

ORIGINAL ARTICLE

Preparation of environmentally resistant conductive silica-based polymer hybrids containing tetrathiafulvalene–tetracyanoquinodimethane charge-transfer complexes

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We report the preparation of conductive glasses based on organic–inorganic hybrids that contain charge-transfer (CT) complexes of tetrathiafulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). Using poly(vinylpyrrolidone) as the organic component, the hybrid materials were prepared with various concentrations of CT complexes. From a series of evaluations, including light absorption and X-ray diffraction (XRD) measurements and microscopy observations, it was confirmed that CT complexes form in the materials and are well dispersed. The hybrids that were synthesized with relatively large loading amounts of CT complexes exhibited a conductivity level similar to that of a semiconductor ($\sim 10^{-1} \text{ S cm}^{-1}$). In addition, the conductivity of the synthesized hybrids was maintained during heating and changed negligibly after exposure to water.

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INTRODUCTION

Organic–inorganic polymer hybrids are mixtures that contain a polymer and an inorganic compound with a domain size at the nano or molecular scale.¹ By processing a polymer into a hybrid with silicate, a robust material can be obtained without loss of polymer functionalities.² Because of their transparency and enhanced stability, various types of thermally stable emissive hybrids can be obtained using optically functionalized polymers that have relatively low durabilities.³ In addition, by immobilizing unstable or transient structures within the matrices, unique characteristics can be observed in the hybrids that originate from these structures.⁴ Although the silica component generally functions as an insulator, there are several examples of silica-based conductive hybrids^{5–9} and composites.^{10–15} Stability can be significantly enhanced by hybrid formation, although a decrease in conductivity is often observed. Thus, the development of conductive hybrids with environmental resistance remains a challenge.

Tetrathiafulvalene (Scheme 1, TTF)-based polymer composites are a promising platform for developing advanced opto- and/or electronic materials.^{16–19} These materials can be prepared using a facile solution process, and have shown a similar level of conductivity ($< 10^{-2} \text{ S cm}^{-1}$) to that of TTF conductive films composed of mixed-valence TTF crystals.²⁰ Following the first report of TTF-containing conductive composites in 1981,²¹ detailed information about the characteristics of TTF species and the properties of TTF films have been reported.^{22–26} Several applications have recently been presented based on TTF-based polymer composites for practical uses,

such as transparent conductive materials and flexible conductors.²⁷ Regulation of the radical concentration in the film through photo-patterning and long-term storage of radical spins in the film have also been achieved, although conductivity was below the detection limit in these films.^{28,29} In addition, it has been demonstrated that conductivity can be tuned by modulating the morphologies,²⁷ additives,³⁰ substituents,³¹ moisture,³² preparation conditions³³ and matrix type.^{34,35} Finally, an improvement in conductivity compared with that of TTF crystals has been achieved through condensation of the TTF species at the film surface.³⁴ By conjugation to silica, the formation of highly ordered structures has been demonstrated.^{36–40} Despite the usability and versatility of TTF polymer composites, there is considerable room to increase the environmental resistance of TTF polymer composites. For example, as shown in our previous work, the conductivity of these composites decreases after heating at temperatures of $> 80^\circ \text{C}$ for several minutes.²⁸ The next challenge is to develop robust TTF-based conductive materials using a facile preparation method.

Herein, we present conductive glasses with environmental resistance based on organic–inorganic hybrids containing TTF and 7,7,8,8-tetracyanoquinodimethane (TCNQ) complexes. By using poly(vinylpyrrolidone) (PVP) as the polymer component, hybrid materials were prepared with various concentrations of CT complexes. Through a series of measurements, the formation of the CT complexes and their dispersion states were investigated. We initially observed that these hybrids exhibit conductivity at a level similar to that of a semiconductor ($\sim 10^{-1} \text{ S cm}^{-1}$). In addition, the change in

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conductivity was monitored during heating and during dipping into water. The synthesized hybrids exhibited high stability against environmental changes. To the best of our knowledge, this is the first study to present a facile strategy for synthesizing conductive glasses with environmental resistance for use in organic conductive materials.

