

Electrochemistry of Novel Phenylene-Bridged Bispyridiniums

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Stable organic redox couples are of interest for a wide variety of applications, ranging from biosensors to electrocatalysis and beyond. In this study, novel phenylene-bridged bispyridinium salts, with the general structure shown in Figure 1, have been synthesized via reaction of the corresponding bispyryliums with appropriate amines, and the products characterized by HPLC/MS and NMR.

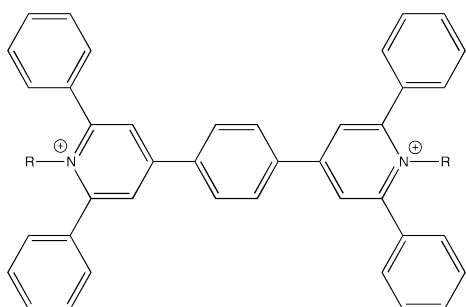


Figure 1: General Structure of bispyridinium ditriflate.

An investigation of the electrochemical properties of these compounds reveals interesting and unexpected behavior that is highly structure dependent. The number of electrons, reduction potential and number of reductions vary with both the electronic and steric properties of the nitrogen constituent and will be discussed in more detail during the presentation.

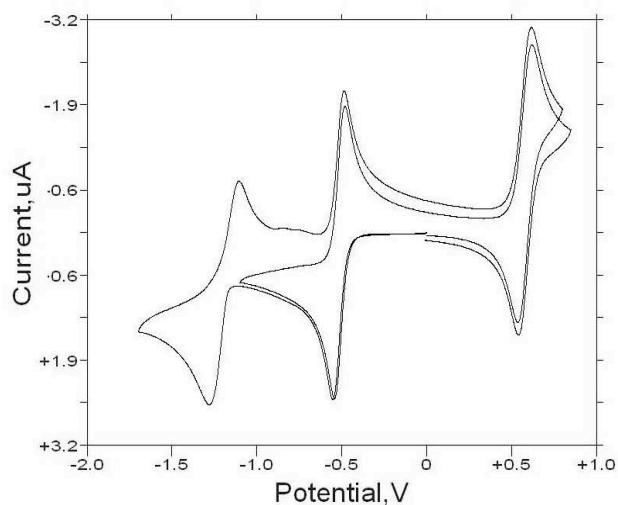


Figure 2: Cyclic voltammograms of bispyridinium (R=phenyl). The first reduction is completely reversible, while the second reduction is clearly more complicated. Couple at ca. +0.5 V is ferrocene.

Typical voltammograms are shown in Figure 2. We hypothesize that the first cathodic wave represents an overall two-electron process, but consists of two sequential one-electron reductions, with a conformational change (planarization around the central phenylene) occurring after the first. In this case, then, the addition of the second electron is thermodynamically favored because of the ability to assume a quinoidal structure. Rigorous

computations performed by Fortage et al.¹ have shown that the analogous model compounds containing a single pyridinium undergo a pyramidalization of the heterocyclic nitrogen upon reduction, and we believe a similar rearrangement is occurring here.

The potential at which the second cathodic peak is observed depends strongly on the nitrogen substituent. The presence, location, and reversibility of the second reduction depend on the electronic and steric properties of the R group.

The triflate salt gives good solubility in many common polar organic solvents, and it can be metathesized to other salt forms giving it a wide range of solubility options. The tunable electronic properties, reversible reductions, and good solubility make these bispyridiniums interesting candidates for both electronic and optoelectronic applications.

1) Fortage, J.; Peltier, C.; Perruchot, C.; Takemoto, Y.; Teki, Y.; Bedioui, F.; Marvaud, V.; Dupeyre, G.; Pospisil, L.; Adamo, C.; Hromadová, M.; Ciofini, I.; Lainé, P.P. *J. Am. Chem. Soc.* **2012** 134 (5), 2691-2705