Anion polarity-induced self-doping in a purely organic paramagnetic conductor, α′-α′-(BEDT-TTF)$_2$(PO-CONH-m-C$_6$H$_4$SO$_3$)·H$_2$O where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and PO is the radical 2,2,5,5-Tetramethyl-3-pyrrolin-1-oxyl

Hiroki Akutsu [a,*], Keita Ishihara [b], Soich Ito [b], Fumiyoshi Nishiyama [a], Jun-ichi Yamada [b], Shin'ichi Nakatsuji [b], Scott S. Turner [c], Yasuhiro Nakazawa [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan
[b] Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan
[c] Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK

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ABSTRACT

A new BEDT-TTF-based salt with an organic free radical, α′-α′-(BEDT-TTF)$_2$(PO-CONH-m-C$_6$H$_4$SO$_3$)·H$_2$O, has been prepared. The crystal structure consists of alternating donor and anion/water layers propagated along the c axis. The anisotropic radical anions form a head-to-head arrangement, which provides a permanent dipole moment. The effect on the nearest donor layer has been estimated to be 4.0 V. The salt has two crystallographically independent donor layers (A and B), one of which (A) is surrounded by the negative ends of the anion layer dipole whereas the B layers are bordered by the positive ends of the dipole. This structural feature suggests that layers A and B have different Fermi levels. To eliminate the imbalance, self-doping occurs whereby electron density is transferred from layer A to B. The temperature dependence of the magnetic susceptibility has 11.1% of extra Curie spins, from which a doping ratio of 12.7% has been estimated.

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1. Introduction

The collective electronic ground states of BEDT-TTF-based organic conductors are dependent on the BEDT-TTF stacking arrangement (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene). A wide variety of conducting behaviors is observed in these salts with the same BEDT-TTF charge but different stacking organisations, designated by Greek letters: α, β, β″, κ, θ, and so on [1]. For example, κ- and β-type salts are often metallic, α- and θ-type salts are usually semiconducting or show metal–insulator transition, and β″-type salts are commonly semimetallic.
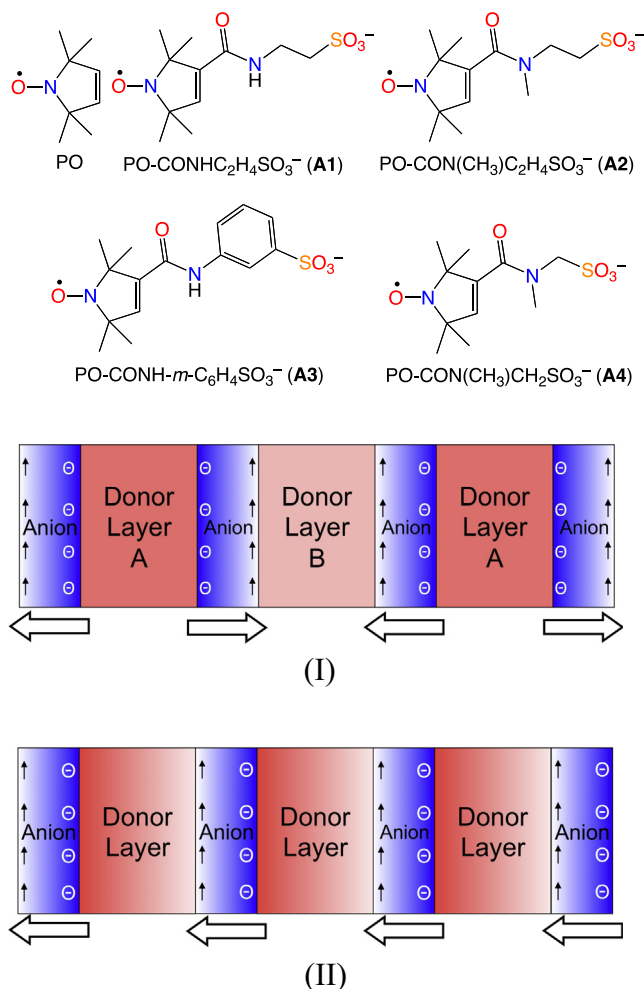
A typical structure for this type of salts consists of conducting BEDT-TTF-based two-dimensional layers separated by anionic layers. Normally the anions play no significant role in the conducting property and prevent BEDT-TTF molecules from approaching one other. Indeed a charge-transfer (CT) salt with smaller anions is often more conductive than an isostructural salt with larger anions. Therefore simple, symmetrical and small anions have been widely used [1–3].