EXPERIMENTAL PROCEDURE

General

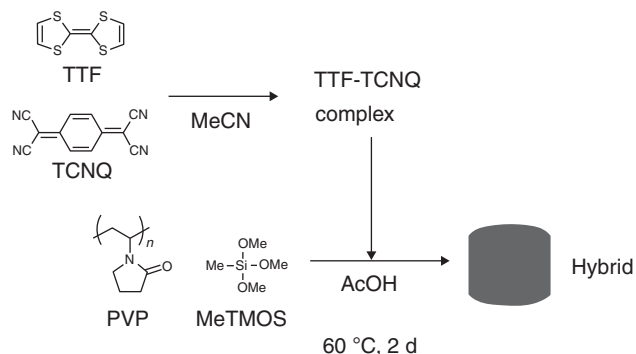
The electrical conductivity of the casting films was measured using the four-probe technique at 25 °C. Scanning electron microscopy images were acquired using a JEOL JSM-5600 (JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 15 kV. Ultraviolet-visible-near infrared absorption spectra were recorded using a SHIMADZU UV-3600 ultraviolet-visible-near infrared spectrophotometer and a JASCO V-570 spectrophotometer (JASCO Co., Tokyo, Japan). Powder X-ray diffraction (XRD) patterns were recorded on a SHIMADZU X-ray diffractometer-6000 (SHIMADZU Co., Ltd., Kyoto, Japan) using high-intensity Cu K α radiation from the 2 θ range of 2–90° at a scan rate of 0.02° s⁻¹. Powder samples for the XRD measurements were prepared by culling the materials. Thermogravimetric analysis was performed on an EXSTAR TG/DTA 6220, Seiko Instruments Inc., Chiba, Japan, with a heating rate of 10 °C per min up to 500 °C under a nitrogen atmosphere. Residual chloroform was removed by heating the samples in a vacuum oven at 100 °C for 1 h before thermogravimetric analysis measurements. TTF, TCNQ and acetic acid were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. PVP (M_w = 630 000) was purchased from Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. Methyltrimethoxysilane (MeTMOS) was purchased from Sigma-Aldrich, Inc., St Louis, MO, USA. These reagents were used without further purification.

Preparation of TTF–TCNQ complexes

To a solution of TTF (165 mg, 0.81 mmol) in acetonitrile (50 ml), TCNQ (165 mg, 0.81 mmol) in acetonitrile (250 ml) was added, and the mixture was stirred for 1 h at room temperature.⁴¹ The black precipitate was filtered and washed with acetonitrile. The product was directly used in the next step.

Preparation of PVP–silica hybrid films doped with various amounts of TTF–TCNQ complexes

Hybrid films doped with TTF–TCNQ complexes were prepared via the acid-catalyzed sol–gel reaction of MeTMOS in the presence of a 0.38 M CH₃COOH aqueous solution. PVP was dissolved in methanol (40 g l⁻¹), and CH₃COOH and MeTMOS were added. After stirring for 5 min, various amounts of TTF–TCNQ complexes were added to the reaction solution, and the sample was subsequently stirred at ambient temperature for 5 min. The reaction solution was poured into a polypropylene vessel and then heated in an oven at 60 °C for 2 days. Black hybrid films were prepared. The names used for the samples consist of the percentage weight of glass contributed by PVP (HYB)



Scheme 1 Chemical structures and the preparation of the hybrids used in this study

and the percentage weight of the material contributed by the TTF–TCNQ complexes (TT) (for example, HYB13TT16 is composed of 13 wt% of glass containing 16 wt% of the complexes).

Conductivity measurements

The surface conductivity was determined using the four-point probe method. To monitor the time courses of the conductivity changes, the samples were placed on a hot plate and the conductivity was recorded by altering the surface temperature. To evaluate the durability in water, the samples were dipped into deionized water. The conductivity was measured after drying under ambient conditions.

