Novel Purely Organic Conductor with an Aminoxyl Radical, α-(BEDT-TTF)$_2$(PO–CONHCH$_2$SO$_3$)$\cdot$2H$_2$O (PO = 2,2,5,5-Tetramethyl-3-pyrrolin-1-oxyl Free Radical)

Hiroki Akutsu,*[1] Shinji Yamashita,[1] Jun-ichi Yamada,[1] Shin'ichi Nakatsuji,[1] and Scott S. Turner[2]
[1]*Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297*
[2]*Department of Chemistry, Warwick University, Gibbet Hill Road, Coventry CV4 7AL, U.K.*

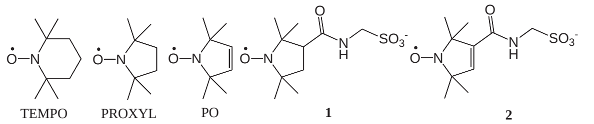
(Received May 7, 2008; CL-080469; E-mail: akutsu@sci.u-hyogo.ac.jp)

A novel bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)-based salt with an aminoxyl radical 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl (PO) has been prepared. The salt has α-type 2-D conducting sheets and is a semiconductor with $\rho_{\mathrm{RT}} = 26\,\Omega\cdot\mathrm{cm}$ and $E_a = 0.31$ eV. The temperature dependence of the magnetic susceptibility suggests that both the aminoxyl radical and the BEDT-TTF layer have local spin moments at room temperature.

Organic magnetic conductors have received increasing attention due to reports of unique properties that emerge from an interplay between the conductivity and magnetism.[1] For this reason, organic free radicals have been incorporated into organic conductors as a magnetic source.[2,3] However, to our knowledge, all of the previously prepared salts do not show metallic behavior.[2] We have also focused on preparing several BEDT-TTF salts with new organic magnetic anions that combine the organic free radical TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) with the sulfonate group ($-SO_3^-$).[3] These salts also show semiconducting behavior, probably because the size of the anions are relatively large compared to inorganic anions in metallic BEDT-TTF salts, such as Cl^-, ClO_4^-, I_3^-, PF_6^-, etc.[4]

Recently, we prepared a sulfonate of the smaller PROXYL radical, PROXYL-CONHCH$_2$SO$_3^-$ (**1**) (Scheme 1). The anion provided a BEDT-TTF salt, β''-(BEDT-TTF)$_2$**1**, that shows metallic behavior down to 210 K.[5] Here, we have chosen the smaller PO radical and report the structure and magnetic properties of the PO-based new sulfonate, PO–CONHCH$_2$SO$_3^-$ (**2**), prepared as a tetraphenylphosphonium (PPh$_4$) salt **3** and the electrochemically synthesized derivative, α-(BEDT-TTF)$_2$**2**$\cdot$2H$_2$O (**4**).

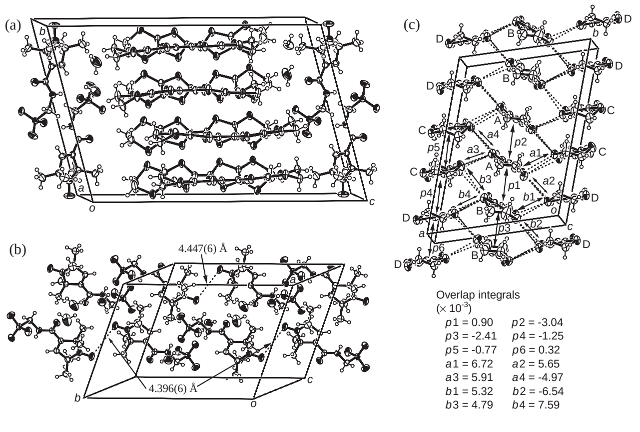
Sulfonic acid H**2** was prepared by reacting 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-oxyl (0.30 g, 1.6 mmol) with aminomethanesulfonic acid (0.22 g, 2.0 mmol) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC, 0.46 g, 2.0 mmol) and 4-dimethylaminopyridine (DMAP, 0.48 g, 3.9 mmol) in 30 mL of dichloromethane at room temperature with stirring over four days. Metathesis with PPh$_4$Br yielded PPh$_4$**2** (**3**) as yellow crystals, which were recrystallized from acetone (yield 54%). Single-crystal X-ray diffraction data were collected on a Rigaku AFC-5R 4-circle diffractometer at room temperature.[6] The asymmetric unit has one PPh$_4$ cation and one anion **2**. The N–O distance in **2** is 1.267(3) Å, almost the same as observed in PO–COOEt [1.270(2)].[7] The magnetic susceptibility of **3** from 2–300 K using a Quantum Design MPMS-5S SQUID magnetometer obeys the Curie–Weiss law with $C = 0.377$ emu K mol^{-1} and $\theta = -0.43$ K.