Recently, we have prepared three new types of conducting charge-transfer (CT) salts, which have relatively large anisotropic organic anions that play a significant role in their electronic structure and conducting properties. These salts can be classified into two types, I and II. Type I salts include κ-β″-(BEDT-TTF)$_2$**A1** (**1**) [4] and (TTF)$_3$(**A2**)$_2$ (**2**) [5], in both of which the anions form in 'head-to-head' (Fig. 1-I). The resultant anisotropy leads to two crystallographically different donor layers (A and B) and a dipole moment (μ) associated with each anion layer. The effect of the dipole on the nearest donor BEDT-TTF layer can be estimated in terms of a voltage [6], which is achieved by using the absolute μ value of the anion(s) and the angle between the dipole's vector and the donor layer plane. The resultant values from the anion layers in **1** and **2** are 3.2 and 7.7 V, respectively. As shown in Fig. 1-I the donor layers A are bordered by negative ends of the dipole and the donor layers B are far from the negative ends. Therefore the cations within layer A are more positively charged compared to those in layer B. Indeed the average charges of donors in the β″-layer (A) and κ-layer (B) are +0.58 and +0.42, respectively

* Corresponding author.
E-mail address: akutsu@chem.sci.osaka-u.ac.jp (H. Akutsu).

PO   PO-CONHC$_2$H$_4$SO$_3^-$ (**A1**)   PO-CON(CH$_3$)C$_2$H$_4$SO$_3^-$ (**A2**)

PO-CONH-*m*-C$_6$H$_4$SO$_3^-$ (**A3**)   PO-CON(CH$_3$)CH$_2$SO$_3^-$ (**A4**)

(I)

(II)

Fig. 1. Schematic schemes of the crystal structures of (I) Type I and (II) Type II where ↑ is a magnetic dipole and ⊖ is a minus charge. ⟹ represents the direction of electrical dipole.

[4,7], indicating that the polar anion layers provide a hole and electron doping effect into the donor layers. However, the crystals of **1** and **2** have no net dipole moment because the dipole moments of successive anionic layers oppose each other. Here we report a new salt, α'-α'-(BEDT-TTF)$_2$(**A3**)·H$_2$O (**3**), which is also a Type I salt, and another dicationic BEDT-TTF salt of **A3**, (BEDT-TTF)(**A3**)$_2$ (**4**). In addition, we have very recently obtained a Type II salt, α -(BEDT-TTF)$_2$(**A4**)·3H$_2$O (**5**), which has a net dipole moment. In the latter salt all polar anions are orientated in the same directions (as shown in Fig. 1-II) to provide a net dipole moment for the whole crystal [7].

2. Material and methods

The acidic PO-CONH-*m*-C$_6$H$_4$SO$_3$H (**A3**) was prepared by reacting aniline-3-sulfonic acid (0.90 g, 5.2 mmol) with 3-carboxy-PO (0.79 g, 4.3 mmol) in the presence of DCC (1.06 g, 5.16 mmol) and DMAP (1.26 g, 10.3 mmol) in 40 mL of CH$_2$Cl$_2$ at room temperature with stirring for 3 days. Metathesis of H**A3** with PPh$_4$·Br gave the PPh$_4$ salt of **A3** as yellow block-like crystals, which were recrystallized from acetonitrile (yield 1.91 g, 64%). X-ray diffraction data of PPh$_4$ of **A3** were collected at 200 K on a Rigaku Mercury II CCD system with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated Mo *K*α radiation [8]. The structure was assigned as PPh$_4$**A3**·H$_2$O. Black needles of **3** were