RESULTS AND DISCUSSION

The general procedure for preparing the hybrids is described here according to our previous paper.⁴ Charge-transfer (CT) complexes were isolated from the mixture of TTF and TCNQ in acetonitrile and used directly in the next step. Hybrid materials doped with the resultant TTF–TCNQ complexes were prepared via the acid-catalyzed sol–gel reaction of MeTMOS using a 0.38 M aqueous acetic acid solution. The feed ratios are listed in Table 1. PVP was dissolved in methanol (40 g l⁻¹), and a 0.38 M acetic acid solution and MeTMOS were added. After stirring for 5 min, various amounts of TTF–TCNQ complexes were added to the PVP solution. The solution was ultrasonicated for 5 min and subsequently stirred for 5 min. The reaction solution was poured into a polypropylene vessel and then heated in an oven at 60 °C for 2 days. Black self-supporting films were obtained (Figure 1). The feed ratios of TTF–TCNQ complexes, PVP and silica are shown in Table 1. When the amount of TTF–TCNQ complexes was increased, the film formability decreased, although all of the samples had measurable electronic properties. The environment responsiveness of the hybrids was evaluated using the hybrids containing 16 wt% TTF–TCNQ complexes.

Table 1 Preparation of TTF–TCNQ complexes containing hybrid films

	TTF–TCNQ complex (mg)	MeTMOS (ml)	PVP/MeOH (ml)	CH ₃ COOH _{aq} (ml)
HYB50TT00	—	0.12	1.42	0.053
HYB50TT01	1.0	0.12	1.42	0.053
HYB50TT08	9.1	0.12	1.42	0.053
HYB50TT16	18.3	0.12	1.42	0.053
HYB50TT24	27.3	0.12	1.42	0.053
HYB50TT32	36.5	0.12	1.42	0.053
HYB50TT40	54.8	0.12	1.42	0.053
HYB00TT16	18.3	—	2.84	0.106
HYB13TT16	18.3	0.03	2.47	0.092
HYB25TT16	18.3	0.06	2.13	0.080
HYB37TT16	18.3	0.09	1.79	0.067
HYB50TT16	18.3	0.12	1.42	0.053

Abbreviations: MeTMOS, methyltrimethoxysilane; PVP, poly(vinylpyrrolidone); TTF–TCNQ, tetrathiafulvalene–7,7,8,8-tetracyanoquinodimethane.

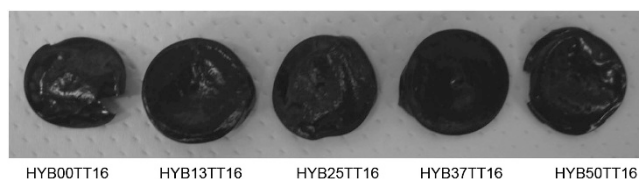


Figure 1 Appearance of the hybrids. A full color version of this figure is available at *Polymer Journal* online.

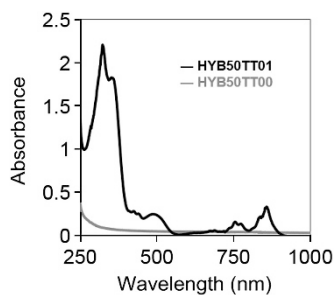


Figure 2 Ultraviolet-visible (UV-vis) spectra of hybrid films containing tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) complexes (HYB50TT01, black line) and not containing these complexes (HYB50TT00, gray line).

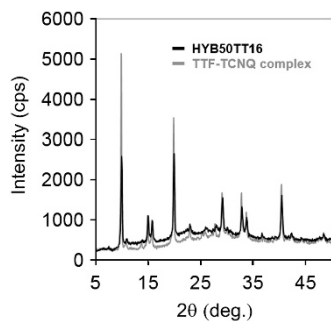


Figure 3 X-ray diffraction (XRD) patterns of tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) complexes (grey line) and of the hybrid films (black line).

