

TTF Derivatives Containing Phosphonic Acid Group As Potent Component for Organic-Inorganic Hybrid

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INTRODUCTION

Like ferrocene, tetrathiafulvalene (TTF) is a well-known electron donor molecule, which exhibits two reversible one-electron redox cycles.¹ The two-step redox processes are shown in *Scheme 1*. Utilizing this property, a lot of TTF derivatives have been investigated for the development of organic magnets, sensors, conducting materials, etc.¹ Various functional compounds such as thiophene,² ferrocene³ and azobenzene,⁴ containing the phosphonic acid group have been investigated for the preparation of organic-inorganic hybrid materials exhibiting catalytic activity, non-linear optical properties and photo-induced sensing. TTF amphiphiles with two phosphonic acid moieties were also investigated for the purpose of developing Langmuir-Blodgett magnetic thin films.⁵

In this study, two mono-phosphonic acid derivatives of TTF (compounds **1b** and **2b** in *Scheme 2*) are synthesized, *via* the corresponding ethyl phosphonate derivatives, and characterized spectroscopically. Their electrochemical and

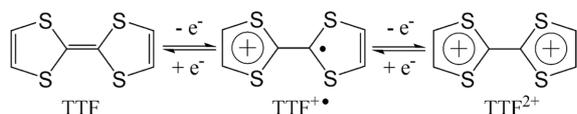
structural characterizations were also carried out. This search for a facile way of synthesizing monophosphonic acid derivatives was intended to be the first step in the preparation of zirconium phosphate-based two-dimensional magnetic materials.⁴

EXPERIMENTAL

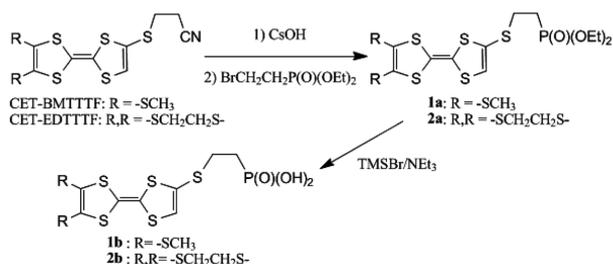
The starting materials (CET-BMTTTF⁵ and CET-EDTTTF⁶) shown in *Scheme 2* were prepared according to the previously reported methods. Cesium hydroxide monohydrate, diethyl 2-bromoethyl phosphonate, triethylamine, bromotrimethylsilane (TMSBr) and HPLC-grade organic solvents were commercially purchased and used as received.

The infrared spectra were recorded by the KBr pellet method on a Perkin Elmer Spectrum 100 in the range of 4000~400 cm⁻¹. The ¹H NMR spectra were obtained on a Bruker Avance 500 or 300 using CDCl₃ as a solvent. Electrochemical studies were carried out at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.) in a CH₂Cl₂ solution containing 0.5 mM of the sample and 0.1 M n-Bu₄NPF₆ as the supporting electrolyte, using a Pt-button (*r* = 1 mm) working electrode, Ag/AgCl reference electrode and Pt-wire (ϕ = 1 mm) counter electrode at a scan rate of 100 mV s⁻¹. All redox potentials were referenced against the standard Fc/Fc⁺ redox couple ($E_{1/2}$ = +0.504 V vs. Ag/AgCl).

Single crystals of compound **2b** suitable for X-ray structure analysis were grown by the slow-evaporation method in CDCl₃. The X-ray crystallographic data was collected at 200(2) K on a SMART APEX CCD SYSTEM (Bruker) equipped with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The structure was solved by the direct method and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program.⁷ The crystal data and



Scheme 1. Two one-electron redox processes of TTF.



Scheme 2. Synthesis of compounds **1** and **2**.