Scheme 1.

Black block-like crystals of α-(BEDT-TTF)$_2$**2**$\cdot$2H$_2$O (**4**) were obtained by the constant-current electrocrystallization method in a mixed solvent of 18 mL of chlorobenzene and 2 mL of acetonitrile with 15 mg of BEDT-TTF and 70 mg of **3**. X-ray diffraction data were recorded using a Quantum CCD 1 area detector on a Rigaku AFC-7R diffractometer at room temperature.[8] The crystal structure of the salt is shown in Figure 1a. Four BEDT-TTF molecules, two anions, and four water molecules are crystallographically independent. The unit cell consists of alternating donor and anion/water layers, along the *c* axis. The anion layer has two independent PO spin dimers about a center of symmetry with short O···O distances of 4.396(6) and 4.447(6) Å, respectively (Figure 1b). There are no short contacts between BEDT-TTF and **2**, suggesting that it is unlikely to show significant interactions between conducting and magnetic electrons. In addition, the N–O distances of the PO moieties are 1.273(5) and 1.282(5) Å, respectively, which are not significantly different from that in **3**.

The packing of the donor layers is shown in Figure 1c. There are two kinds of BEDT-TTF stacks (AABB and CCDD) which propagate along the *b* axis and interact with each other in a side-by-side fashion along the *a* axis, giving an α-type 2-D



Overlap integrals
($\times 10^{-3}$)
$p1 = 0.90$ $p2 = -3.04$
$p3 = -2.41$ $p4 = -1.25$
$p5 = -0.77$ $p6 = 0.32$
$a1 = 6.72$ $a2 = 5.65$
$a3 = 5.91$ $a4 = -4.97$
$b1 = 5.32$ $b2 = -6.54$
$b3 = 4.79$ $b4 = 7.59$

Figure 1. (a) The BEDT-TTF and anion/water layers of **4**. (b) The anion and water layers of **4**. (c) View of the BEDT-TTF layers along the central C=C bonds of **4**. Dashed lines indicate S···S contacts shorter than the van der Waals distance (3.7 Å). The overlap integrals (bottom) were calculated using extended Hückel method.[9]

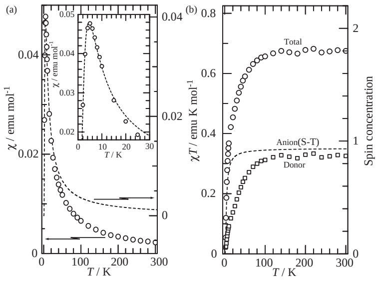


Figure 2. (a) χ–T plots for salt **4** where χ is the molar magnetic susceptibility per (BEDT-TTF)$_2$**2**$\cdot$2H$_2$O. Inset is the expansion from 2–30 K. Dashed line is calculated on the basis of a singlet–triplet (S–T) model.[10] (b) χT–T plots where $\chi_{\mathrm{Donor}} = \chi_{\mathrm{Total}} - \chi_{\mathrm{Anion}}$ (S–T). See text for explanation.

conducting sheet. There are many short interstack S···S contacts but no short intrastack contacts. We have calculated the intermolecular overlap integrals by means of extend Hückel method as shown in Figure 1c.[9] The values of $p1$–$p6$ are smaller than those of $a1$–$a4$ and $b1$–$b4$, confirming that the BEDT-TTF side-by-side interactions are stronger than the face-to-face interactions.

