Dication Salts of the Organic Donor Bis(ethylenedithio)tetrathiafulvalene

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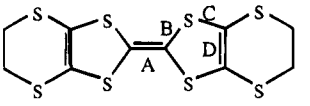
Dication salts of the organic π-donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have been isolated as tetrafluoroborate and perchlorate salts. The salts are prepared by electrocrystallization from an oxidizing solvent mixture. Optical spectroscopy shows that BEDT-TTF is first chemically oxidized to the monocation in the electrolyte media followed by electrochemical oxidation to the dication. BEDT-TTF$(BF_4)_2$ **(1)** crystallizes in the $P2_1/n$ space group with $a = 5.824(1)$ Å, $b = 9.490(2)$ Å, $c = 17.593(3)$ Å, $\beta = 91.61(1)°$, $V = 972.0(3)$ Å^3, and $Z = 2$. BEDT-TTF$(ClO_4)_2$ **(2)** is isostructural to the BF_4^- salt with $a = 5.867(1)$ Å, $b = 9.579(2)$ Å, $c = 17.669(3)$ Å, $\beta = 92.06(2)°$, and $V = 992.4(3)$ Å^3. Optical transmittance spectra from **2** show no evidence for low-frequencey metallic behavior. Two localized transitions at 855 nm (11 700 cm^{-1}) and 714 nm (14 000 cm^{-1}), each strongly polarized along the crystallographic b axis, are observed by optical reflectance.

Introduction

The organic π-donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is the basis of a large number of conducting and superconducting cation-radical molecular solids.[1–7] Conductivity in these materials occurs via the donor-ion network that results from close intermolecular contacts in the solid. The donor-ion networks are often stacks or sheets that are separated by the counterions.[3,8] The most common route to pure crystalline samples of conducting cation-radical salts is through electrochemical oxidation of the donor in the presence of an appropriate counterion. Salts are generally formed where the oxidation state of the donor ranges from $+1/2$ to $+1$, and all of the current superconducting examples have donor oxidation states of $+1/2$ or $+2/3$.[4,9]

In principle, solids where the donor has a nonintegral oxidation state between +1 and +2 could also be conductors with potentially interesting properties. Such examples would have degrees of band filling different from the presently known materials. In practice, however, there are only a few examples of BEDT-TTF cation-radical salts where the degree of oxidation is greater than +1.[10–12] If high-oxidation state salts are to be prepared by electrocrystallization, methods need to be developed to stabilize the donor cations in solution and prevent precipitation of the more common "low-oxidation state" salts. In this paper, we describe the preparation of dication salts of BEDT-TTF where the donor is first chemically oxidized to the monocation followed by electrochemical oxidation to the dication. Tetrafluoroborate and perchlorate[13] salts of the BEDT-TTF dication have been isolated, and their crystal structures are described. While optical reflectivity shows that these dication salts are not conducting, the route used to isolate them appears to be general and could be used to pursue cation-radical salts of BEDT-TTF and related donors with nonintegral oxidation states greater than +1.



BEDT-TTF

Experimental Section

Materials. BEDT-TTF was synthesized by the method of Larsen and Lenoir.[14] Tetra-*n*-butylammonium tetrafluoroborate, tetraethylammonium perchlorate, and tetra-*n*-butylam-

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monium perchlorate were obtained from Southwestern Analytical Co. (Austin, TX) and then twice recrystallized from an ethyl acetate–pentane mixture. Benzonitrile (C_6H_5CN, 99%) and chloroacetyl chloride ($ClCH_2COCl$, 98%) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Benzonitrile was purified by distillation, and chloroacetyl chloride was used without further purification. Carbon disulfide (CS_2) was purchased from Fisher Scientific Co. (Pittsburg, PA) and used without further purification.

BEDT-TTF$(BF_4)_2$ (1). *Method 1:* BEDT-TTF (10 mg) was placed in the working electrode arm of a two-electrode H-cell containing a total of 2 mL of 2.5×10^{-2} M tetrabutylammonium tetrafluoroborate in 10% $CS_2/ClCH_2COCl$. A constant current density of 1 $\mu A/cm^2$ was maintained at room temperature between the platinum working and counter electrodes that were separated by two glass frits. After a few days, needles could be seen on the electrode surface and at the bottom of the H-cell. Small blue needles were collected after 28 days. *Method 2:* BEDT-TTF (7 mg) was dissolved in 36 mL of 1.0×10^{-2} M tetrabutylammonium tetrafluoroborate in 10% $ClCH_2COCl$/benzonitrile and oxidized in an H-cell as described above. The cells were maintained at room temperature with a constant current density of 1.5 $\mu A/cm^2$. As above, crystals were observed within a few days and were collected after 21 days.

