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TTF derivative of 2,5-aromatic disubstituted pyrrole, synthesis and electronic study

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ABSTRACT

TTF derivative of substituted pyrrole was obtained by means electrochemical synthesis, the resultant colored mix was characterized by Mass spectrometry, NMR and EPR studies, its intrinsic electronic behavior was measured by a four point probe method, besides theoretical calculations were carried out on the possible structures of the resultant molecular adduct. All the results show that there is a net transfer of an electron between both organic moieties in solution giving place to a semiconductor species.

1. Introduction

The study of electronic materials has been growing and opening new important areas [1–3], the study of this kind of compounds takes account mainly on the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and the orbital interactions. These last interactions are fundamental for the communication between two different pair of molecules that can show interesting electronic interchanges [4].

The combination of TTF (tetrathiafulvalene) (Fig. 1) with several organic molecules showing electron donor-acceptor and charge transfer complexing abilities has given place to several interesting chemical mixes with important semiconducting behavior [3–7].

TTF molecule is known since 1970 [8–10] and one of the groups interested in its synthesis was the one to find the very important redox behavior of this substance [10]. The authors [10] suggest for the first time that the molecule can reach an aromatic situation on the consecutive lack of two electrons (Fig. 2), therefore, this ion can interact with an electron acceptor counterpart in such a way that the HOMO of TTF and the LUMO of the other species give place to an electronic flux making a redox complex with semiconductor behavior. One of the most studied pairs is that in which TTF interacts with TCNQ [11] which has demonstrated a very good organic semiconductor behavior; however, this is only one example of a large quantity of combinations with interesting electronic characteristics [12].

In other context, the synthesis, characterization and study of the semiconductor behavior of 2,5-aromatic disubstituted pyrrole derivatives have been an interest of our research group [13]. These studies have yielded interesting results in which the importance of the substituent of the aromatic ring joint to the nitrogen atom of the pyrrole unit have been established as a promotion agent of semiconductor behavior.

The goal of this work is to show the nature of the redox complex arising from the interaction among pyrrole derivative and TTF in order to get semiconductor species. The method of electrochemical synthesis, the characterization by several spectroscopic techniques and the study of conductivity are included. A theoretical study of the interaction between TTF and one of the derivatives (the one with the $-NO_2$ substituent) is also shown, the results show a very interesting pathway of electronic promotion and give a chance

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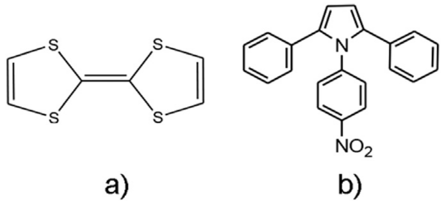

Fig. 1. Molecular structures of TTF (a) and 1-(4-nitrophenyl)-2,5-diphenyl-pyrrole (b) studied in this work.

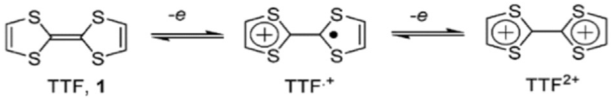

Fig. 2. TTF redox transformation.

for other kind of studies which have started in our group and will be reported in short time.

2. Experimental part

2.1. Synthesis

The synthesis and characterization of 1, 4-diphenylbuta-1, 3-diyne (compound 1); 1-(p-nitro-phenyl)-2, 5-triphenylpyrrole (compound 2) and 1-(p-carboxy-phenyl)-2,5-triphenylpyrrole (compound 3) have been recently described [13,14].

2.2. Electrochemical synthesis

Voltammetric analysis of fresh solutions of substrates, TTF and 1-(4-nitrophenyl)-2,5-diphenylpyrrole, in order to determined the electrochemical oxidation properties prior to bulk electrolysis, was carried out.