Table 1. Crystal data and structure refinement parameters for **2b**·Et₃N·H₂O

E.F	C ₁₆ H ₂₆ N O ₄ P S ₇
F.W	551.77
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	9.8469(10)
<i>b</i> (Å)	10.1450(10)
<i>c</i> (Å)	13.0893(14)
α (°)	79.241(3)
β (°)	84.258(3)
γ (°)	74.892(2)
<i>V</i> (Å ³)	1238.4(2)
<i>Z</i>	2
<i>D_c</i> (Mg/m ³)	1.480
Abs. coeff. (mm ⁻¹)	0.724
<i>F</i> (000)	576
Crystal size (mm ³)	0.21×0.17×0.06
θ range for data collec.	1.59 to 28.27°
Index ranges	-13≤ <i>h</i> ≤13, -13≤ <i>k</i> ≤13, -17≤ <i>l</i> ≤12
Reflec. Collec.	9343
Indep. Reflec.	6073 [R(int) = 0.0739]
Completeness to $\theta = 28.27^\circ$	98.8%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	6073/0/262
GOF on F ²	0.770
Final R indices [I>2σ(I)]	R1 = 0.0696, wR2 = 0.1220
Largest diff. peak and hole	0.632 and -0.642 e.Å ⁻³

structure refinement parameters for **2b**·Et₃N·H₂O are listed in Table 1. The detailed crystallographic information is available from the author on request.

Preparation of 1a To an anhydrous DMF solution (20 mL) of CET-BMTTTF (1.5 mmol, 572 mg) degassed for 30min was added dropwise to a minimum amount of a methanol solution of cesium hydroxide monohydrate (1.65 mmol, 277 mg) over a period of 20 min. During the course of this addition, the color of the solution mixture became dark (red-orange solution). After stirring this mixture for an additional 30 min, diethyl 2-bromoethyl phosphonate (1.4 mmol, 0.25 mL) was added. The resulting dark brown mixture was stirred for 3 h. The white precipitate was filtered off, and the solvent was removed in vacuo. The product was separated by column chromatography (SiO₂, acetone: diethyl ether=3:2) as orange-brown oil. Yield: 62% (425 mg), ¹H NMR (300 MHz, CDCl₃, ppm) 6.44 (1H, CH, s), 4.15-4.06 (4H, CH₂, m), 2.99-2.90 (2H, SCH₂, m) 2.43 (6H, SCH₃, s), 2.17-2.02 (2H, CH₂P, m), 1.36-1.32 (6H, CH₃, t), FT-IR (KBr, cm⁻¹) 2982, 2921 (-CH₃,

-CH₂CH₂-), 1477, 1424, 1391, 1368 (-CH₂S-), 1243 (P=O), 1054, 1027, 964 (P-OEt), 888 (asym S-C-S str), 784, 771 (P-C), 528 (R(RO)₂P=O).

Preparation of 2a Compound **2a** was prepared by the same method as that employed for compound **1a** using DMF (25 mL), CET-EDTTTF (0.70 mmol, 265 mg), CsOH (0.77 mmol, 129 mg), and diethyl 2-bromoethyl phosphonate (0.77 mmol, 0.14 mL). Yield: 92% (318 mg), ¹H NMR (300 MHz, CDCl₃, ppm) 6.44 (1H, CH, s), 4.17-4.06 (4H, CH₂, m), 3.26 (4H, CH₂CH₂, s) 2.98-2.93 (2H, SCH₂, m), 2.13-2.02 (2H, CH₂P, m), 1.36-1.31 (6H, CH₃, t), FT-IR (KBr, cm⁻¹) 2980, 2926, 2853 (-CH₂CH₂-), 1716 (C=C), 1463, 1442, 1411, 1391, 1367 (-CH₂S-), 1241 (P=O), 1056, 1028, 961 (P-OEt), 886 (asym S-C-S str), 803, 772 (P-C).

