

TTF derivative of 2,5-aromatic disubstituted pyrroles, experimental and theoretical study

Lioudmila Fomina¹, Christopher León¹, Montserrat Bizarro¹, Alejandro Baeza², Victoria Gómez-Vidales³, Luis E. Sansores¹ and Roberto Salcedo¹

¹Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n. C.U. A. Postal 70-360, Delegación Coyoacán. C.P. 04510. México D.F., México

²Facultad de Química, Universidad Nacional Autónoma de México, Circuito, Escolar s/n, Ciudad Universitaria, Coyoacán 04510, México D.F., México

³Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, Coyoacán 04510, México D.F., México

ABSTRACT

In the last decades the interest in organic conductors has growth, so they have become the object of study of many research groups that are interested in developing new materials with important conducting properties. The charge transfer complexes (CTC) represent an important kind of organic conductors, because they exhibit high conductivity values, as well as versatility for their design.

In this work, the charge transfer complex (CTC) formed by substituted pyrrole and tetrathiofulvalene (TTF) 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 a solution giving place to a semiconductor species.

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].

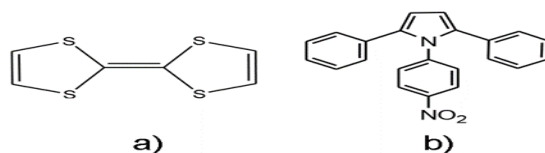


Fig. 1. Molecular structures of TTF (a) and 1-(4-nitrophenyl)-2,5-diphenyl-pyrrole (b) studied in this work.

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].

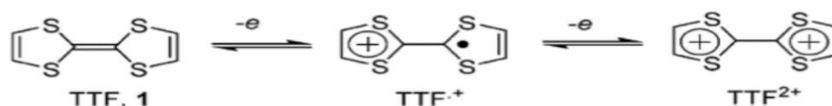


Fig. 2. TTF redox transformation.

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 technics and the study of conductivity are included. A theoretical study of the interaction between TTF and one of the derivatives (the one with the -NO₂ substituent) is also shown, the results show a very interesting pathway of electronic promotion and give a chance for other kind of studies which have started in our group and will be reported in short time.

EXPERIMENTAL DETAILS

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].

Electrochemical Synthesis

Complejo de Transferencia de Carga 1-(4-nitrophenyl)-2,5-diphenylpirrol – TTF (CTC 2-4).

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 cm² was used. A silver wire immersed in a solution of 0.01 mol/L in AgNO₃ 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 cm² 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. 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).

IR (cm⁻¹): ν (Csp₃-H) 2950, 2980, ν (Csp₃-H) 1370, ν (C-CH₂ o CH₃) 1450, ν (perchlorate ion) 600, 1100 cm⁻¹. ¹H RMN (400 MHz, CDCl₃): δ (ppm) 6.50 (s, 2H. H-1), 7.02 – 7.06 (m, 4H. H-5), 7.14 (d, 2H. H-6), 7.20 - 7.22 (m, 6H. H-4, H-8), 8.068 (d, 2H. H-9).

¹³C RMN (100 MHz, CDCl₃): δ (ppm) 111.24 (C1), 124 (C8), 125.93 (C6), 128.225 (C4), 128.95 (C5), 129.311 (C9), 132.516 (C3), 135.74 (C2), 144.518 (C7), 146.085 (C10).

Espectroscopía UV-Visible: λ_{max} = 294 nm; 4.21 eV.

EM: 242 m/z (tetrabutylammonium ion); 340 m/z (**2**); 204 m/z (**4**⁺⁺).

EPR: factor $g = 2.00882$; coupling constante (mT)=0.145; peak broad (mT)=0.089; central signal (mT)=335.747.

Computational Details

All calculations were carried out using a pure DFT method for energy evaluations, and it was applied Becke's gradient corrections [15] for exchange and Perdew-Wang's for correlation [16]. This scheme gives place to the B3PW91 method which forms part of the Gaussian09 code [17]. All calculations were performed using the 6-31G** basis set. Frequency calculations were carried out at the same level of theory to confirm that the optimized structures were at a minimum of the potential surfaces.

DISCUSSION

Synthesis

The diacetylenic molecule 1,4-diphenylbuta-1,3-diyne (**1**) (see **Fig. 3**) was prepared following the Glaser method taking into account the modification of Hay [18,19] which considers the oxidative coupling of terminal alkynes with copper salts as catalysts and a bidentate ligand, TMEDA, in the present particular case.