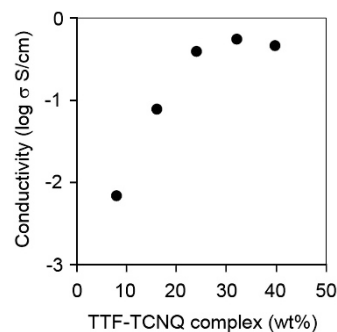


Figure 5 Conductivities of the hybrids containing various amounts of tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) complexes (wt%). The thicknesses of the films were 0.08–0.20 mm.

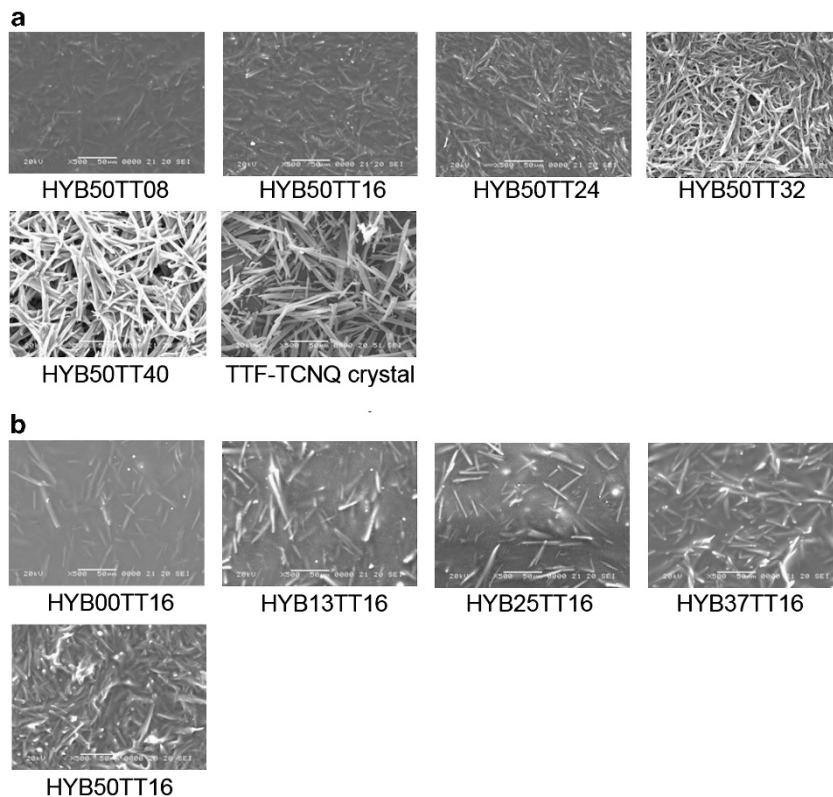


Figure 4 Scanning electron microscopy (SEM) images of the hybrid films (a) with various concentrations of tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) complexes and (b) with same concentration of the complexes and different ratios between organic and inorganic components. The scale bars represent 50 μm .

the hybrids containing TTF–TCNQ complexes. Sharp peaks were observed from the hybrids. In particular, almost identical peak patterns were obtained from both samples. These data also indicate that TTF–TCNQ complexes were maintained in the hybrids.

The surface morphology was investigated using scanning electron microscopy imaging (Figure 4). The formation of nanofiber structures was observed in the TTF–TCNQ complex-containing composites (Figure 4a). Correspondingly, the synthesized hybrids containing TTF–TCNQ complexes exhibited fiber structures at the surface. Moreover, by increasing the amount of TTF–TCNQ complex in the material, the number of fiber structures clearly increased at the surface. These data clearly indicate that nanofibers based on CT complexes form in the hybrids. Furthermore, from the comparison

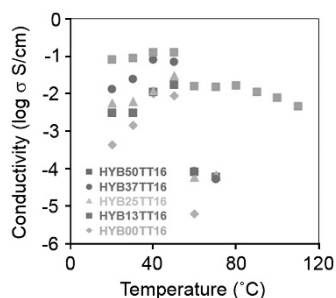


Figure 6 Dependencies of the conductivities of the hybrids on temperature. The thicknesses of the films were 0.16–0.19 mm.

