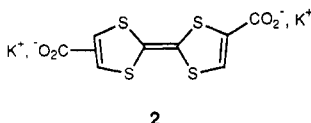
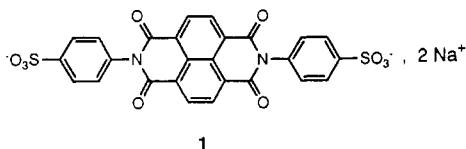


Tetrathiafulvalene  $\pi$ -Stacks in WaterMichael E. Benz, Ibro Tabakovic, and  
Larry L. Miller\*Department of Chemistry, University of Minnesota  
Minneapolis, Minnesota 55455

Received November 23, 1993

Revised Manuscript Received February 8, 1994

In this study we set out to discover an example of the solution-phase self-assembly of cation radicals into  $\pi$ -stacks.  $\pi$ -Stacks of this kind are the structural entities responsible for the electrical conductivity of most crystalline molecular conductors,<sup>1</sup> and such a discovery would have significance for understanding both self-assembly and molecular conductors. Furthermore, we believe that studies of solution  $\pi$ -stacks, which are unconstrained by crystal forces, will lead to the preparation of several new types of conductive materials. Because the archetypical conductive structure is a stack of oxidized tetrathiafulvalene (TTF) molecules and some of the most interesting results concern oxidized TTF derivatives,<sup>1</sup> we focused attention on such compounds. Previous studies<sup>2</sup> have identified a  $\pi$ -dimer of the TTF cation radical (TTF<sup>+</sup>)<sub>2</sub>, but no evidence for TTF  $\pi$ -stacks in solution exists.<sup>3</sup> Publications<sup>5</sup> from this laboratory elucidated solution-phase anion radical  $\pi$ -stacks from diimide derivatives such as 1<sup>-</sup>. This singular case is



not well connected to the large literature on conducting salts, and it seemed appropriate to use a TTF derivative to make this connection. We also anticipated the advantage of air stability from TTF cation radicals, a quality that imide anion radicals lack. Our anion radical studies showed among other things that (1) water was a necessary solvent for forming stacks and (2) near-infrared (NIR) absorption bands (optical conduction bands) provided a signature for these aggregates which have electrons delocalized intermolecularly along the stack direction. On this basis we chose to study the water-soluble dipotassium

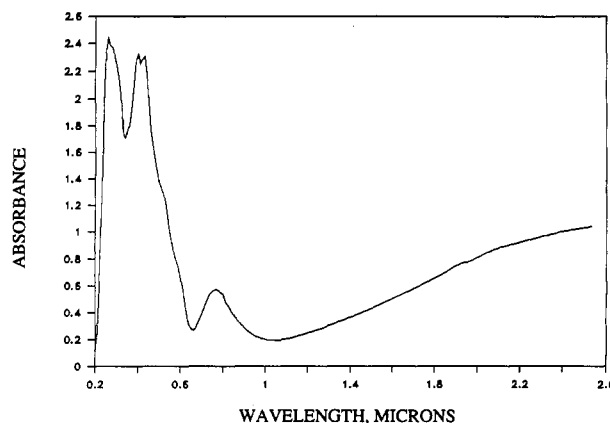


Figure 1. UV-vis-NIR spectrum of 2<sup>+</sup>, 5 mM in D<sub>2</sub>O. Oxidized by bulk electrolysis without added electrolyte.

tetrathiafulvalene dicarboxylate 2 and to focus attention on optical spectroscopy.

Compound 2,<sup>6</sup> synthesized from the diester, was dried and stored in the dark, under vacuum to prevent air oxidation. Dissolved in D<sub>2</sub>O (H<sub>2</sub>O has strong overtones in the NIR), it was oxidized with 0.5 mol equiv of the two-electron oxidant, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, or by preparative one-electron oxidation at a platinum electrode in D<sub>2</sub>O, with or without 0.01 M K<sub>2</sub>SO<sub>4</sub>. Similar spectra for the cation radical were obtained using the two oxidation methods. In both cases reduction (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> or cathodic) regenerated neutral 2 in high yield. The optical spectra from coulometric oxidations without added electrolyte indicated that below 0.06 mM 2 in D<sub>2</sub>O the cation radical 2<sup>+</sup> was present in monomeric form with  $\lambda_{\max}$  600 and 429 nm. Oxidation of the 2 diacid in DMF gave a similar spectrum. At higher concentration in D<sub>2</sub>O there was a new band at 764 nm, which was assigned to a  $\pi$ -dimer by comparison with (TTF<sup>+</sup>)<sub>2</sub> ( $\lambda_{\max}$  714 nm).