Preparation of 1b and 2b Triethylamine (0.58 mL, 28 eq.) was added to a dichloromethane solution (4 mL) of **1b** (0.15 mmol, 74 mg) or **2b** (0.15 mmol, 73 mg), to which TMSBr (0.56 mL, 28 eq.) was slowly added from a syringe. During this addition, a white precipitate became evident in the flask. After stirring for 2 h, the solution was concentrated in vacuo and methanol (4 mL) was added to the resulting residue followed by additional stirring for 4 h. The product was concentrated in vacuo, dissolved in dichloromethane, and extracted by distilled de-ionized water. The extraction procedure using dichloromethane resulted in the product being obtained as orange brown oil. Single crystals of **2b** were obtained in CDCl₃.

1b: Yield: 54%, ¹H NMR (500 MHz, CDCl₃, ppm) 10.72 (2H, OH, br), 6.26 (1H, CH, s), 3.11 (2H, SCH₂, br) 2.44 (6H, SCH₃, s), 2.02 (2H, CH₂P, br), FT-IR (KBr, cm⁻¹) 2972, 2919 (-CH₃, -CH₂CH₂-), 2687 (P-OH), 1735 (C=C), 1456, 1428 (-CH₂S-), 1291 (P=O), 1159 (P-O-H), 1047, 935 ((OH)₂P=O), 804 (asym S-C-S str), 771 (P-C).

2b: Yield: 77%, ¹H NMR (500 MHz, CDCl₃, ppm) 11.84 (2H, OH, br), 6.36 (1H, CH, s), 3.29 (4H, CH₂CH₂, s), 3.02-2.99 (2H, SCH₂, m), 1.98-1.91 (2H, CH₂P, m), FT-IR (KBr, cm⁻¹) 2977, 2928 (-CH₂CH₂-), 2678 (P-OH), 1488, 1452, 1422, 1392 (-CH₂S-), 1287 (P=O), 1126 (P-O-H), 1073, 1061, 939, 920, 893 ((OH)₂P=O), 835, 804 (asym S-C-S str), 771 (P-C).

RESULTS AND DISCUSSION

The TTF derivatives with ethylcyanide groups (CET-BMTTTF and CET-EDTTTF) synthesized by the phosphite-based cross-coupling reaction⁶ were transformed into the corresponding diethyl phosphonate derivatives (**1a** and **2a**, respectively). Subsequently, their treatment with

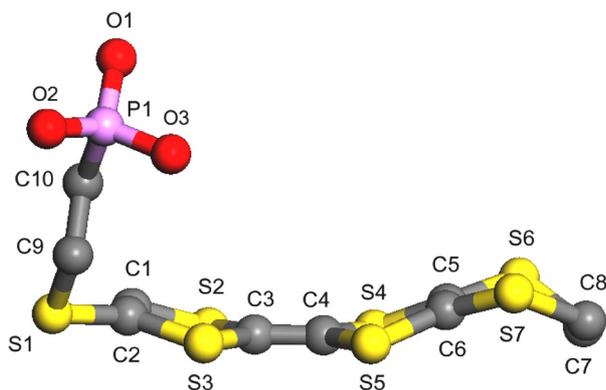


Fig. 1. Molecular structure of **2b** with numbering scheme. The hydrogen atoms and solvated molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): C1-C2 1.323(9), C3-C4 1.351(8), C5-C6 1.340(8), C7-C8 1.415(10), C9-C10 1.511(9), C10-P1 1.809(7), P1-O1 1.493(5), P1-O2 1.507(5), P1-O3 1.552(5), C4-C3-S2 123.3(5), C4-C3-S3 122.3(5), S2-C3-S3 114.4(4), C3-C4-S5 124.2(5), C3-C4-S4 121.9(5), S5-C4-S4 113.9(4), O1-P1-O2 115.5(3), O1-P1-O3 110.1(3), O2-P1-O3 109.9(3).

TMSBr in the presence of triethylamine afforded the phosphonic acid derivatives (**1b** and **2b**, respectively). The isolated compounds were identified with ^1H NMR and FT-IR spectroscopies.