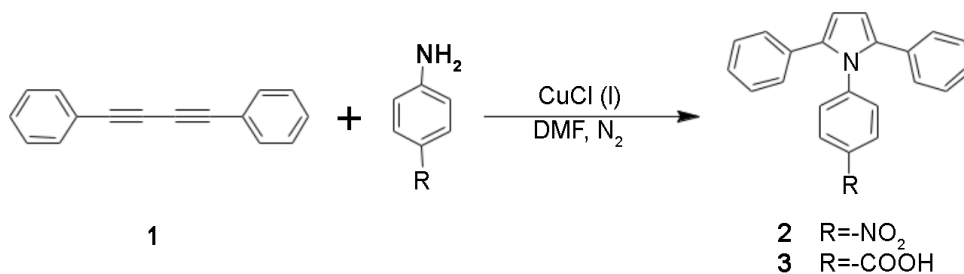


Fig. 3. Chemical reaction of 1,4-diphenylbuta-1,3-diyne (1) with different amines used to obtain the pyrrole derivatives.

As shown in **Fig. 3**, 1-(p-nitro-phenyl)-2,5-triphenylpyrrole (**2**) and 1-(p-carboxy-phenyl)-2,5-triphenylpyrrole (**3**) were synthesized by the reaction of diphenyldiacetylene with different aromatic amines employing copper chloride (I) as catalyst, the synthesis and characterization of these compounds have been recently described [13, 14]. These compounds were obtained by a modification of a reported procedure [20].

Electrochemical Synthesis

The proposed electrochemical reaction is shown in **Fig. 4**.

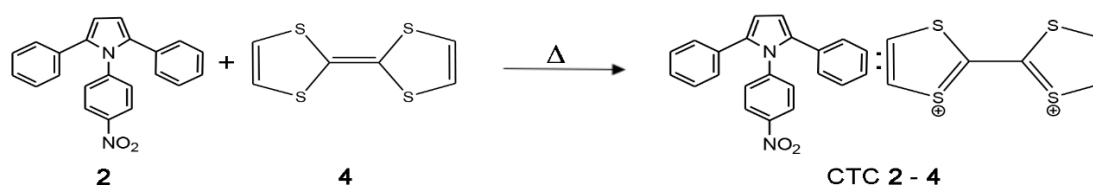


Fig. 4. Proposed reaction of formation of CTC 2-4.

The idea is to prepare a transfer charge complex between compounds **2** and **4**, in a first step, a voltamperometric study of both compounds (**Figs. 5 and 6**) was carried out in order to determinate the nature and potentials for each participant in the reaction, after the compounds were mixed and the electrosynthesis was carried out by means the chronoamperometric technics (**Fig. 7**). The cyclic voltamperograms of **4** and **2** compounds are shown in **Figs. 5 and 6**, respectively; the potential scan was from -1000 to 1800 mV vs an Ag/AgCl electrode and the solvent was anhydride acetonitrile.

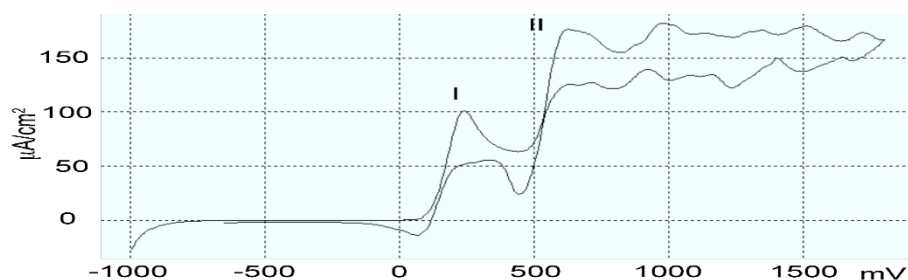


Fig. 5. Voltammetric behavior of compound **4** (TTF), (1mM), $\nu = 10$ mV/s, at platinum disk in 0.1 M TBAP in acetonitrile. I: $\text{TTF} - 1e^- \rightarrow \text{TTF}^+$; II: $\text{TTF}^+ - 1e^- \rightarrow \text{TTF}^{2+}$.

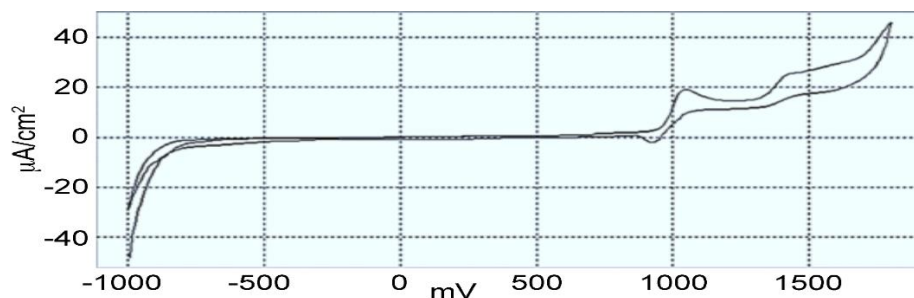


Fig. 6. Voltammetric behavior of compound **2**, (1mM), $\nu = 10$ mV/s, at platinum disk in 0.1 M TBAP in acetonitrile.