BEDT-TTF$(ClO_4)_2$ (2). Using method 1, described above, with 6×10^{-2} M tetraethylammonium perchlorate as electrolyte, crystals were isolated as thin blue plates. Crystals were also prepared according to method 2 with 1.0×10^{-2} M tetrabutylammonium perchlorate as electrolyte.

Crystallographic Data Collection and Structure Determination. X-ray data for **1** and **2** were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation. In each case, 50 reflections with $20.0° \leq 2\theta \leq 22.0°$ were used to refine the cell parameters. Four reflections (013, $12\bar{3}$, 113, $\bar{2}21$) for **1**, and ($02\bar{1}$, $13\bar{5}$, 011, 011) for **2**, were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections were applied based on measured crystal faces using *SHELXTLplus*.[15]

The structures were solved by direct methods in *SHELXTLplus*[15] from which the locations of the non-H atoms were obtained. The structures were refined in *SHELXTLplus* using full-matrix least squares. The non-H atoms were treated anisotropically. In **1**, the CH_2CH_2 units of the cation are disordered (site occupation factors were refined to 0.64 for the C4–C5 unit and 0.36 for the C4′–C5′ unit with an esd of 0.02). The disordered H atoms were calculated in idealized positions and their isotropic thermal parameters fixed at 0.08. In **2**, the CH_2CH_2 units of the cation are also disordered (site occupation factors were refined to 0.65 for the C4–C5 unit and 0.35 for the C4′–C5′ unit with an esd of 0.03). Each of the disordered CH_2 units has a H atom of full occupancy (H4 or H5, common to both disordered units) and a disordered H atom (H4a and H4a′ on C4 and C4′, respectively; H5a and H5a′ on C5 and C5′, respectively). H4a′ and H5a′ were calculated in idealized positions, and their isotropic thermal parameters fixed at 0.08. H4, H5, H4a, and H5a were refined without any constraints. 146 and 162 parameters for **1** and **2**, respectively, were refined and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) $= (I_{peak} - I_{background})$ (scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$ (scan rate), k is the correction due to decay and Lp effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography*.[16] Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[17] with anomalous-dispersion corrections from Cromer and Liberman,[18] while those of hydrogen atoms were from Stewart et al.[19]

Optical Measurements. Two crystals with large enough surface area (1×1 mm^2) were selected for optical measurements. The principal optical axes in the (001) face were identified by observing the extinction point when rotating the sample under an Olympus (Tokyo, Japan) Model BHM microscope with crossed polarizers. The a and b axes in the crystal coincide with the directions of maximum optical anisotropy. Polarized reflectance along these two axes was measured in the frequency range 3000–32 000 cm^{-1} using a Perkin-Elmer (Norwark,CT) monochromator. Each sample was mounted by fixing it onto a frame with a 1 mm diameter hole. A piece of Al-coated glass was mounted the same way as the sample and used as the reference. The surface of the sample was flat and smooth, giving a nearly specular reflectance. Transmittance of one sample was measured in the far- and mid-IR (100–4000 cm^{-1}) using a fast-scanning Bruker (Billerica,MA) IFS-113V Fourier interferometer. Solution UV–vis spectra were obtained with a Perkin-Elmer 330 spectrophotometer.

Results and Discussion

Synthesis and Structure. The BEDT-TTF dication salts were isolated during attempts to define conditions where small molecules can be purposefully incorporated into cation-radical salts to form ternary structures. Incorporation of small neutral molecules into the lattice represents a way to vary donor ion packing by changing the unit cell volume. Previously,[20] we have isolated a salt, $(BEDT\text{-}TTF)_2PF_6 \cdot ClCH_2COCl$, where the BEDT-TTF packing is different than observed in other PF_6^- salts and is similar to that seen in the conductor β'-$(BEDT\text{-}TTF)_2AuBr_2$.[21,22] The dication salts were initially isolated from a standard constant-current electrocrystallization cell using a solvent mixture of 10% CS_2 in $ClCH_2COCl$ and have since been reproduced using a 10% $ClCH_2COCl$/benzonitrile solvent mixture according to the conditions described in the Experimental Section. In all cases, the donor ion is slowly oxidized by the solvent medium to form a solution containing the BEDT-TTF monocation. The dication is then formed electrochemically and is isolated at the anode by crystallization with the electrolyte anion. Optical spectroscopy shows that BEDT-TTF is slowly oxidized by $ClCH_2COCl$. Figure 1 compares the optical spectrum of a 6.75×10^{-4} M solution of BEDT-TTF in 1,1,2-trichloroethane with the spectrum from the same solution containing a 2-fold excess of $ClCH_2COCl$. Bands between 400 and 600 nm are intramolecular transitions of the BEDT-TTF monocation.[23] The band at 960 nm is an intermolecular charge-transfer band resulting from the formation of dimers in solution.[24]

