

Synthesis and characterization of new materials with pyrrole units and their semiconductor behavior

Olivia Monroy¹, Lioudmila Fomina¹, 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

ABSTRACT

New organic materials with semiconductor behavior were prepared from diphenyldiacetylene and aromatic amines with withdrawing groups by Reisch-Schulte reaction and characterized by IR, RMN spectroscopy. The obtained materials share the property of having electron withdrawing groups joint to the attached aromatic ring, it seems this feature accounts in large fashion to improve the semiconducting behavior of this kind of substances, this topic was studied by means theoretical calculations and the results are also discussed. The calculations were carried out by means the Gaussian09 software and all the involved species were geometrically optimized.

INTRODUCTION

Recently, organic materials have started to play an important role in electronic and photonic technologies. Organic semiconductors are very useful because they have electrical properties similar to those of inorganic semiconductors, but manifest the same properties as plastic (low cost, easily processed, flexibility and versatility of chemical synthesis).

Extensive research [1, 2], using both experimental and theoretical approaches has been carried out in an attempt to endow a low HOMO/LUMO gap to organic materials. One strategy employed in order to decrease the band gap in organic molecular materials consists of substitution with electron-withdrawing groups [3]. In this work, 2,5-diphenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrrole and 1-(4-nitro-3-(trifluoromethyl)phenyl)-2,5-diphenyl-1H-pyrrole were synthesized using a modification of the Reisch-Schulte reaction, as previously described [4, 5] and characterized by IR, RMN spectroscopy and theoretically studied to explain the origin of their semiconducting behavior.

EXPERIMENTAL DETAILS

Reagents were provided by Aldrich Chemical Company and used as purchased. FT-IR spectra were taken, using Nicolet 510p spectrophotometer. NMR ¹H and ¹³C spectra were recorded using a Bruker Avance 400 MHz spectrometer. The chemical shifts are reported in ppm, scaled relative to TMS. Melting points are uncorrected.

Synthesis of the monomer compounds

Synthesis of the precursor

(2) 1, 4-diphenylbuta-1,3-diyne. Copper (I) chloride (0.4g, 4 mmol) and N, N, N', N'-tetramethylethylenediamine (TMEDA), 0.1 mL (0.0775g, 0.666 mmol) were added to the

solution of phenyl acetylene (2.042 g, 20 mmol) in isopropanol. The mixture was left stirring under an oxygen atmosphere for 3 hours, and the resulting solution added to acidified water. The product was separated by filtration, dried in vacuum and purified by recrystallization from hexane. Yield: 90%, white solid, m.p. 87-88°C. NMR ^1H (400 MHz, CDCl_3): δ (ppm) 7.33 (m, 3H), 7.50 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 73.9 (CC), 81.6(CC), 121.8, 128.5, 129.2, 132.5.

Synthesis of the monomer compounds

A typical procedure was as follows. A mixture of diacetylene (0.5056 g, 2.5 mmol), copper (I) chloride (0.1979g, 2 mmol) and the corresponding amine (5 mmol), in *N,N*-dimethylformamide (10 mL), was refluxed under nitrogen for 48 hours at 153°C in an oil-bath, and allowed to cool to room temperature. The solvent was removed in vacuum and the product was purified by column chromatography using hexane-acetone (9:1) as eluent.

(4a) 2,5-diphenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrrole. Yield: 37%, white solid, m.p.: 132-134°C. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 6.49 (s, 1H, H-1), 7.04 (m, 1H, H-8), 7.10 (d, 1H, H-6), 7.19 (m, 2H, H-5), 7.25 (s, 1H, H-9), 7.48 (d, 2H, H-4). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 110.68, 125.79, 125.84, 126.64, 128.10, 128.88, 129.06, 132.81, 135.77, 142.01.