obtained by the constant-current electrocrystallization method in PhCl with 10% acetonitrile (total 15 mL) with 15 mg of BEDT-TTF and 70 mg of PPh$_4$**A3**·H$_2$O. Single crystal X-ray diffraction data of **3** were collected with a Rigaku Rapid 191R imaging plate system with FR-E SuperBright High-Brilliance rotating-anode X-ray generator with confocal monochromated Mo *K*α radiation, at room temperature [9]. A small amount of black blocks of **4** were found in an electrocrystallization cell filled with 18 mL of PhCl and 2 mL of EtOH with 10 mg of BEDT-TTF and 70 mg of PPh$_4$**A3**·H$_2$O. The crystal structure of **4** was determined using the same instrument as for PPh$_4$**A3**·H$_2$O, at 273 K [10]. However, the obtained yield of **4** was so small that we were not able to determine its physical properties. Electrical resistivity was measured by a standard four-probe method using a HUSO HECS-994C multi-channel conductometer. Magnetic susceptibility of a polycrystalline sample from 2–300 K was measured using a Quantum Design MPMS-2S SQUID magnetometer. For **3**, the magnetic susceptibility data were corrected for a contribution from an aluminum foil sample holder and the sample diamagnetic contributions were estimated from Pascal's constants.

3. Results and discussion

3.1. PPh$_4$**A3**

Analysis of single crystal X-ray diffraction data indicates that the asymmetric unit has one PPh$_4$ cation, one **A3** anion, and one water molecule [8]. The water molecule interacts with an oxygen of the –SO$_3^-$ group and an oxygen of the amido groups of **A3** *via* hydrogen bonds. Temperature-dependent magnetic susceptibility of the powder sample of PPh$_4$**A3**·H$_2$O obeys a Curie-Weiss law with a Curie constant $C = 0.371$ emu K mol^{-1} and Weiss constant $\theta = -0.18$ K.

3.2. α'-α'-(BEDT-TTF)$_2$(**A3**)·H$_2$O (**3**)

Compound **3** contains two independent donor molecules (A and B) and one crystallographically independent **A3** anion [9]. The donor B and **A3** anion are so distorted that rigid model restraints were applied for these molecules. Due to the relatively high *R*-value of 15.2%, the discussion is limited to the gross molecular arrangement. The crystal structure of **3** is shown in Fig. 2a. Both donor layers, A and B, have α'-type packing motifs as shown in Fig. 2b. The anions form a 'head-to-head' arrangement, which provides a dipole moment. The unit cell includes two anion layers, which are related by a two-fold operation. Therefore the directions of successive pairs of dipole moments are opposite, indicating that the crystal has no net dipole moment. Thus the compound is a Type I structure as described above (see Fig. 1-I), in which the donor layer A is surrounded by negative charge and is itself more positive than more negative donor layer B, which is far from negative charges. In this circumstance, the A and B layers have different Fermi levels, and to eliminate the charge imbalance, self-doping is necessary. In addition, we calculated the dipole moment (μ) of the crystallographically independent **A3** anion using MOPAC7 [11], giving a value of 21.9 Debye. The effect of the dipole moment on the nearest donor layer can be calculated in terms of voltage [6], the resultant value of which is 4.0 V.

The electrical resistivity of **3** was measured by a conventional four-probe method. The salt is a semiconductor with room temperature resistivity (ρ_{RT}) of 0.36 Ω cm and activation energy (E_a) of 20 meV. I. D. Parker et al. reported [12] that three α'-type salts, α'-(BEDT-TTF)$_2$X salts where X = AuBr$_2$, CuCl$_2$, and Ag(CN)$_2$ (**6**, **7**, and **8**, respectively), each have similar $\rho_{RT} \approx 20$ Ω cm and $E_a \approx 300$ meV. Values for compound **3** are two orders of magnitude