

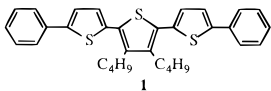
Single-Crystal X-ray Structure of the Cation Radical of 3',4'-Dibutyl-2,5''-diphenyl-2,2':5',2''-terthiophene: Definitive Evidence for π -Stacked Oxidized Oligothiophenes

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A popular model for the electrical conductivity of oxidatively doped polymers like polythiophene and polypyrrole suggests that conduction results when polarons (cation radicals) and bipolarons (dications) migrate along the conjugated polymer chain.¹ In 1992, we suggested² that cation radical π -dimers were a structural alternative to bipolarons and that these diamagnetic π -dimers provided a mechanism for interchain charge transport. Since that time spectroscopic evidence has accumulated from studies^{3–8} of oxidized oligomers to support the importance of interchain π -dimers and π -stacks, and it has been shown that oxidized oligomers are, indeed, electrically conductive.^{3b,c} Conspicuously absent, however, is an X-ray diffraction structure conclusively demonstrating a π -stack structure. We now report the synthesis, single-crystal X-ray structure, and electrical conductivity of the radical cation of 3',4'-dibutyl-5,5''-diphenyl-2,2':5',2''-terthiophene **1**.



1 was synthesized via a sequence of Ni-catalyzed ring couplings of brominated precursors.⁹ The capped and sterically stabilized compound, which is soluble in most common organic solvents, was characterized by ¹H NMR, UV–vis–IR, and

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(9) Experimental procedures and characterization of **1** and $[1^+]\text{PF}_6^-$ are available as supporting information.

elemental analysis.⁹ A cyclic voltammogram of a 0.55 mM solution of **1** in 0.1M (tbaPF₆)/dichloromethane (tba = tetrabutylammonium) exhibits two reversible one-electron processes with $E^{\circ}_{1+/0} = 0.89$ V and $E^{\circ}_{2+/1+} = 1.29$ V (vs Ag/AgCl; glassy carbon electrode). The formation of a blue/green solution near the electrode surface when the electrode was poised at potentials positive of the first process suggested that the radical cation species was relatively stable and might be isolated as the PF₆⁻ salt.

Hexafluorophosphate salts of the cation radical **1**⁺ were synthesized by chemical oxidation of **1** with NOPF₆ and by electrochemical oxidation.⁹ When a benzene solution of **1** was treated with 1 equiv of NOPF₆ in acetonitrile, a dark purple solid was isolated from the reaction mixture in 87% yield. Characterization of this material is consistent with its formulation as $[1^+]\text{PF}_6^-$. Electrochemical oxidation of **1** at 10 $\mu\text{A}/\text{cm}^2$ in 2:1 mixtures of benzene:dichloromethane with tbaPF₆ as the supporting electrolyte produced a crystalline coating of dark purple solid on the surface of the platinum foil electrode. The purple solid did not passivate the electrode, and millimolar quantities of the compound were produced by this method. Redissolving the solids produced chemically or electrochemically in dichloromethane gave vis–near-IR spectra, ($\lambda_{\text{max}} = 655$ and 1105 nm), similar to those of other α -capped oligothiophene cation radicals;^{2–7} these spectra suggested that the solids were the salt $[1^+]\text{PF}_6^-$. The locations of the these two bands in the vis–near-IR region are more similar to alkyl substituted oligothiophene cation radicals with three thiophene rings ($\lambda_{\text{max}} = 580–620$, 890–939 nm)^{2,4a,6a} than those with four ($\lambda_{\text{max}} = 670–693$, 1117–1181 nm)^{4a,6a} or five ($\lambda_{\text{max}} = 725–756$, 1252–1393 nm)^{4a,6a} rings. Attenuated total reflectance and transmission spectra of the solids taken on CaF₂ disks showed additional strong absorptions in the near-IR extending into the IR, as expected for a structure containing delocalized stacks of cation radicals.^{3b,c}

Electrocrystallization with the above electrolyte solution, a Pt wire electrode, and a current of 160 $\mu\text{A}/\text{cm}^2$ produced needle-like crystals (C2/c space group¹⁰) of $[1^+]\text{PF}_6^-$. Examination of atomic occupancy factors suggests there is no deviation from the stoichiometry (i.e. partial oxidation) suggested by the formula. The structure consists of columnar stacks of **1**⁺ cations and channels, which contain the PF₆⁻ anions, parallel to the needle axis (the (001) direction) of the crystals (Figures 1 and 2). The thiophene rings adopt a transoid orientation for the sulfur atoms; both the thiophene and phenyl rings form a nearly perfect planar structure. The planar cations overlap in π -fashion with the nearest neighboring cations in the unit cells above and below to form the infinite stacks. In the plane perpendicular to the stacking direction, the cations form sheets that exhibit no unusually close contacts between cations in the same layer. The partially disordered butyl groups are arranged in a manner to form the channels occupied by the PF₆⁻ anions.