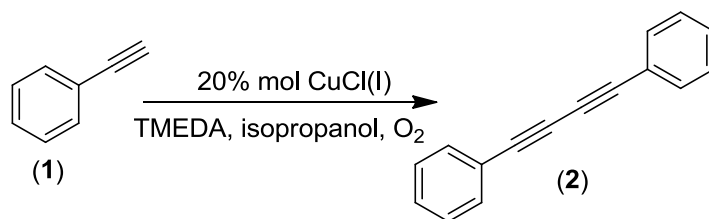
(4b) 1-(4-nitro-3-(trifluoromethyl)phenyl)-2,5-diphenyl-1H-pyrrole. Yield: 20%, yellow solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 6.51 (s, 2H, H-1), 7.04 (m, 2H, H-6), 7.21(dd, 4H, H-5), 7.26 (d, 1H, H-13), 7.32(s, 4H, H-4), 7.71 (d, 1H, H-12), 7.75 (dd, 1H, H-8). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 111.70, 125.75, 127.39, 127.84, 128.47, 128.64, 129.18, 130.65, 132.11, 135.61, 142.56, 145.37.

Computational Details

All density functional (DFT) calculations were carried out, using full geometry optimizations, without symmetry constraints. Becke's gradient corrections [6] for the exchange and Perdew-Wang's for the correlation [7] were used for optimization and total energy evaluation. Thus, BPW91 represents the corresponding functional which has given an excellent performance for this kind of system [8]. All calculations were carried out using the 6-31-G** basis set. The version used was that included in the Gaussian03 code [9].

DISCUSSION

The 1,4-diphenyl-1,3-diyne precursor (**2**) was synthesized by Glaser reaction in Hay modification (**Scheme 1**) which consists of the oxidative coupling of terminal alkynes (phenylacetylene (**1**)) using as catalyst CuCl (I) and TMEDA (*N,N,N',N'*-tetramethylethylenediamine) as a complexing bidentate ligand.



Scheme 1. Oxidative dimerization of phenylacetylene.

The precursor (2) was characterized by infrared spectroscopy. **Figure 1** shows the characteristic absorption signals of phenylacetylene ($\nu_{\text{C-H}} 3287\text{cm}^{-1}$, $\nu_{\text{C=C}} 2107\text{cm}^{-1}$, $\delta_{\text{C-H}} 615\text{cm}^{-1}$), the bands of $\equiv\text{C-H}$ disappeared to form the compound (2).

The synthesis of materials with pyrrole units (4) was carried out by Reisch-Schulte reaction (**Scheme 2**) by the addition of substituted aromatic amines (3) on the triple bond of compound 2. The reaction conditions were 48 hours under reflux of DMF (153°C).

The obtained compounds were characterized by infrared and nuclear magnetic resonance (^1H , ^{13}C) spectroscopy.

Infrared spectra of compounds 4a and 4b are shown in **Figure 2**, where we can see the disappearance of the characteristic band of precursor 2 ($\nu_{\text{C=C}} 2148\text{cm}^{-1}$) and the appearance of the bands corresponding to the pyrrol unit of the obtained compounds: 4a $\nu_{\text{C-H}} 3061\text{cm}^{-1}$ and 4b $\nu_{\text{C-H}} 3068\text{cm}^{-1}$.