Single crystals of **2b** were grown and its crystal structure was analyzed by the X-ray diffraction method. The molecular structure of **2b** (Fig. 1) shows that the TTF moi-

ety is slightly folded-up with the peripheral ethylene moiety folded downwards and the ethylphosphonic acid moiety is approximately vertical to the EDTTTF plane. The intramolecular bond lengths and angles fell in the range of their averaged values.⁸ Only one intermolecular interaction shorter than the sum of their van der Waals radii (3.70 Å)⁸ is observed, viz. S4...S5* (3.583 Å; *-x+1, -y+1, -z).

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements of **1b** and **2b** were performed and their parameters are listed in Table 2. The two compounds show the same redox behavior, exhibiting two reversible redox-cycles (Fig. 2) at almost the same potentials. These cycles are undoubtedly attributable to the two redox-steps of the TTF moiety. The half-wave potentials of the EDTTTF moiety in **2b** ($E_{1/2}^1=0.610$ V and $E_{1/2}^2=1.035$ V) are slightly more anodic than those of BMTTTF (0.608 V and 1.000 V), possibly due to the additional peripheral 6-membered ring.

In summary, two TTF derivatives with the mono-phosphonic acid group, which can be utilized as a potent component for functional organic-inorganic hybrids such as zirconium phosphate, were successfully synthesized in a facile way of reacting the corresponding ethyl phosphonate with bromotrimethylsilane (TMSBr) and triethylamine, and characterized by ^1H NMR and FT-IR spectroscopies. Their electrochemical properties also indicate the pres-

Table 2. The CV parameters (in V) of **1b** and **2b**.^a

Compound	E_{pa}^1	E_{pa}^2	E_{pc}^1	E_{pc}^2	$E_{1/2}^1$ ^b	$E_{1/2}^2$ ^b
1b	0.665	1.058	0.550	0.941	0.608	1.000
2b	0.674	1.100	0.545	0.970	0.610	1.035

^aThe samples are dissolved in CH_2Cl_2 containing 0.1 M TBA- PF_6 electrolyte and analyzed using a scan rate of 0.1 V/s, Pt-disk working electrode, Pt-wire counter electrode, and Ag/AgCl ref. electrode. All potential values are referenced to the Fc/Fc⁺ couple ($E_{1/2} = +0.504$ V).

^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$

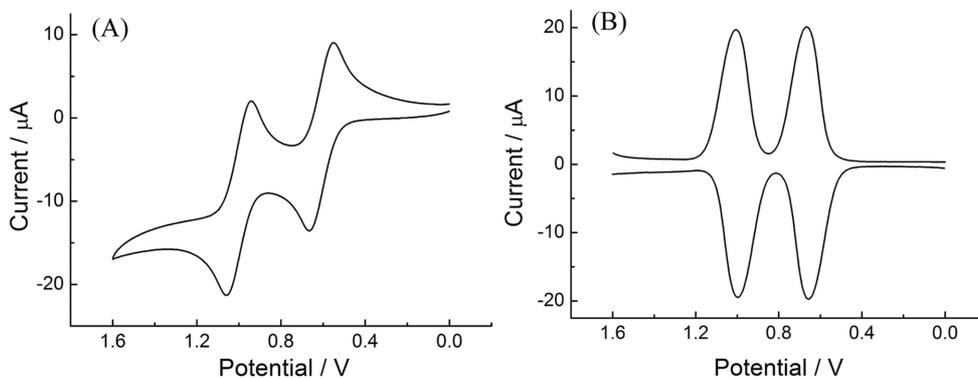


Fig. 2. The CV (A) and its DPV (B) of **1b** measured in CH_2Cl_2 (Fc/Fc⁺=0.504 V vs. Ag/AgCl). Compound **2b** shows identical patterns in its CV and DPV to those of **1b**.

ence of the TTF moiety in the compounds. One of the compounds was also analyzed by the X-ray diffraction method.

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