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# Electrical properties of new organic composites obtained by mechanochemical synthesis

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We present new results on organic semiconductive and metallic composites obtained by direct solid-solid charge-transfer (CT) reaction. By this method, samples of arbitrarily large size are readily achievable. In the present study, we consider composites formed from the reaction between the following pairs of donors and acceptors: TTF and iodine, BEDT-TTF and TCNQ, BEDT-TTF and TCNE, BEDT-TTF and AuI as well as BEDT-TTF and $AuI_3$. Most of the composites show semiconducting properties only. Two of them, however, (BEDT-TTF)/(AuI) and $(BEDT\text{-}TTF)_2/(AuI_3)$, exhibit a metallic behavior. © *2001 Kluwer Academic Publishers*

## 1. Introduction

Tetrathiafulvalene: TTF, and derivatives, in particular bis(ethylenedithio)tetrathiafulvalene: BEDT-TTF, are the donor molecules most commonly used in the preparation of electrically conducting organic metals and superconductors [1, 2]. The first organic metal appeared in 1973 [3]. It is the charge-transfer (CT) salt: TTF-TCNQ, between TTF and the acceptor molecule tetracyanoquinodimethane: TCNQ, which is metallic down to 54 K. TTF forms also a large series of compounds with halogens, X. Structurally ordered mixed-valence compounds: TTF-$X_n$, with metallic properties, are formed for high halogen /TTF proportions ($0.7 < n < 0.8$) [4].

The most important group of organic superconductors consists of salts derived from the BEDT-TTF donor molecule; this group comprises more than a dozen different crystalline phases, with transition temperatures $T_c$ ranging from 1 K to 13 K [1, 2]. In this case, linear, inorganic, symmetrical, monovalent anions, such as $I_3^-$, $IBr_2^-$, $AuI_2^-$, were found to be most appropriate for stabilization of the superconducting state [5].

For all these organic metals and superconductors, however, only very small single crystals, of submillimeter dimensions, can be grown by standard procedures, such as electrocrystallization, and they have, in addition, poor mechanical properties which make them unpracticable for any potential application. For this reason, there has been various attempts to obtain organic conductive materials in other forms, including reticulate doping of polymeric films [6], evaporation of thin conducting films [7] or fabrication of polycrystalline samples [8]. All of them have some specific advantages, but still strong limitations.

The way chosen here to overcome these inconveniences has already been widely explored by our group. It consists of producing the conductive material, as a composite material, by the way of a charge-transfer reaction produced directly in the solid state between the organic electron donor and acceptor moities [9–11]. We have established that CT reactions between almost any two organic, donor and acceptor, components are realizable directly in the solid state, simply by grinding the two components together [9–11]. Such a reaction is at first evidenced by a sharp color change. Various conductive composites of interest have so been obtained under appropriate mechanical and thermal treatments [11]. The method is quite easy and inexpensive; it works for almost any donor-acceptor couple and it is a convenient way to produce samples of nearly unlimited size.

Recently, we presented a detailed study of an interesting composite material: $(BEDT\text{-}TTF)_2/I_3$. It was shown to have a marked metallic character down to, at least, 0.34 K, with the onset of a superconducting transition below 5 K [12–14] and it is very stable. On the contrary,

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the composite material: (BEDT-TTF)$_y$/(AuBr$_3$) [15] was shown to have non-metallic properties.

In this paper we report experimental results on several new composite materials of interest produced by a direct solid-solid CT reaction.

## 2. Experimental

The realization of the following new composite materials is considered in the present paper: (TTF)/I, (BEDT-TTF)/(TCNQ), (BEDT-TTF)/(TCNE), (BEDT-TTF)/(AuI$_3$) and (BEDT-TTF)/([Bu$_4$N]I), in which Bu stands for butyl group. In the AuI$_n$ series the composite materials: (BEDT-TTF)/(AuI) has already been produced and briefly investigated [15] and the materials (BEDT-TTF)/(AuI$_2$) can not be prepared by the present method. The donor and acceptor molecules utilized to realize the composite materials have been selected for their specific CT activity. The method of fabrication of the materials is quite similar to that described elsewhere in the cases of (BEDT-TTF)/I [12, 13] and (BEDT-TTF)/(AuBr$_3$) [15] series.