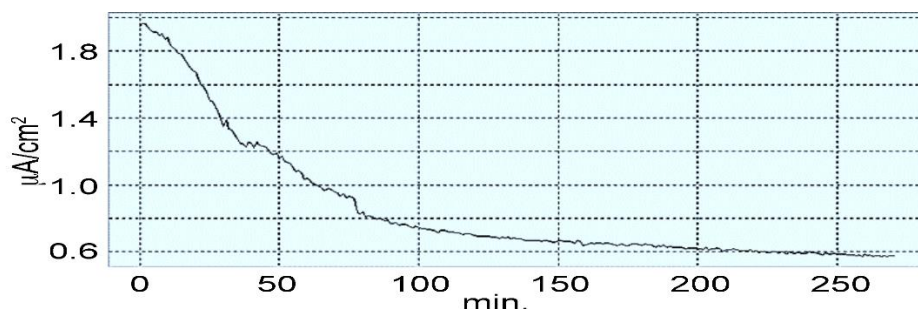


Fig. 7. Chronoamperometric plot during bulk electrolysis of compounds **4** (TTF) and **2**, 1 mM each, at platinum plate in 1 mM M TBAP in acetonitrile. The color of solution changes from orange to deep red.

Fig. 8 shows the voltammetric behavior, at 10 mV/s, of the mixture of TTF (**4**) and compound **2**, both 1 mM, on platinum in 1 mM TBAP in AN after 250 min of bulk electrolysis. From this figure it is observed that the voltammetric profile is strongly modified since only the first oxidation peak of TTF is observed. The $(E_p^a - E_p^c) = 0.173$ V of the original electrochemical oxidation of TTF is strongly increased until $(E_p^a - E_p^c) = 0.554$ V.

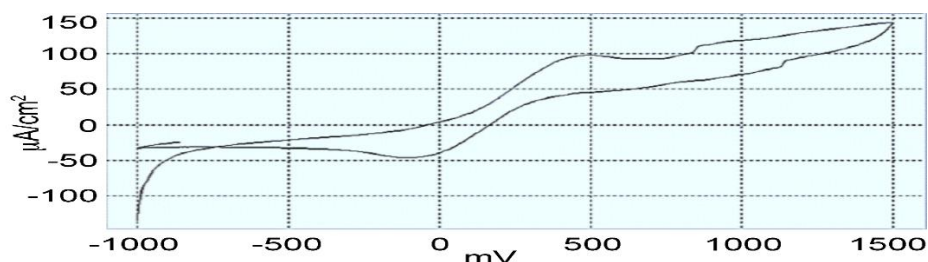
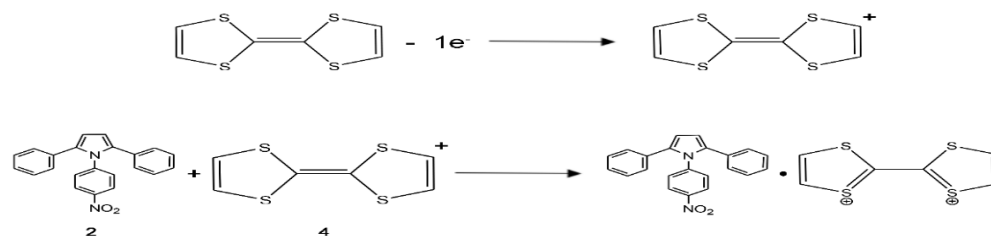


Fig. 9. Voltammetric behavior of compounds **2** and TTF (**4**) (1mM each), $\nu = 10$ mV/s, at platinum disk in 1 mM M TBAP in acetonitrile, *after 250 min bulk electrolysis*.

Since the first oxidation of TTF is the electrochemical process that leads the whole mechanistic reaction between compound **2** and TTF (**4**), an electrochemical mechanism of the type E_rC_r is proposed where TTF^+ is stabilized by the presence of **2** according to scheme:



Conductivity and Theoretical Calculations

Table 2 shows the eigenvalues of the frontier molecular orbitals of both studied derivatives of pyrrole, in both cases the values correspond to the classification of semiconductors, in fact, the present study contains conductivity measurements which will be discussed below. In the same table is registered the corresponding band gap value of the charge transfer complex, the value is 4.6 eV, but this result even being classified as an insulator should be handled with care because it is a salt susceptible to narrow its gap in solution or by means a dopant agent.

