

Electrochemical behaviour of some BEDT-TTF and TTF derivatives

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Abstract

The electrochemical behavior of eight bis(ethylenedithio)tetrathiafulvalene and three tetrathiafulvalene derivatives has been investigated to explore the influence of electron withdrawing and donating groups attached to the peripheral dithiin and thiophene rings.

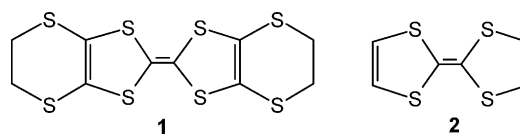
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1. Introduction

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) **1** derivatives have been studied extensively due to their ability to form both stable cation and dication radicals with mono anions and electron acceptors such as tetracyanoquinodimethane (TCNQ), which makes the molecule acquire metallic behaviour. Such cations exhibit superconducting, conducting and semiconducting properties [1–6], and can form Lagmuir–Blodgett (LB) films, which can be utilized in the field of organic conductors as well as in the production of sensors and electrochemical storage devices [7–14]. This wide range of application possibilities has led research groups to synthesize the derivatives of BEDT-TTF. Particular attention has been devoted to the preparation of systems having increased conjugation and functional groups for intermolecular hydrogen bonding, which would allow an increase in the stability of the cation radical and control the intermolecular architecture in the material, respectively [2,7]. Although the effects of various peripheral functional groups on the electrochemical behaviour of the tetrathiafulvalene **2** systems have been

widely investigated [7,15–17], there are limited examples for BEDT-TTF systems. The most recent example available in the literature is a report of the effects of amphiphilic and non-amphiphilic long chains at the peripheral sulfur atoms of BEDT-TTF on its redox properties [18].



Here, we present a detailed electrochemical study of some BEDT-TTF and TTF derivatives, containing various electron donating or withdrawing peripheral groups, which were prepared by employing a recently developed 1,8-diketone ring closure reaction using Lawesson's reagent (LR) or P₄S₁₀ (Tables 1 and 2) [19–21]. Using such a reaction as a tool, substituted dithiin or thiophene rings were easily introduced into the TTF system of compounds **3–13**, including the fully unsaturated BEDT-TTF derivatives, **7–10** (see Scheme 1).

It is obvious that having an additional double bond at the ethylene bridge, in most cases in conjugation with a phenyl ring, could be an advantage in stabilizing the radical cations in charge transfer salts. The same advantage could be seen for the systems where fused thiophene rings are incorporated in conjugation with

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