BEDT-TTF$(BF_4)_2$ (**1**) forms as small six-sided needles and slowly degrades in air over a period of days while

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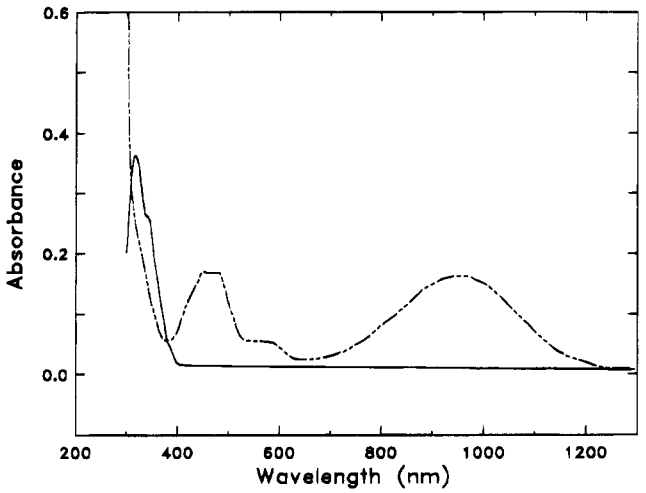

Figure 1. Optical spectra of 6.75×10^{-4} M BEDT-TTF in 1,1,2-trichloroethane (solid line) and in the same solution containing a 2-fold excess of $ClCH_2COCl$ (dashed line). Bands between 400 and 600 nm are localized transitions of the BEDT-TTF monocation, while the band at 960 nm is an intermolecular transition resulting from the formation of dimers in solution.

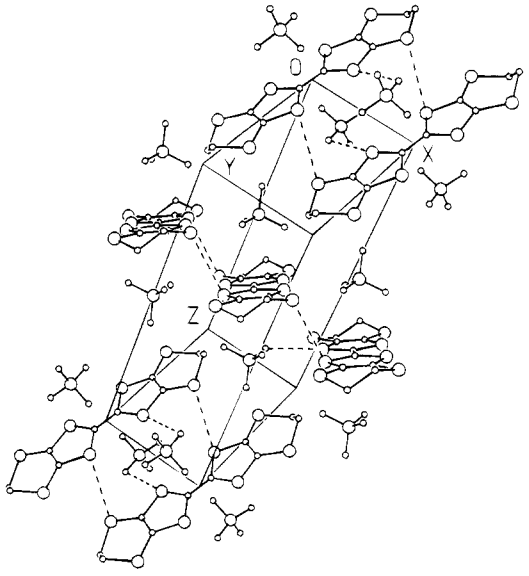

Figure 2. Crystal structure showing the molecular packing of **1**.

BEDT-TTF$(ClO_4)_2$ (**2**) forms as very thin hexagonal plates and is stable in air for several months. Both salts exhibit a blue tint. The two salts are isostructural, crystallizing in the monoclinic space group $P2_1/n$. Crystallographic data for both salts are presented in Table 1. Atomic coordinates are listed in Table 2, and bond lengths and angles are presented in Table 3 for both **1** and **2**. Complete crystallographic data for **2** have been deposited previously.[13] Figure 2 shows a packing diagram for **1** including both anions and cations. All BEDT-TTF dications are equivalent and are surrounded by six counterions in a distorted octahedron. Intermolecular overlap between donor molecules is weak, and the nearest intermolecular S−S contacts are 3.620 Å in **1** and 3.621 Å in **2** from an inner ring sulfur to an outer ring sulfur on adjacent molecules.

