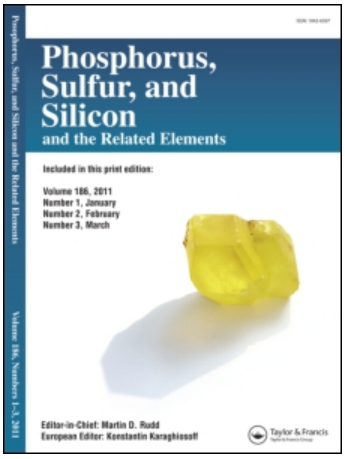

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Recent Results in the Preparation of Molecular Conductors Based on P-Type Doped π-Radicals

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RECENT RESULTS IN THE PREPARATION OF MOLECULAR CONDUCTORS BASED ON P-TYPE DOPED π-RADICALS

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Abstract The p-type doping of neutral polyfunctional π-radicals with iodine has revealed interesting electronic and structural features. Alternative preparative routes such as electrocrystallization have allowed the isolation of compounds not normally obtainable via sublimation methods.

INTRODUCTION

We are interested in the design of molecular conductors based on neutral π-radicals. This approach is hampered by the fact that materials based on neutral radicals give rise to a half-filled energy band (Figure 1A) which, in a one-dimensional arrangement, is prone to a Peierls distortion (Figure 1B), essentially a dimerization driven by charge density waves (CDWs). This distortion results in a loss of conductivity.[1] However, p-type doping of the radicals depletes the energy band away from the half-filled level and stabilizes the metallic state (Figure 1C). Recently we have investigated the use of halogens as dopants, and have prepared several mixed valent salts based on the bifunctional 1,2,3,5-dithiadiazolyl radicals **1**, **2**, **3** and **4** (E = S).[2]

THERMAL AND ELECTROCHEMICAL DOPING

The doped materials can be prepared by cosublimation of the neutral radical and halogen along carefully controlled temperature gradients. As an alternative method electrocrystallization is now being employed to isolate compounds that normally break down under the harsh thermal conditions required for sublimation. Iodine doped derivatives of the

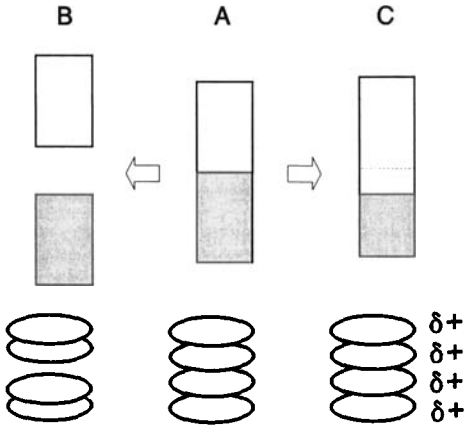
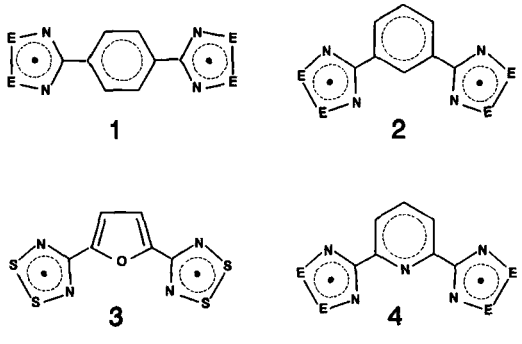


FIGURE 1 (A) Half-filled energy band associated with a uniformly spaced one-dimensional array of radicals. (B) Band gap produced by Peierls distortion. (C) Stabilization of uniform stacking by p-type doping.

The crystal structures (293K) of the doped materials consist of stacks of evenly spaced diradicals linked by disordered iodines. The compounds are metallic at room temperature, but upon cooling a CDW-driven instability causes a sharp decrease in conductivity.



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