Table 2. Energies of orbitals calculated by *Gaussian*.

| Compound | HOMO (eV) | LUMO (eV) | E _g (eV) |
|--|-----------|-----------|---------------------|
| 1-(4-nitrophenyl)-2,5-diphenylpyrrole (2) | 5.578 | 2.558 | 3.02 |
| 1-(4-carboxyphenyl)-2,5-diphenylpyrrole (3) | 5.363 | 1.621 | 3.741 |
| CTC of 1-(4-nitrophenyl)-2,5-diphenylpyrrole (2)–TTF (4) | 9.93 | 5.33 | 4.6 |

The measurements of conductivity of both pyrrole derivatives **2** and **3** and CTC **2-4**, were carried out by means the four point probe. The conductivity of compounds **2**, **3** and CTC **2-4** are 3.5×10^{-7} , 3.94×10^{-7} and 1.07×10^{-9} S/cm, respectively.

CONCLUSIONS

In this work, the synthesis and characterization of organic compounds containing 2,5-disubstituted pyrroles was carried out. These compounds were the 1-(4-nitrophenyl)-2,5-diphenylpyrrole and 1-(4-carboxyphenyl)-2,5-diphenylpyrrol. There are previous reports of their synthesis by our group.

We also conducted the synthesis and characterization of CTC formed by 1-(4-nitrophenyl)-2,5-diphenylpyrrole and tetrathiofulvalene (TTF) (which has no previous reports in literature) by electrochemical method. The results of the characterization of the CTC synthesized show that the compounds involved share an electron from the TTF that migrates to the structure of 1-(4-nitrophenyl)-2,5-diphenylpyrrole.

It was also carried out the calculation of the difference in HOMO-LUMO energy levels (band gap) of compounds 1-(4-nitrophenyl)-2,5-diphenylpyrrole, 1-(4-carboxyphenyl)-2,5-diphenylpyrrole and CTC 1-(4-nitrophenyl)-2,5-diphenylpyrrole–TTF. We found the three compounds to exhibit *band gaps* that place them within the classification of materials with potential semiconducting behavior, and this can be demonstrated by analyzing their electrical properties.

We obtained a good approximation of the theoretical *band gap* compared with the *band gap* obtained experimentally by UV-Visible spectroscopy, which value may be considered among materials with semiconducting behavior.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Teresa Vázquez, Oralia Jiménez for technical help and to Joaquín Morales Rosales and Alberto Lopez for computers support. Thanks are also due to Gerardo Cedillo for the assistance in NMR- analysis, to Miguel Angel Canseco for IR analysis.

REFERENCES

1. G.G. Mallaras, *Biochim. Et Biophys. Acta, General Subjects* **1830**, 4286 (2013).
2. A. Saeki, Y. Koizumi, T. Aida and S. Seki, *Acc. Chem. Res.* **45**, 1193 (2012).
3. M. Bendikov, F. Wudl and D.F. Perepichka, *Chem. Rev.* **104**, 4891(2004).
4. V. Coropceanu, J. Cornil, D.A. da Silva-Filho. Y. Olivier, R. Silbey, and J.C. Brédas, *Chem. Rev.* **104**, 926(2004).
5. M.R. Bryce, *J. Mater. Chem.* **10**, 589 (2000).
6. M.B. Nielsen, C. Lomholt, and J. Becher, *Chem. Soc. Rev.* **29**, 153 (2000).
7. J.L. Segura, and N. Martín, *Angew. Chem., Int. Ed.* **40**, 1372 (2001).
8. D.L. Coffen, J.Q. Chambers, D.R. Williams, P.E. Garrett, and N.D. Canfield, *J. Am. Chem. Soc.* **93**, 2258 (1971).
9. S. Hünig, G. Kiesslich, D. Scauzow, R. Zhrandik and P. Carsky, *Int. J. Sulfur Chem., Part C* 109 (1971).
10. F. Wudl, G.M. Smith and E.J. Hufnagel, *J. Chem. Soc., Chem. Commun.* 1453 (1970).
11. J. Ferraris, D.O. Cowan, V.V., Jr. Walatka, J.H. Perlstein, *J. Am. Chem. Soc.* **95**, 948 (1973).
12. J.C. Brédas, D. Beljonne, V. Coropceanu and J. Cornil, *Chem. Rev.* **104**, 4971 (2004).
13. L. Fomina, G. Zaragoza- Galán, M. Bizarro, J. Godínez- Sánchez, I.P. Zaragoza and R. Salcedo, *Mater. Chem. and Phys.* **124**, 257 (2010).
14. G. Huerta-Angeles, L. Fomina, L. Rumsh, M. G. Zolotukhin, *Polymer Bulletin*, **57**, 433 (2006).
15. A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
16. J. P. Perdew & Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
17. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford CT, 2009.
18. M.F. Shostakovskii. & A.V. Bogdanova, *The Chemistry of Diacetylenes*, John Wiley and Sons, New York, 1974.
19. A.S. Hay, *J. Org. Chem.* **27**, 3320 (1962).
20. K.E. Schulte & J. Reisch, *Angew. Chem.* **73**, 241 (1961).