Oxidation of BEDT-TTF results in an increase in the C−C bond lengths and a decrease in the C−S bond lengths of the fulvalene core.[10-13,25-28] This is consistent with MO calculations that show the BEDT-TTF HOMO

Table 1. Crystallographic Data

	1	**2**
A. Crystal Data (298 K)		
a, Å	5.824(1)	5.867(1)
b, Å	9.490(2)	9.579(2)
c, Å	17.593(3)	17.669(3)
β, deg	91.61(1)	92.06(2)
V, Å^3	972.0(3)	992.4(3)
d_{calc}, g cm^{-3} (298 K)	1.908	1.953
empirical formula	$C_{10}H_8S_8^{2+}(BF_4^-)_2$	$C_{10}H_8S_8^{2+}(ClO_4^-)_2$
formula wt, g	279.13	291.77
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
Z	2	2
crystal size (mm^3)	0.34 × 0.13 × 0.08	0.28 × 0.22 × 0.02
B. Data Collection (298 K)		
radiation, λ (Å)	Mo Kα, 0.710 73	
mode	ω-scan	
scan range	symmetrically over 1.2° about Kα$_{1,2}$ maximum	
background	offset 1.0 and −1.0 in ω from Kα$_{1,2}$ maximum	
scan rate, deg min^{-1}	2−4	2−4
2θ range, deg	3−50	3−50
range of hkl	$0 \le h \le 6$	$0 \le h \le 6$
	$-11 \le k \le 11$	$0 \le k \le 11$
	$-20 \le l \le 20$	$-21 \le l \le 21$
total reflections measured	3800 (2 sets)	2053
unique reflections	1710	1742
absorption coeff. μ (Mo Kα), mm^{-1}	0.99	1.21
min, max transmission	0.885, 0.936	0.787, 0.982
C. Structure Refinement		
S, goodness-of-fit	1.43	1.44
reflections used	1441, $I > 2\sigma(I)$	1385, $I > 2\sigma(I)$
no. of variables	146	162
R, wR^* (%)	4.30, 4.33	3.31, 4.07
R_{int} (%)	0.0187	0.0113
max shift/esd	0.001	0.001
min peak in diff Fourier map (e Å^{-3})	−0.20	−0.26
max peak in diff Fourier map (e Å^{-3})	0.31	0.34

[a] Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

is predominately contained within the fulvalene core and has nodes at the C−S bonds.[13,29-30] The bond lengths of the TTF core of **1** and **2** are listed in Table 4 and are compared to the bond lengths in a series of salts with different BEDT-TTF formal oxidation states. The central C−C bond, in the dication salts is long, 1.430 Å in **1** and 1.439 Å in **2**, with the latter being the longest central C−C bond observed in a BEDT-TTF cation-radical salt. The C−S bonds in **1** and **2** are shorter than the comparable bonds in salts where the BEDT-TTF oxidation state is ≤1.

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Table 2. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å²) for the Non-H Atoms of Compounds 1 and 2

atom	*x*	*y*	*z*	*U*
		Compound **1**		
S1	0.10314(13)	0.21502(8)	0.02273(5)	0.0413(2)
S2	−0.26559(13)	0.05037(7)	0.07803(4)	0.0405(2)
S3	−0.0049(2)	0.47397(8)	0.10514(5)	0.0521(3)
S4	−0.46598(14)	0.27055(8)	0.17201(5)	0.0469(3)
C1	−0.0351(5)	0.0586(3)	0.0225(2)	0.0320(8)
C2	−0.0745(5)	0.2997(3)	0.0840(2)	0.0351(9)
C3	−0.2524(5)	0.2210(3)	0.1105(2)	0.0342(9)
C4	−0.2645(13)	0.5321(6)	0.1461(6)	0.045(2)
C4′	−0.182(3)	0.5025(13)	0.1856(9)	0.046(4)
C5	−0.352(2)	0.4364(9)	0.2072(5)	0.041(2)
C5′	−0.431(3)	0.4604(13)	0.1764(13)	0.051(4)
B	0.2002(6)	0.3236(4)	0.3501(2)	0.0403(11)
F1	0.1799(4)	0.4685(2)	0.34556(13)	0.0715(7)
F2	0.0988(4)	0.2779(2)	0.41713(12)	0.0661(8)
F3	0.0981(4)	0.2607(3)	0.28799(13)	0.0757(9)
F4	0.4320(3)	0.2911(2)	0.35371(12)	0.0655(7)
		Compound **2**		
S1	0.1024(2)	0.21253(8)	0.02324(5)	0.0412(3)
S2	−0.2630(2)	0.04883(8)	0.07734(5)	0.0404(3)
S3	−0.0058(2)	0.46836(9)	0.10523(6)	0.0533(3)
S4	−0.4619(2)	0.26610(9)	0.17077(6)	0.0468(3)
C1	−0.0355(6)	0.0579(3)	0.0227(2)	0.0326(10)
C2	−0.0742(6)	0.2964(3)	0.0840(2)	0.0366(11)
C3	−0.2515(6)	0.2173(3)	0.1100(2)	0.0323(10)
C4	−0.265(2)	0.5254(8)	0.1438(9)	0.049(3)
C4′	−0.187(3)	0.498(2)	0.1844(12)	0.039(4)
C5	−0.353(2)	0.4336(10)	0.2050(8)	0.043(3)
C5′	−0.432(4)	0.453(2)	0.172(2)	0.044(5)
Cl	0.1979(2)	0.31952(8)	0.34856(5)	0.0403(3)
O1	0.1731(5)	0.4678(3)	0.3410(2)	0.0649(11)
O2	0.0939(5)	0.2740(3)	0.4169(2)	0.0614(11)
O3	0.0945(5)	0.2514(3)	0.2847(2)	0.0685(12)
O4	0.4361(5)	0.2876(3)	0.3528(2)	0.0584(10)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit-cell vectors.