The electrical resistivity was measured by a standard four-probe method. The salt shows semiconducting behavior with $\rho_{\mathrm{RT}} = 26\,\Omega\cdot$cm and $E_\mathrm{a} = 0.31$ eV. The ρ_{RT} and E_a values are higher than those of other BEDT-TTF$^{0.5+}$ salts.[4] The magnetic susceptibility of a polycrystalline sample of **4** from 2–300 K was measured using a Quantum Design MPMS-5SH SQUID magnetometer (Figure 2a). The curve has a maximum at 5 K (Inset of Figure 2a), below which χ decreases with decreasing temperature. The χ value at 2 K ($\chi_{2\,\mathrm{K}} = 0.027$ emu mol^{-1}) is smaller than 2/3 of that at the maximum ($\chi_{\max}$ (=0.048) $\times$ 2/3 = 0.032 emu mol^{-1}), suggesting that the ground state is not antiferromagnetic ($\chi_{0\,\mathrm{K}} = 2\chi_{\max}/3$ for polycrystals) but is diamagnetic. In fact the data from 2–20 K can be modeled well by a singlet–triplet model[10] (dashed line in Figure 2a) with $C = 0.351$ emu K mol^{-1} and $J = -3.7$ K. The C value is 94% of that from an $S = 1/2$ spin (0.375 emu K mol^{-1}), suggesting that the PO radical part in the salt dominates the S–T term. Since the anions **2** form spin dimers with short >N–O···O–N< contacts the intra-dimer interaction is likely to produce the antiferromagnetic S–T situation. The large deviation between the circles and the dashed line from 40–300 K in Figure 2a indicates that there is another magnetic contribution. The χT–T plots in Figure 2b (Total) indicate that there are approximately two spins at room temperature. This suggests that there is a magnetic contribution from the BEDT-TTF layers. To obtain the χT–T curve for the donor layers, we subtracted the anionic S–T term (Anion(S-T) in Figure 2b) from the total data. The resultant curve is shown in Figure 2b (Donor). The room temperature χT value of 0.326 emu K mol^{-1} is 87% of that of the $S = 1/2$ spin, suggesting that approximately one spin is localized on each two BEDT-TTF molecules, like a Mott insulator. In the overlap integrals along the stacks ($p1$–$p6$ in Figure 1c), $p2$, $p3$, and $p4$ are larger than $p1$, $p5$, and $p6$, suggesting that AA ($p2$), BB ($p3$), CD, and DC ($p4$) molecules are dimers, on which the spins may be localized. The results of the band calculations[11] indicate that the bands are split to lower and upper bands and that the upper band is half-filled. Below 100 K, the χT value gradually decreases with deceasing temperature to become approximately zero at 2 K.

In conclusion a smaller anion **2** compared to **1** which provided a metallic BEDT-TTF salt[5] does not provide a metal but a semiconductor. The result contradicts the "rule of thumb" that smaller anions provide a more stable metallic state. However, this salt has incorporated solvent molecules (H$_2$O), which may prevent the salt from becoming metallic. The observation of the significant magnetic interaction between itinerant electrons and local spins would likely require the salt being metallic at low temperature. Preparation of other BEDT-TTF salts of **2** without included solvent is in progress.

References and Notes

1 H. Kobayashi, H. Cui, A. Kobayashi, *Chem. Rev.* **2004**, *104*, 5265; E. Coronado, P. Day, *Chem. Rev.* **2004**, *104*, 5419; T. Enoki, A. Miyazaki, *Chem. Rev.* **2004**, *104*, 5449.