The interplanar contact distance between the cations (3.47 Å) is somewhat longer than we expected, but it is still consistent with bonding between molecules in the stack.¹¹ Significantly, the stacks are only slightly slipped along the packing direction

(10) Crystal data for $[1^+]\text{PF}_6^-$: MW = 657.73, C₃₂H₃₂F₆PS₃, dark purple needles (green reflectance) (0.52 × 0.156 × 0.13 mm), monoclinic, space group C2/c, $a = 18.0188(3)$ Å, $b = 20.6230(3)$ Å, $c = 8.4926(2)$ Å, $\alpha = 90^\circ$, $\beta = 91.009(1)^\circ$, $\gamma = 90^\circ$, $V = 3155.4(1)$ Å³, $\rho_{\text{calc}} = 1.385$ Mg m⁻³, $Z = 4$; $2\theta_{\text{max}} = 50.04^\circ$; Mo K α radiation ($\lambda = 0.71073$ Å), $T = 293(2)$ K. X-ray data were collected using the Siemens SMART system, and the structure was solved via direct methods. Full matrix least-squares refinement on F² with SHELXTL-V5.0 converged with R = 0.0727 and wR² = 0.2148 for 2791 independent reflections with $I > 2\sigma(I)$ and 199 parameters and 12 restraints.

(11) This contact distance is slightly shorter than the 3.5 Å reported for a neutral oligothiophene (3,3''-dimethoxy-2,2':5',2''-quaterthiophene) that exhibits a slipped stack structure. See: Miller, L. L.; Yu, Y. *J. Org. Chem.* **1995**, *60*, 6813.

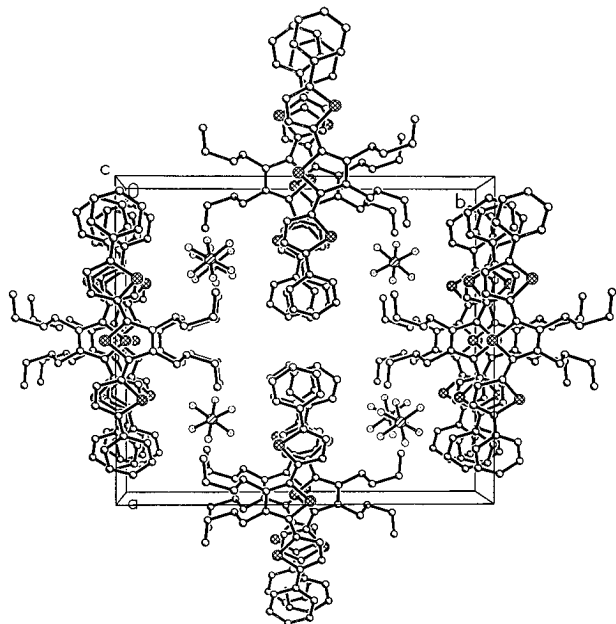


Figure 1. View down the slipped packing direction (*c* axis) showing the channels for the PF_6^- anions formed by the butyl group packing.

so that there is still extensive intermolecular overlap. In comparison, neutral oligothiophenes, including **1**, do not have extensive intermolecular contacts. This intermolecular bonding leads to the near-IR spectral results above and to electrical conductivity.

Pressed pellets of the chemically oxidized or electro-oxidized salts gave four probe conductivities at room temperature of $1-3 \times 10^{-3}$ S/cm; two probe single-crystal measurements gave $\sigma = 10^{-2}$ S/cm along the needle axis which corresponds to the stack axis. Similar pressed pellet values have been reported for other oligothiophene radical cation salts.^{3b,c} The oligomer data²⁻⁸ form a consistent set, and with the X-ray structure in hand it is now established that cation radicals of these oligomers

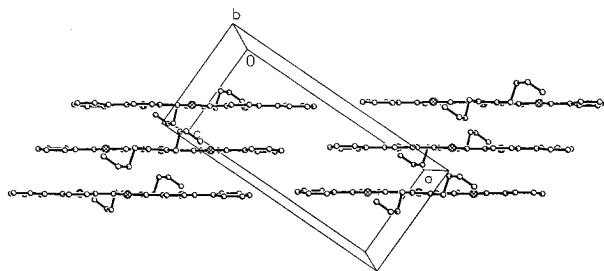


Figure 2. View of the packing structure of $[1^+]\text{PF}_6^-$ parallel to the *ac* plane normal; PF_6^- anions left out for clarity.

form stacks in solution and the solid state and that these stacks are conductive. We note further that since a polymer containing oxidized oligothiophene units alternating with aliphatic units in the main chain¹² gives $\sigma = 0.8$ S/cm², the importance of stack conductivity in polymers is also now clear. Finally, we suggest that single-crystal samples in which extended conjugated chains run perpendicular to a stack structure present some interesting, as yet unstudied, possibilities for nonpolymeric conductors.

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Supporting Information Available: Experimental procedures and analytical data for **1** and 1^+ ; Full details of the X-ray crystal structure of $[1^+]\text{PF}_6^-$ including structure determination summary and tables listing positional parameters, isotropic and anisotropic displacement parameters, and bond lengths and angles; Ortep diagrams that show the atomic numbering scheme and a stereoview (19 pages). Ordering information is given on any current masthead page.

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