For electrical conductivity measurements the samples were in the form of bars onto which gold contacts were evaporated in four-probe geometry. Silver wires were then stuck to these contacts with silver paint. In general, all measurements down to 77 K were performed with a lock-in amplifier PAR model 124, and measurements down to 2 K, with a Keithley 220 programmable current source and a Keithley 182 sensitive voltmeter. Voltage versus current linearity were checked up to 250 $\mu$A, in any case, but the current neither exceeds 100 $\mu$A during the measurements being 10 $\mu$A at low temperature.

The absorption spectra of the composite samples dispersed in KBr matrices were investigated at room temperature in the spectral range 500–7000 cm$^{-1}$ with the help of a FT-IR Perkin Elmer 1725X spectrometer.

## 3. Results and discussion

In this study, the “best” conductive régime is thus researched for each composite material, requiring first a careful determination of the following parameters to be optimized independently: the proportion of the two components, donor D and acceptor A, given here by $x$, the ratio of acceptor to donor molecules: D/A$_x$, the time of mechanical grinding, the time and temperature of annealing. The optimal $x$-value is defined as that corresponding to a conductivity maximum.

In this study the optimal grinding times are generally between 1 and 8 hours. The optimal stoichiometries are $1:0.72$ ($x = 0.72$), for composites (TTF)/I$_x$, $1:1$ ($x = 1$), for composites (BEDT-TTF)/(TCNQ)$_x$ and (BEDT-TTF)/(TCNE)$_x$, $1:1.5$ ($x = 1.5$), for composites (BEDT-TTF)/I$_x$ [12, 13], as shown in Fig. 1. It is symptomatic that the optimal compositions $x$, for materials obtained by direct solid-solid charge-transfer reaction, are the same as those for single crystals obtained in solution with the same components [15–19]. In the case of (BEDT-TTF)/(AuI) and (BEDT-TTF)/(AuI$_3$) composite materials, the optimal composition $x$ has not yet been investigated and only an indicative study was made for compositions $x = 1$: (BEDT-TTF)/(AuI), for the first one and $x = 0.5$: (BEDT-TTF)$_2$/(AuI$_3$), for the second.

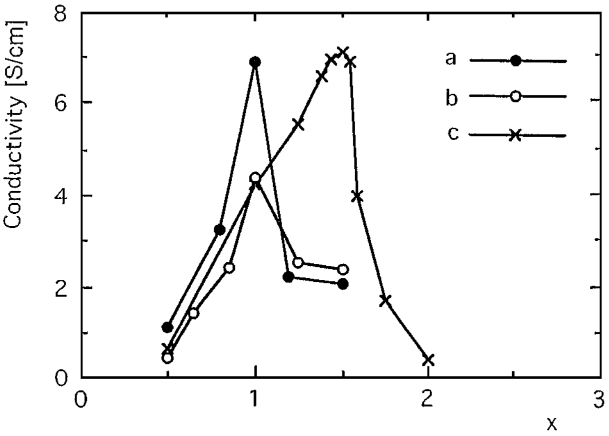

*Figure 1* Room temperature DC electrical conductivity of composite materials: (BEDT-TTF)/(TCNQ) (a) and (BEDT-TTF)/(TCNE) (b), versus $x$, the ratio of acceptor to donor molecules. The conductivity of (BEDT-TTF)/I composite materials is also shown for comparison (c).

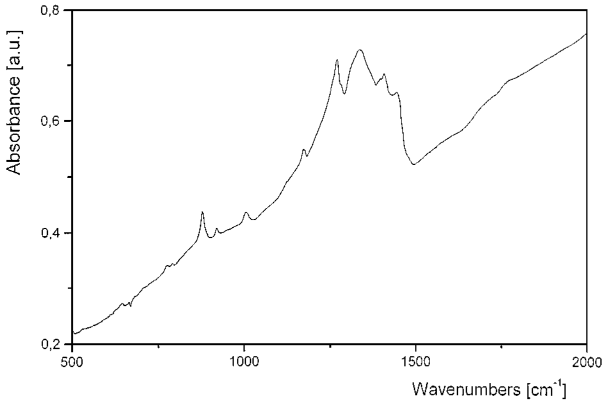

*Figure 2* Room temperature IR absorption spectrum of (BEDT-TTF)/(AuI) composite material, in KBr, in the frequency range of the molecular vibrations of the donor molecule.