Donor ion bond lengths have been used to assign oxidation states in charge transfer salts and mixed-valent cation-radical salts of BEDT-TTF.[10-13,25-28] Characterization of BEDT-TTF dication salts will now help extend these correlations to salts with oxidation states greater than +1. For example, in Table 4, bond-length correlations are used to confirm the coexistence of $BEDT\text{-}TTF^+$ and $BEDT\text{-}TTF^{2+}$ ions in the mixed-valent salts $(BEDT\text{-}TTF)_3(ZnCl_4)_2$[10] and $(BEDT\text{-}TTF)_3(MnCl_4)_2$.[12] The central C−C bond is most sensitive to changes in oxidation state,[10-13,25-28] and a bond length of 1.438 Å on one donor molecule in $(BEDT\text{-}TTF)_3(ZnCl_4)_2$ shows that the BEDT-TTF dication is present in this salt, coexisting with BEDT-TTF monocations where the central C−C bond length is 1.378 Å.

Optical Properties. Transmittance spectra for **2** were measured from 100 to 3000 cm^{-1} in two polarizations. There is no evidence for low-frequency metallic behavior in the IR. This is not surprising as the donor HOMO is fully oxidized in the dication leaving no partially filled levels in the solid. In addition, the crystal structure shows that the donor molecules are essentially isolated from one another, and intermolecular interactions are weak.

Figure 3 shows the room-temperature reflectance parallel to the *a* and *b* axes of **2** from 200 to 2900 nm. The spectra were identical for two samples, and only one set of data is shown. The fringe patterns at low energy arise from the interference of light reflected off the front and back surfaces of the very thin crystal (13.5 μm). For nonabsorbing materials, the spacing of the fringes, $\Delta\nu$, is given by $n = {}^1/_2 d\Delta\nu$, where *d* is the thickness of the sample and *n* is the refractive index.[31] Above 1200 nm, single-bounce reflectance values (shown by squares and triangles in Figure 3) were calculated using the refractive index estimated from the fringes. A fit[31] of the reflectance data to a Lorentzian model dielectric function is also plotted in Figure 3. The values

Table 3. Bond Lengths (Å) and Angles (deg) for the Non-H Atoms of Compounds 1 and 2