At concentrations above 2 mM the spectral shape again changed as a new, intense NIR-IR band grew in at about 2400 nm (the maximum is obscured by solvent absorption) at the expense of the monomer and dimer bands. We propose that this band is due to  $\pi$ -stacks of 2<sup>+</sup>. NIR absorbance at such long wavelengths can be best explained by excitation of a valence electron along a delocalized stack, an excitation that corresponds to the electrical conductivity along stacks in solids.

In experiments in which chemical oxidations were sequentially performed to varying extents (0.5, 0.6, 1.0, 1.2 electrons/molecule) or in which solutions coulometrically oxidized to 1 electron/molecule were diluted it was shown that the  $\lambda_{\max}$  values of these two bands were independent of concentration (Figure 1). Thus, the preliminary indication is that one kind of  $\pi$ -stack (or a specific mixture) formed, and there was no evidence for the formation of mixed valence aggregates when 2 was partially oxidized or overoxidized. In further experiments it was found that addition of surfactant converted stacks to dimers.

The monomer, dimer, stack scheme outlined above is in agreement with cyclic voltammetry (CV, Figure 2) and

(1) (a) Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic Press: Orlando, FL, 1987. (b) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 1-3.

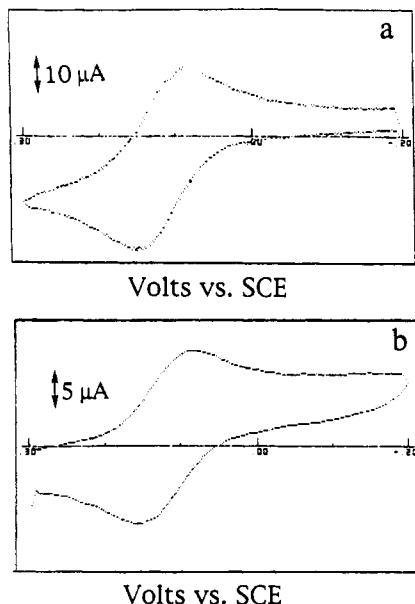
(2) Torrance, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. E. *Phys. Rev. B* 1979, 19, 730.

(3) Attention is drawn to solution-phase self-assembled  $\pi$ -stacks of porphyrins and to discotic liquid crystals.<sup>4a</sup> To our knowledge, there is only one example of a cation radical liquid crystal.<sup>4b</sup>

(4) (a) Wegner, G. *Ber. Bunsen-Ges. Phys. Chem.* 1991, 95, 1326. Pasternack, R. F.; Giannetto, A.; Pagano, P.; Gibbs, E. J. *J. Am. Chem. Soc.* 1991, 113, 7799. (b) Saeva, F. D.; Reynolds, G. A.; Kaszczuk, L. *J. Am. Chem. Soc.* 1982, 104, 3524.

(5) (a) Penneau, J.-F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem. Mater.* 1991, 3, 791. (b) Zhong, C. J.; Kwan, W. S. V.; Miller, L. L. *Chem. Mater.* 1992, 4, 1423.

(6) Melby, L. R.; Hartzler, H. D.; Sheppard, W. A. *J. Org. Chem.* 1974, 39, 2456. The dicarboxylate may be a mixture of "cis and trans" isomers, since HPLC shows two peaks. We expect that the cation radical will undergo cis-trans isomerization and have reserved for the future an elucidation of this stereochemical point.



**Figure 2.** (a) CV of 1 mM **2**, D<sub>2</sub>O-0.01 M K<sub>2</sub>SO<sub>4</sub>, scanned from -0.2 to 0.3 V at 100 mV/s, glassy carbon electrode. (b) CV of 1 mM **2**<sup>+</sup>, D<sub>2</sub>O-0.01 M K<sub>2</sub>SO<sub>4</sub>, scanned from 0.3 to -0.2 V at 100 mV/s, glassy carbon electrode.