The solid-solid CT reaction has also been confirmed by means of infrared spectroscopy. A broad absorption band is observed usually with a maximum between 2500 and 3500 cm$^{-1}$. Such an absorption band is generally assigned to electronic interband transitions in the CT complexes. The room temperature infrared absorption spectrum in KBr of composite (BEDT-TTF)/(AuI), in the particular region of the molecular vibrations of the donor molecule, is shown in Fig. 2. This spectrum presents several non-symmetrical bands, typical of an interaction between conducting electron states and molecular vibration states, in particular totally symmetric molecular vibrations [20].

In (BEDT-TTF)/(AuI) composite material, the bands attributable to intermolecular vibrations of BEDT-TTF ions and those resulting from coupling between electrons and molecular vibrations present the same shapes and frequencies for different values of the donor to acceptor ratio. This seems to indicate that in composite materials with the same stoichiometry are produced by solid-solid CT reaction - any component in excess, donor or acceptor, remaining neutral in the mixtures.

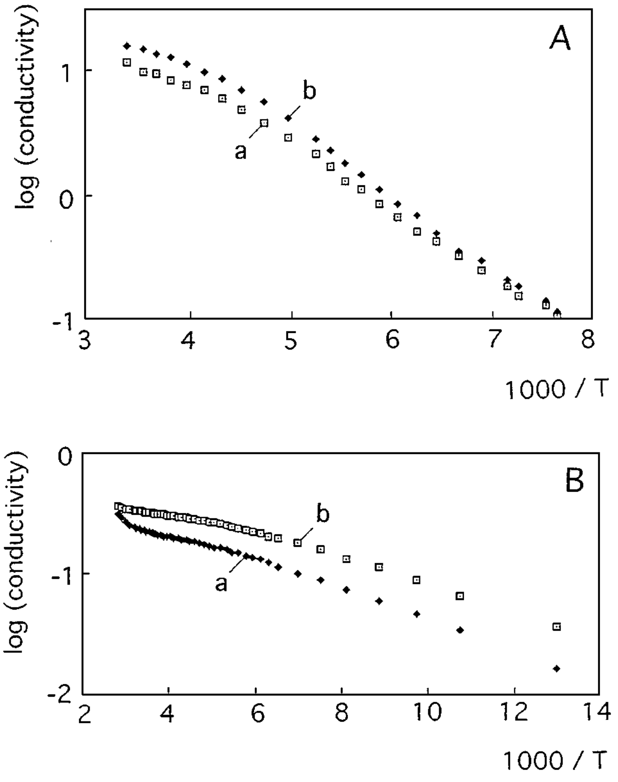

*Figure 3* Temperature dependence of DC electrical conductivity, before annealing (a), and after annealing (b), of semiconductive composite materials: (TTF)/$I_{0.72}$ (Fig. 3A) and (BEDT-TTF)/(TCNQ) (Fig. 3B).

The annealing procedure we choose to apply here is the one with which the metallic state has been obtained for composites: $(BEDT\text{-}TTF)_2/I_3$ investigated previously [12, 13]. It consists of two steps: heating the samples for 2 hours at 85°C and then for 5 minutes at 155°C.

The DC electrical conductivity data of two composite materials: (TTF)/$I_{0.72}$ and (BEDT-TTF)/(TCNQ), are presented as examples in Fig. 3, in the form of Arrhenius plots. In this case, measurements are made on the samples before annealing at 85°C, curves *a*, and after annealing, curves *b*. It is clear from the figure that the samples exhibit semiconducting behaviour only. Upon subsequent heating at 155°C the samples continue to exhibit semiconducting behaviour with first signs of decomposition.

Table I presents for each of the composite materials: (TTF)/$I_{0.72}$, (BEDT-TTF)/(TCNQ) and (BEDT-TTF)/(TCNE), the particular stoichiometry corresponding to maximum of conductivity, together with the room temperature conductivity value, the low temperature activation energy value and the sign of thermopower at room temperature. These parameters are compared to those already found for composite material (TTF)/(TCNQ) [11].