1	2	3	1−2	1−2−3
		Compound **1**		
C1	S1	C2	1.689(3)	96.77(14)
C2	S1		1.715(3)	
C1	S2	C3	1.684(3)	96.91(14)
C3	S2		1.718(3)	
C2	S3	C4	1.740(3)	100.7(2)
C4	S3		1.781(9)	
C2	S3	C4′		100.1(4)
C4′	S3		1.80(2)	
C3	S4	C5	1.737(3)	100.8(3)
C5	S4		1.810(9)	
C3	S4	C5′		102.3(6)
C5′	S4		1.814(13)	
C1a	C1	S1	1.430(4)	122.8(2)
C1a	C1	S2		122.0(2)
S1	C1	S2		115.2(2)
C3	C2	S1	1.369(4)	115.7(2)
C3	C2	S3		128.3(2)
S1	C2	S3		116.0(2)
S2	C3	S4		115.9(2)
S2	C3	C2		115.4(2)
S4	C3	C2		128.8(2)
C5	C4	S3	1.507(13)	114.2(5)
S4	C5	C4		114.0(6)
C5′	C4′	S3	1.51(2)	116.5(13)
S4	C5′	C4′		112.1(10)
F1	B	F3	1.382(4)	110.8(3)
F1	B	F4		107.9(3)
F2	B	F1	1.403(4)	108.6(3)
F2	B	F3		110.7(3)
F3	B	F4	1.366(4)	110.0(3)
F4	B	F2	1.385(4)	109.0(3)
		Compound **2**		
C1	S1	C2	1.688(3)	96.6(2)
C2	S1		1.717(3)	
C1	S2	C3	1.678(3)	97.0(2)
C3	S2		1.714(3)	
C2	S3	C4	1.734(3)	100.4(3)
C4	S3		1.774(12)	
C4′	S3	C2	1.81(2)	100.3(5)
C3	S4	C5	1.729(3)	101.3(5)
C5	S4		1.821(11)	
C5′	S4	C3	1.80(2)	101.7(9)
C1a	C1	S1	1.439(4)	122.1(2)
C1a	C1	S2		122.2(2)
S1	C1	S2		115.7(2)
C3	C2	S1	1.379(5)	115.5(2)
C3	C2	S3		128.4(3)
S1	C2	S3		116.1(2)
S2	C3	S4		116.3(2)
S2	C3	C2		115.2(2)
S4	C3	C2		128.5(2)
C5	C4	S3	1.50(2)	114.8(7)
C5′	C4′	S3	1.51(3)	115.(2)
S4	C5	C4		113.8(9)
S4	C5′	C4′		111.9(13)
O1	Cl	O2	1.434(3)	109.5(2)
O1	Cl	O3		110.0(2)
O2	Cl	O3	1.440(3)	110.2(2)
O2	Cl	O4		109.5(2)
O3	Cl	O4	1.421(3)	109.4(2)
O4	Cl	O1	1.430(3)	108.2(2)

(31) Wooten, F. *Optical Properties of Solids*; Academic Press: New York, 1972.

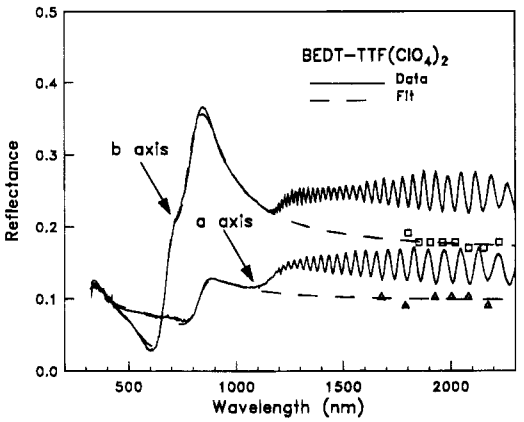

Figure 3. Optical reflectivity data from **2** polarized along the *a* and *b* axes. Lorentz fits to the data are shown as the dashed lines. Interference fringes are observed at low energy where the thin crystal becomes transparent. Squares and triangles are single-bounce reflectance values calculated as described in the text.

Table 4. Bond Lengths[a] of the TTF Core in BEDT-TTF$^{+\varrho}$ Cation-Radical Salts

compound	ϱ	bond length (Å) A[b]	B	C	D
BEDT-TTF[c]	0	1.312(12)	1.757(7)	1.754(8)	1.332(7)
$(BEDT\text{-}TTF)_2ClO_4\text{-}(TCE)_{0.5}$[d]	1/2	1.359	1.729	1.755	1.294
$(BEDT\text{-}TTF)_3(ClO_4)_2$[e]	2/3	1.366(7)	1.731(7)	1.743(5)	1.345(9)
ϵ-$(BEDT\text{-}TTF)ClO_4$[f]	1	1.390(7)	1.721(3)	1.738(4)	1.365(6)
$(BEDT\text{-}TTF)_3(ZnCl_4)_2$[g]		1.378(7)	1.721(6)	1.738(6)	1.360(6)
$BEDT\text{-}TTF(ClO_4)_2$	2	1.439(4)	1.683(3)	1.716(3)	1.379(5)
$BEDT\text{-}TTF(BF_4)_2$		1.430(4)	1.687(3)	1.717(3)	1.369(4)
$(BEDT\text{-}TTF)_3(ZnCl_4)_2$[g]		1.438(7)	1.680(6)	1.710(6)	1.369(7)
$(BEDT\text{-}TTF)_3(MnCl_4)_2$[h]		1.431	1.685	1.715	1.361
$(BEDT\text{-}TTF)_5Hg_5Br_{11}$[i]		1.43	1.68	1.71	1.34
$(BEDT\text{-}TTF)_5Hg_5Br_{11}$[i]		1.41	1.69	1.72	1.37