Pure acetonitrile, AN, (AR grade) dried over molecular sieves was used as solvent. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP, reagent grade), dried at 90 °C overnight before use. As working electrode a platinum disk microelectrode of about 0.031 cm^2 was used. A silver wire immersed in a solution of 0.01 mol/L in $AgNO_3$ was used as quasi-reference electrode. The silver reference potential according to couple ferrocene/ferricinium was 0.4V. A great surface Au foil is used as auxiliary electrode. Constant potential bulk electrolysis was performed in a 50 mL electrolytic cell using a great surface platinum plaque of about 20 cm^2 with constant stirring using a fresh solution containing 1 mM of compounds 1-(4-nitrophenyl)-2,5-diphenylpyrrole and TTF in presence of TBAP 1 mM as well.

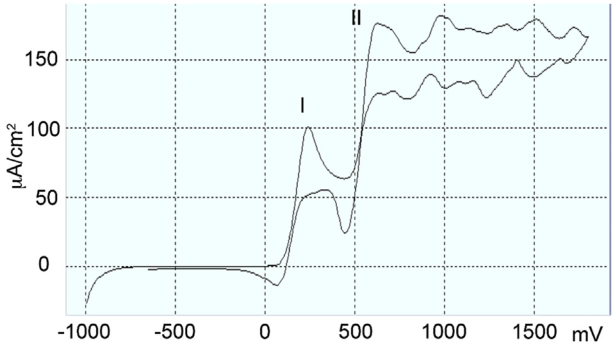

Fig. 5. Voltammetric behavior of compound **4** (TTF), (1 mM), $v = 10$ mV/s, at platinum disk in 0.1 M TBAP in acetonitrile. I: TTF − $1e^-$ → TTF^+; II: TTF^+ − $1e^-$ → TTF^{2+}.

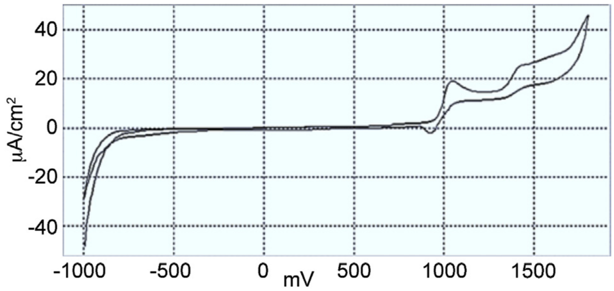

Fig. 6. Voltammetric behavior of compound **2**, (1 mM), $v = 10$ mV/s, at platinum disk in 0.1 M TBAP in acetonitrile.

The cells were maintained in a pure nitrogen atmosphere at all times. Voltammograms and chronoamperometric bulk electrosynthesis were obtained with a DEI-digital electrochemical analyzer (Radiometer-Tacussel).

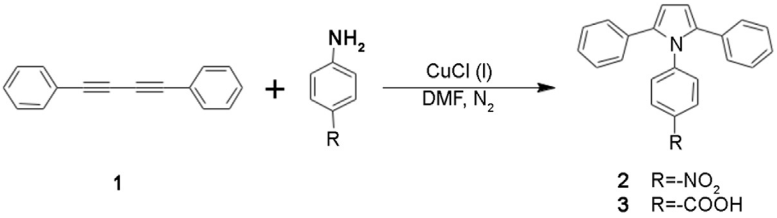

Fig. 3. Chemical reaction of diphenylacetylene with different amines used to obtain the pyrrole derivatives.

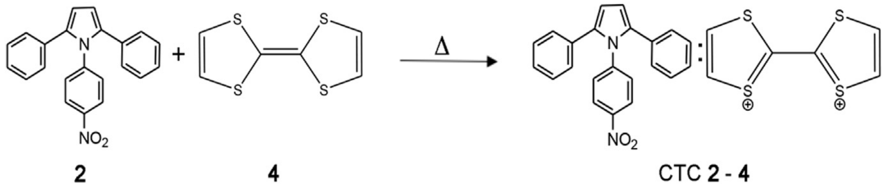

Fig. 4. Proposed reaction of formation of CTC **2**–**4**.