The properties of the composite material: $(BEDT\text{-}TTF)_2/I_3$ have been investigated in great detail by Smirani *et al.* [12–14] and they are quite different from those reported above. After appropriate annealing (2 hours at 85°C and 5 minutes at 155°C), this material exhibits definite metallic behaviour from room temperature down to at least 0.34 K, the lowest temperature limit available in the experiment. Below 5 K, the onset of superconducting transition has even been observed [12–14].

TABLE I Summary of the parameters characterizing conductive organic composites with semiconducting behaviour

| Composite materials | Stoichiometry | RT conductivity $(\Omega\cdot cm)^{-1}$ | Activation energy (eV) | Sign of thermopower |
|---|---|---|---|---|
| (TTF)/$I_{0.72}$ | 1 : 0.72 | 6 | 0.12 | + |
| (BEDT-TTF)/ (TCNQ) | 1 : 1 | 1.5 | 0.01 | + |
| (BEDT-TTF)/ (TCNE) | 1 : 1 | 1.1 | 0.04 | + |
| (TTF)/(TCNQ) [11] | 1 : 1 | 7.5 | 0.025 | 0 |

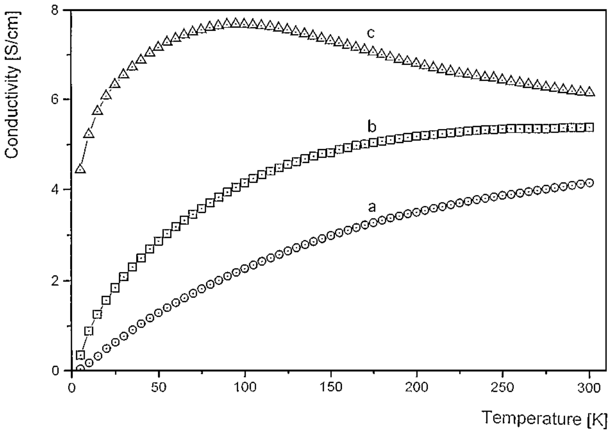

*Figure 4* Temperature dependence of DC electrical conductivity of $(BEDT\text{-}TTF)_2/(AuI_3)$ composite material before annealing (a) and after annealing: for 2 hours at 85°C (b); for 2 hours at 85°C and 5 minutes at 155°C (c).

For this reason we also consider here the production and properties of closely related composite materials based on BEDT-TTF, as the donor, and on acceptors containing iodine in different chemical forms: AuI, $AuI_3$ and $[Bu_4N]I$. It is observed that the solid-solid charge-transfer reaction is realizable only with the two Au-iodine derivatives.

The electrical transport properties of composite materials formed from BEDT-TTF and AuI or $AuI_3$ are found to be significantly different from the properties of materials reported in Table I. Both (BEDT-TTF)/(AuI) and $(BEDT\text{-}TTF)_2/(AuI_3)$ samples are semiconducting before annealing. In each case, upon annealing, DC conductivity has a slightly higher room temperature value and now exhibits a well defined metallic character at room temperature, down to at least 2 K for (BEDT-TTF)/(AuI), and down to 90 K for $(BEDT\text{-}TTF)_2/(AuI_3)$, Fig. 4. This figure illustrates also the progressive effect of thermal treatment on the electrical conductivity of the material and the progressive change from a semiconductive to metallic character. It suggests that a still more suitable annealing procedure could stabilize the metallic phase in the samples to lower temperatures.

In conclusion, this paper reports on several new conducting organic composite materials produced by solid-solid charge-transfer reactions between TTF or

BEDT-TTF, as the donor, and iodine, TCNE, TCNQ, AuI or $AuI_3$, as the acceptor. The electrical properties of these materials are characterized by means of DC conductivity measurements and IR spectroscopy. It is observed that before annealing all these materials are semiconductors. Upon annealing the two composite materials: (BEDT-TTF)/(AuI) and $(BEDT\text{-}TTF)_2/(AuI_3)$ are observed to be metallic as for $(BEDT\text{-}TTF)_2/I_3$ composite material [12–14]. The other materials of the present study have their semiconducting behaviour almost unchanged by the annealing procedure so that their practical importance seems to be limited. In consequence, we shall concentrate in next studies mainly on charge-transfer composite materials made from acceptors which are iodine derivatives.

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