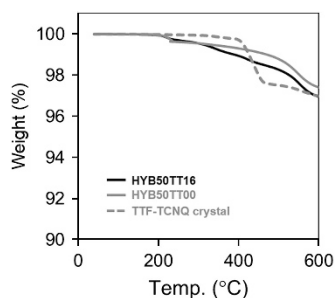


Figure 7 Thermogravimetric analysis (TGA) thermograms of the tetrathiafulvalene–7,7,8,8-tetracyanoquinodimethane (TTF–TCNQ) crystals and of the hybrids with a heating rate of 10 °C per min under a nitrogen atmosphere.

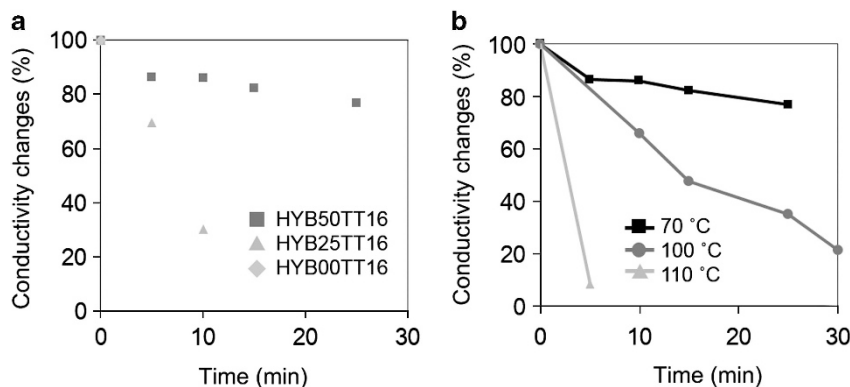


Figure 8 (a) Time courses of the conductivity changes of the hybrids (HYB25TT16 and HYB50TT16) and of the poly(vinylpyrrolidone) (PVP) composite (HYB00TT16). The samples were heated on a hot plate at 125 °C, and the surface temperature was 70 °C. (b) Time courses of the conductivity changes of HYB50TT16 at various surface temperatures.

study with various amounts of the glass component, it was observed that the nanofiber structures were well developed and entangled at the surface of hybrids with a larger percentage of the glass component (Figure 4b). It is hypothesized that the TTF–TCNQ component is condensed at the surface of the material because of the low compatibility of the TTF–TCNQ complexes with the glass component. It is expected that this condensation effect of the nanofiber at the surface contributes to improving the surface conductivity of the materials.³⁴ From the data, including the absorption and XRD measurements and the scanning electron microscopy observations, we concluded that CT complexes form between TTF and TCNQ and that charge transport is responsible for the nanofibers of TTF–TCNQ CT complexes, resulting in increased conductivity.

The conductivity was evaluated using the four-point probe method. The probe was pressed onto the material surface, and the surface resistance of one side of the film was measured. The conductivity was calculated as the inverse of the resistance. When the amount of TTF–TCNQ complexes increased, the conductivity increased (Figure 5). These data can be explained by the scanning electron microscopy observations. Increasing the amount of TTF–TCNQ complexes promoted fiber formation at the surface, and the resultant increase in carrier-transporting pathways contributed to the enhancement in conductivity. Notably, the hybrid films exhibited higher conductivities than that of the cast film composed of TTF–TCNQ complexes ($9.36 \times 10^{-3} \text{ S cm}^{-1}$). It is hypothesized that the assembly of the TTF–TCNQ complexes at the surface contributes to improving the carrier-transport efficiency, leading to enhanced conductivity.

