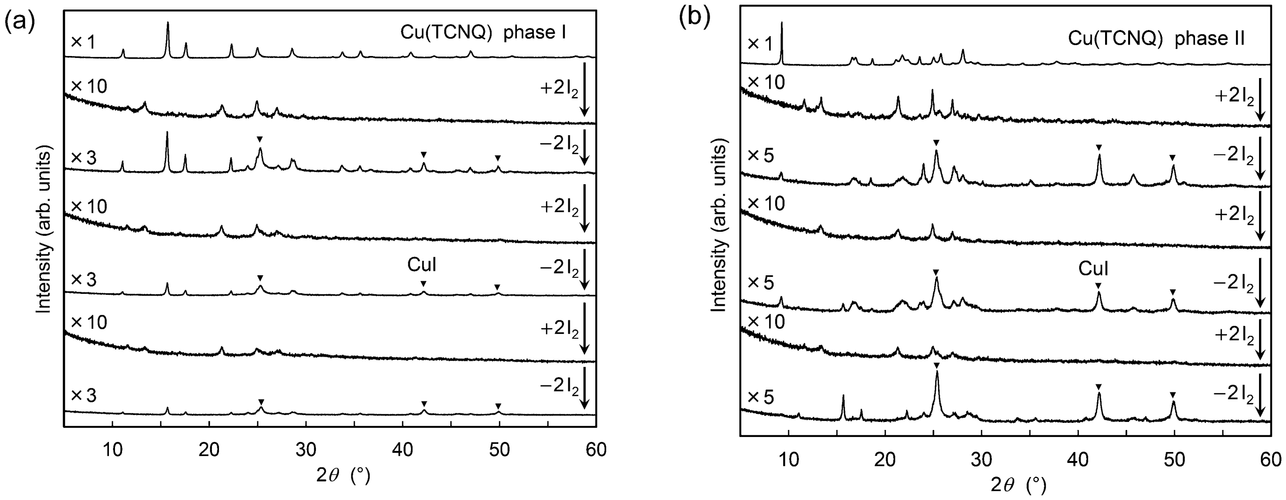

Fig. S1 Powder XRD patterns of (a) phase I and (b) phase II Cu(TCNQ) in the repeated absorption–desorption experiments. Triangles indicate peaks for CuI.

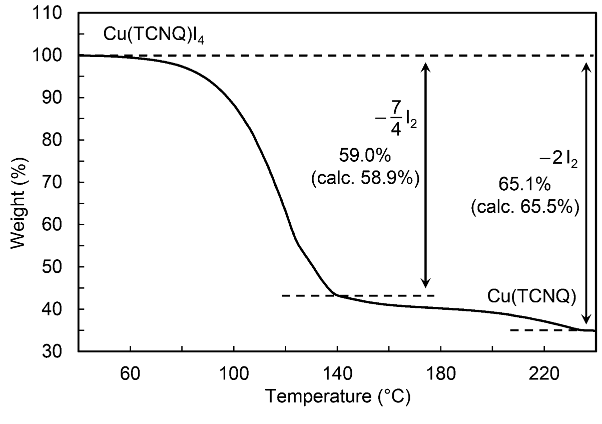

Fig. S2 Thermogravimetric traces of Cu(TCNQ)I$_4$ prepared by solid-state reactions of phase II Cu(TCNQ).

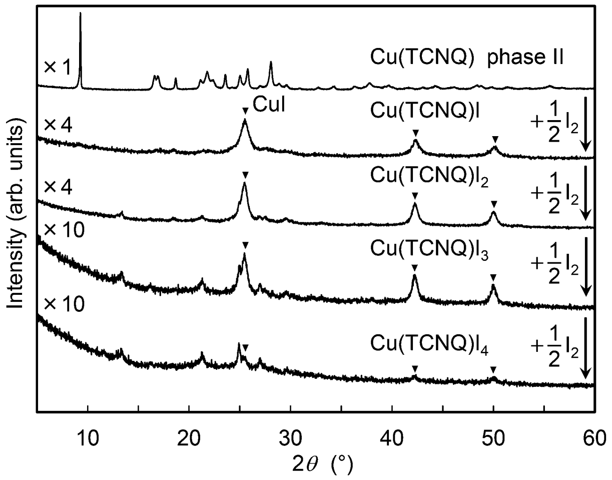

Fig. S3 Powder XRD patterns of Cu(TCNQ)I_n (n = 1, 2, 3, and 4) obtained from stepwise solid-state reactions of phase II Cu(TCNQ). Triangles indicate peaks for CuI.

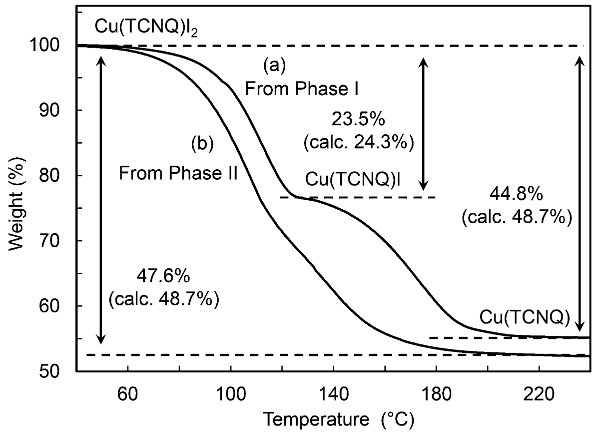

Fig. S4 Thermogravimetric traces of Cu(TCNQ)I_n (n = 2) formed by solid-state reactions of phase I Cu(TCNQ) and phase II Cu(TCNQ).