[a] Bond lengths are averaged assuming D_{2h} symmetry for the TTF core. [b] Bonds refer to those labeled on the structure shown in the text. [c] Reference 33. [d] Reference 34. [e] Reference 24. [f] Reference 35. [g] Reference 10. [h] Reference 12. [i] Reference 11.

Table 5. Lorentz Fit Parameters for the Measured $R(w)$ in the (001) Face of $BEDT\text{-}TTF(ClO_4)_2$

oscillator no.	w_j (cm^{-1})	w_{pj} (cm^{-1})	γ_j (cm^{-1})
	E//b		
1	11 625	15 566	2 283
2	13 992	5 918	1 813
3	31 000	22 000	7 500
	E//a		
1	11 810	6 388	2 189
2	30 430	14 914	4 146

[a] For each case, $\epsilon_\infty = 3.1$.

for the center frequency, ω_j, oscillator strength, ω_{pj}, and scattering rate, γ_j, for each band determined from the fit are listed in Table 5. Figure 4 shows the optical absorption coefficient obtained from Kramers–Kronig analysis. Two bands strongly polarized along the *b* axis are observed in the near-IR near 855 nm (11 700 cm^{-1}) and 714 nm (14 000 cm^{-1}), in agreement with the ω_j found in the fit. These transitions are probably localized excitons and not charge-transfer transitions as are sometimes observed in BEDT-TTF cation-radical salts.[32] The direction of closest contact between BEDT-TTF ions

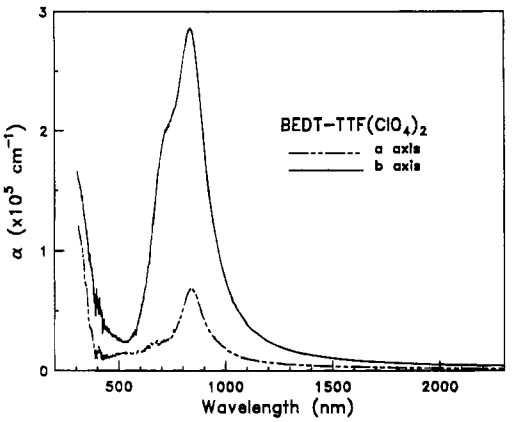

Figure 4. Polarized absorption coefficient of **2**, obtained from Kramers–Kronig analysis of the data in Figure 3.

is along the *a* axis and any intermolecular transitions are expected to be polarized along this direction. The long axis of the BEDT-TTF ion projects primarily along the *b* direction suggesting that the 855 and 714 nm bands are localized excitons polarized along the long axis of the molecule. Similar transitions are observed in monocation salts although at higher energy.[32] Some intensity is observed in the *a* polarization as a result of the monoclinic space group. The band at 323 nm (31 000 cm^{-1}) is nearly isotropic in the *ab* plane, and the high energy suggests this band is also an intramolecular excitation.

Conclusions

Dication salts of the organic donor BEDT-TTF have been isolated by first stabilizing a solution of the monocation followed by electrochemical oxidation and crystallization as the BF_4^- and ClO_4^- salts. Optical spectroscopy shows no evidence for metallic behavior in these salts which is to be expected if the singly degenerate HOMO is completely oxidized. The method of preparation appears to be general, and could be used in attempts to prepare other examples of high-oxidation state cation-radical salts. Examples where the donor oxidation state is between +1 and +2 could be particularly interesting.

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Supplementary Material Available: Anisotropic thermal parameters for the non-H atoms of **1**, fractional coordinates and isotropic thermal parameters for the H atoms of **1**, bond lengths and angles of the H atoms of **1** (2 pages); structure factor amplitudes of **1** (7 pages).

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