A similar situation was observed in the hybrid upon increasing the proportion of the silica component. Figure 6 presents the influence of temperature on the conductivity of hybrids containing various proportions of silica. Higher conductivities of the hybrids than that of the crystals were observed in the series of plots recorded at 25 °C. The TTF–TCNQ complexes, which are responsible for carrier transport, should be condensed at the surface, leading to an improvement in conductivity. On heating the samples, diverse behaviors were observed. In the absence of the silica component (polymer composite), an increase in conductivity was observed that is consistent with the literature.²⁵ In contrast, the conductivity changes decreased on increasing the proportion of the silica component. In HYB50TT16, the conductivity was maintained even at surface temperatures of > 100 °C. In contrast, the conductivity drastically decreased in the absence of the silica component (HYB00TT16), even at ~60 °C.

These data clearly indicate that formation of the hybrid enhances the thermal stability of the conductivity. Figure 7 shows thermogravimetric analysis thermograms of the TTF–TCNQ complexes and hybrids. At temperatures of $>200\text{ }^\circ\text{C}$, the thermal stability of the complexes was improved by the formation of the hybrid. The robust silica framework suppressed the molecular motions of the TTF–TCNQ complexes, leading to constant conductivity during heating. These data clearly indicate that the conductive hybrids containing TTF–TCNQ complexes possess high thermal stability.

To demonstrate the thermal stability of the hybrids, we monitored the time courses of the conductivity changes at constant temperatures (Figure 8). The samples were heated on hot plates, and surface temperatures were measured. Then, the conductivity changes were recorded using the four-point probe method. As shown in Figure 8a, a critical loss of conductivity was observed in the PVP composite lacking the silica component (HYB00TT16) after heating at $70\text{ }^\circ\text{C}$ for 5 min. In contrast, HYB25TT16 showed conductivity over the detectable region ($<10^{-6}\text{ S cm}^{-1}$) after 10 min. Notably, HYB50TT16, which had the highest percentage of silica among the samples, maintained its conductivity even after heating for 25 min. These results indicate that the formation of the hybrid improved the thermal stability of the TTF–TCNQ conductive crystals. In addition, HYB50TT16 showed conductivity after heating at $100\text{ }^\circ\text{C}$ for 25 min (Figure 8b). These data, including the results shown in Figure 6, clearly indicate that hybrid formation is a valid strategy for enhancing the thermal stability of organic conductive materials.

Finally, we examined the change in conductivity after exposure to water. The hybrids were dipped into deionized water at ambient temperature for 1 min and then dried in air. Conductivity was monitored under these conditions. Before treatment, the conductivities of the hybrid HYB50TT16 and of the PVP composite HYB00TT16 were determined to be 2.7×10^{-2} and $2.5 \times 10^{-3}\text{ S cm}^{-1}$, respectively. The conductivity of the PVP composite was lost after the composite was dipped in water because the films were immediately desorbed from the substrate in water. In contrast, the hybrids maintained conductivity at similar levels after water treatment ($5.6 \times 10^{-2}\text{ S cm}^{-1}$). The TTF–TCNQ crystals yielded similar results to the PVP composites. These data clearly indicate that hybrid formation enhances durability to moisture. After dipping in water for 2 min, the conductivity of the hybrid HYB50TT16 was not in the detectable range (Supplementary Figure S1).

CONCLUSION

We present the introduction of TTF–TCNQ complexes into organic–inorganic hybrids and describe their properties. In our experiments, three significant results were obtained with respect to hybrid formation. First, silica plays a significant role in the condensation of TTF–TCNQ complexes at the surface of the hybrids, leading to an enhancement in conductivity. Poor compatibility could be responsible for this effect. Second, the silica component improves the environmental resistance of the materials. The conductivity is preserved even after heating and exposure to water. Third, molecular motion is efficiently suppressed in the hybrids. Consequently, conductivity changes during heating are suppressed. These properties could be important not only for extending the application of TTF-based materials but also for designing thermally stable organic devices.

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