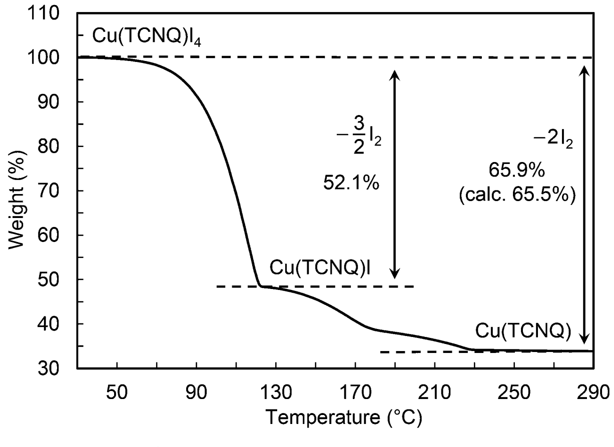

Fig. S5 Thermogravimetric trace of Cu(TCNQ)I_4 prepared by liquid-phase reaction of phase I Cu(TCNQ).

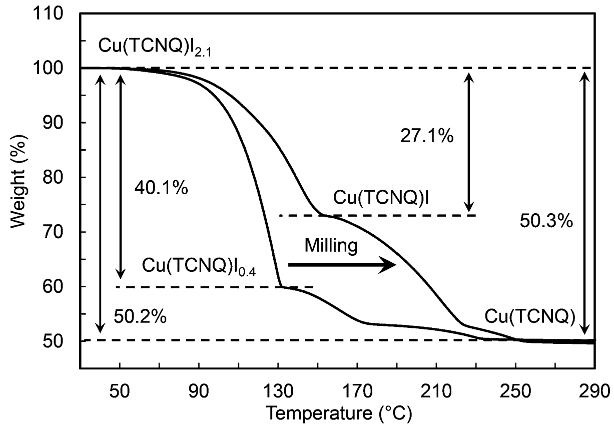

Fig. S6 Thermogravimetric trace of $\mathrm{Cu(TCNQ)I}_n$ ($n = 2.1$) obtained from liquid-phase reaction of phase I Cu(TCNQ). TG trace after grinding phase II Cu(TCNQ) sample ($n = 2.1$) is also shown.

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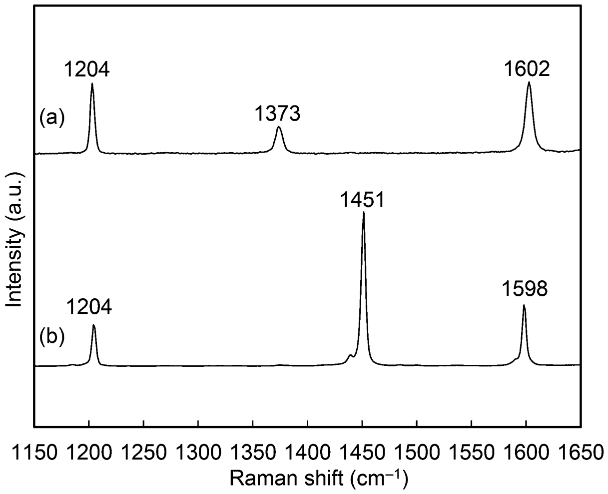

Fig. S7 Raman spectra of (a) phase I Cu(TCNQ) and (b) $\mathrm{Cu(TCNQ)I}_4$ prepared by liquid-phase reaction of phase I.

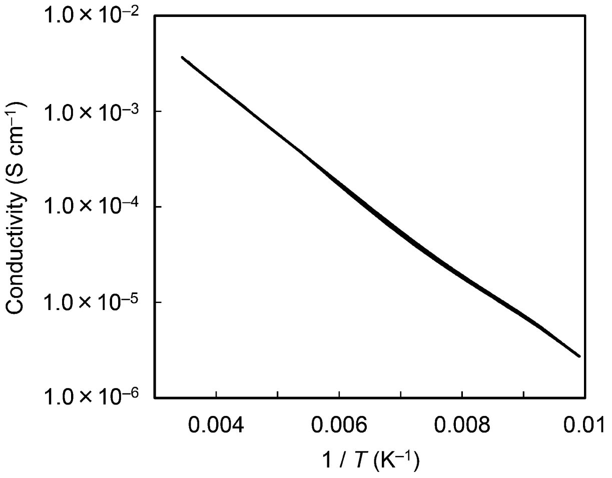

Fig. S8 Temperature dependence of electrical conductivity of compaction pellet of $\mathrm{Cu(TCNQ)I}_n$ ($n = 3.7$) prepared from phase I Cu(TCNQ) using liquid-phase reaction.