ESR studies. CV showed fully reversible one-electron oxidation starting from **2**, but when **2**<sup>+</sup> was generated coulometrically and then studied, the cathodic peak current decreased by about 50% and the peak was slightly broadened, as if aggregated cation radical species were present that diffused more slowly and reduced at more negative potentials than the monomeric **2**<sup>+</sup>. ESR in dilute D<sub>2</sub>O showed the expected three-line spectrum for monomeric **2**<sup>+</sup>. As concentration increased the spin count (percent of **2**<sup>+</sup> as radical) went down as  $\pi$ -dimers and stacks formed. At 4 mM 23% of **2**<sup>+</sup> was ESR active.

The NIR band found in solution is similar to those found for oxidized TTF in infinite stacks,<sup>2</sup> truncated stacks,<sup>7</sup>

polymeric materials,<sup>8</sup> and films.<sup>9</sup> These bands in the solid-state materials are proposed<sup>2</sup> to arise from intermolecular excitation along mixed-valence stacks. We propose that similar stacks are present in solution and give rise to NIR "optical conduction bands", but it appears that the solution stacks are not mixed valent. Comparison of the data for **1**<sup>-</sup> and **2**<sup>+</sup> shows interesting differences. (**1**<sup>-</sup>)<sub>2</sub> absorbs in the NIR at 1140 nm and the  $\pi$ -stacks appear nearby at 1300-1800 nm. (**2**<sup>+</sup>)<sub>2</sub> absorbs in the visible (770 nm), and the  $\pi$ -stack absorbance is far removed in the spectrum (2400 nm). This suggests that the structures (geometry, size, or bonding) of the two stacks are quite different.

Solids formed by precipitation of **2**<sup>+</sup> and polymers containing **2**<sup>+</sup> are electrically conductive<sup>10</sup> and also have a NIR-IR band ( $\lambda_{\text{max}}$  2500 nm). Future studies will attempt to define the structure, understand the differences between **1**<sup>-</sup> and **2**<sup>+</sup>, and use these air-stable stacks of **2**<sup>+</sup> to form anisotropic conducting polymers<sup>11</sup> and other unusual materials.

**Acknowledgment.** This work was supported by the National Science Foundation. ESR and solid-state measurements were made by Yaoliang Hong.

(7) (a) Maceno, G.; Garrigou-Lagrange, Ch.; Delhaes, P.; Bechtel, F.; Bravic, G.; Gaultier, J.; Lequan, M.; Lequan, R. M. *Synth. Met.* **1988**, *27*, B57. (b) Ouahab, L.; Fettouhi, M.; Halet, J. F.; Yartsev, V. M.; Garrigou-Lagrange, Ch.; Delhaes, P.; Sourisseau, C. *New J. Chem.* **1993**, *17*, 399. (c) Garrigou-Lagrange, Ch.; Rozanski, S. A.; Kurmoo, M.; Pratt, F. L.; Maceno, G.; Delhaes, P.; Lequan, M.; Lequan, R. M. *Solid State Commun.* **1988**, *67*, 481.

(8) (a) Kaufman, F. B. *IBM J. Res. Dev.* **1981**, *25*, 303. (b) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1980**, *102*, 483.

(9) Cooke, G.; Dhindsa, A. S.; Song, Y. P.; Williams, G.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K.; Petty, M. C.; Yarwood, J. *Synth. Met.* **1993**, *55-57*, 3871.

(10) Unpublished work of M. E. Benz and Y. Hong. A pressed pellet containing precipitated **2**<sup>+</sup> has  $\sigma$  0.5 S cm<sup>-1</sup>; a film of 10% **2**<sup>+</sup> in poly(vinyl alcohol) has  $\sigma$  10<sup>-3</sup> S cm<sup>-1</sup>. These conductivities are primarily electronic, not ionic (ohmic, no polarization).

(11) Miller, L. L.; Zhong, C. J.; Kasai, P. *J. Am. Chem. Soc.* **1993**, *115*, 5982.