2 T. Sugano, T. Fukasaka, M. Kinoshita, *Synth. Met.* **1991**, *43*, 3281; E. Fujiwara, S. Aonuma, H. Fujiwara, T. Sugimoto, Y. Misaki, *Chem. Lett.* **2008**, *37*, 84; S. Otsubo, H. Cui, H.-J. Lee, H. Fujiwara, K. Takahashi, Y. Okano, H. Kobayashi, *Chem. Lett.* **2006**, *35*, 130; M. M. Matsushita, H. Kawakami, Y. Kawada, T. Sugawara, *Chem. Lett.* **2007**, *36*, 110; T. Sugimoto, S. Yamaga, M. Nakai, K. Ohmori, M. Tsujii, H. Nakatsuji, H. Fujita, J. Yamauchi, *Chem. Lett.* **1993**, 1361; K. A. Hutchison, G. Srdanov, R. Menon, J.-C. P. Gabriel, B. Knight, F. Wudl, *J. Am. Chem. Soc.* **1996**, *118*, 13081; S. Nakatsuji, H. Anzai, *J. Mater. Chem.* **1997**, *7*, 2161; Y. Nakamura, N. Koga, H. Iwamura, *Chem. Lett.* **1991**, 69; K. Mukai, N. Senba, T. Hatanaka, H. Minakuchi, K. Ohara, M. Taniguchi, Y. Misaki, Y. Hosokoshi, K. Inoue, N. Azuma, *Inorg. Chem.* **2004**, *43*, 566; S. Aonuma, H. Casellas, C. Faulmann, B. G. Bonneval, I. Malfant, P. Cassoux, P. G. Lacroix, Y. Hosokoshi, K. Inoue, *J. Mater. Chem.* **2001**, *11*, 337.

3 H. Akutsu, J. Yamada, S. Nakatsuji, *Chem. Lett.* **2003**, *32*, 1118; H. Akutsu, J. Yamada, S. Nakatsuji, *Synth. Met.* **2005**, *152*, 377; H. Akutsu, K. Masaki, K. Mori, J. Yamada, S. Nakatsuji, *Polyhedron* **2005**, *24*, 2126; A. Yamashita, H. Akutsu, J. Yamada, S. Nakatsuji, *Polyhedron* **2005**, *24*, 2796; H. Akutsu, J. Yamada, S. Nakatsuji, S. S. Turner, *Solid State Commun.* **2006**, *140*, 256.

4 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini. M.-H. Whangbo, *Organic Superconductor (Including Fullerenes): Synthesis, Structure, Properties and Theory*, Prentice Hall, Englewood Cliffs, NJ, **1992**.

5 H. Akutsu, K. Sato, S. Yamashita, J. Yamada, S. Nakatsuji, S. S. Turner, *J. Mater. Chem.*, doi: 10.1039/b806694a.

6 Crystal data for **3**: C$_{34}$H$_{36}$N$_2$O$_5$PS, $M_\mathrm{r} = 615.70$, triclinic, space group $P\bar{1}$, $a = 11.603(5)$, $b = 13.889(6)$, $c = 11.241(4)$ Å, $\alpha = 98.79(3)$, $\beta = 96.52(4)$, $\gamma = 114.51(4)°$, $V = 1597.1(12)$ Å^3, $T = 295$ K, $Z = 2$, μ(Mo Kα) = 0.195 mm^{-1}, $D_{\mathrm{calcd}} = 1.28$ g/cm^3, 7715 reflections measured, 7309 independent ($R_{\mathrm{int}} = 0.0737$), 4362 reflections ($I > 2\sigma(I)$), $R = 0.057$, $R_W = 0.064$ (CCDC-692094).

7 J. Duskova, J. Labsky, J. Hasek, I. Cisarova, *Acta Crystallogr., Sect. E* **2001**, *57*, o85.

8 Crystal data for **4**: C$_{30}$H$_{36}$N$_2$O$_7$S$_{17}$, $M_\mathrm{r} = 1081.64$, triclinic, space group $P\bar{1}$, $a = 12.0326(11)$, $b = 16.7631(14)$, $c = 23.419(2)$ Å, $\alpha = 105.5151(12)$, $\beta = 90.591(3)$, $\gamma = 108.0455(19)°$, $V = 4305.3(7)$ Å^3, $T = 294$ K, $Z = 4$, μ(Mo Kα) = 0.899 mm^{-1}, $D_{\mathrm{calcd}} = 1.67$ g/cm^3, 38808 reflections measured, 18821 independent ($R_{\mathrm{int}} = 0.0354$), 11597 reflections ($I > 3\sigma(I)$), $R = 0.065$, $R_W = 0.067$ (CCDC-692095).

9 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627.

10 B. Bleaney, K. D. Bowers, *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) July 19, 2008; doi:10.1246/cl.2008.882