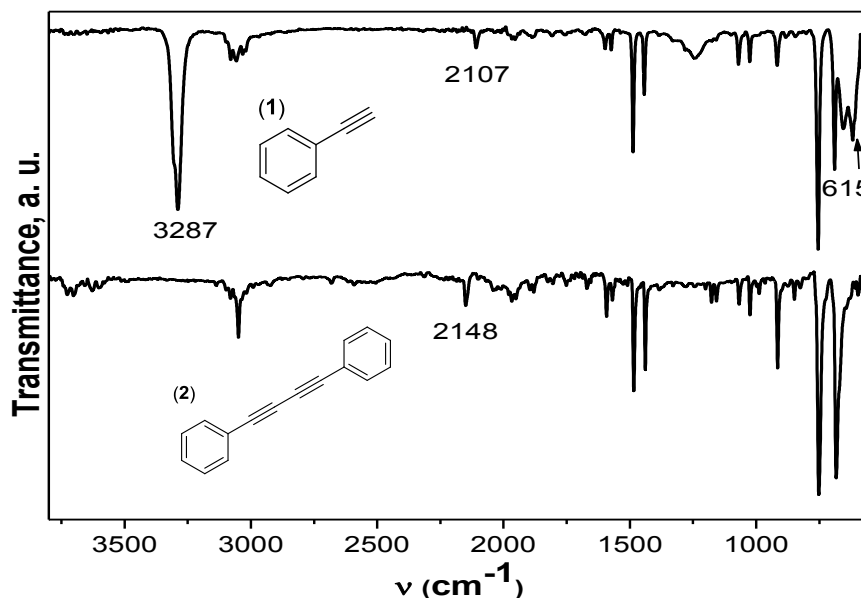
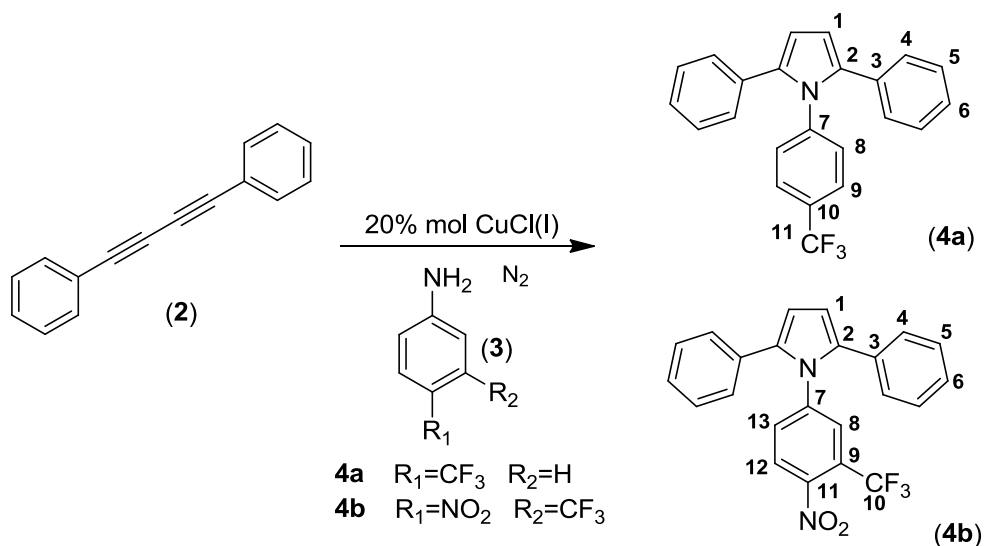


Figure 1. Infrared spectrum of compounds 1 and 2.



Scheme 2. Synthesis of derivatives of pyrrole monomers substituted with electron withdrawing groups.

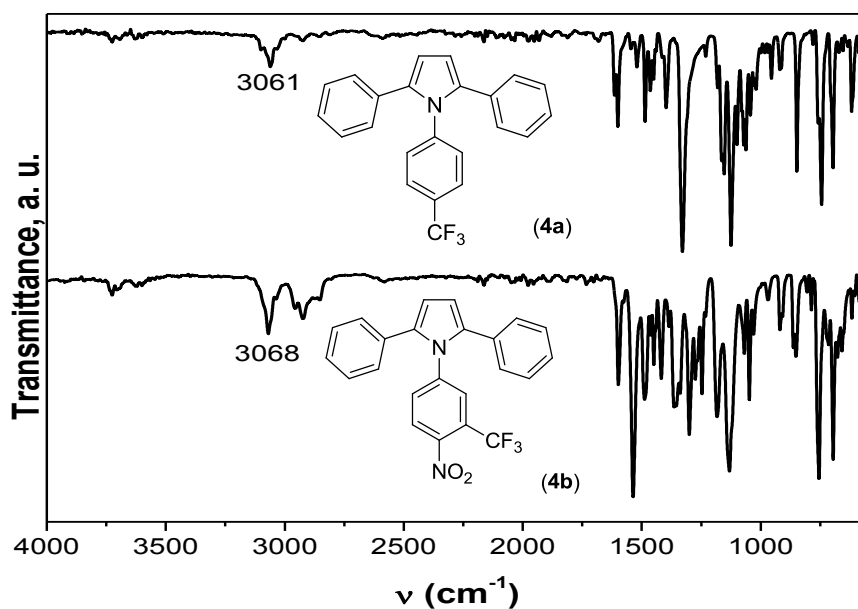


Figure 2. Infrared spectra of compounds **4a** and **4b**.

Figures 3 and 4 show ^1H NMR spectra of compounds **4a** and **4b** with nonequivalent listed hydrogen atoms. In each spectrum we can see the singlet corresponding to atom H1 (**4a**: 6.49ppm and **4b**: 6.51ppm), which is characteristic of the pyrrole ring.

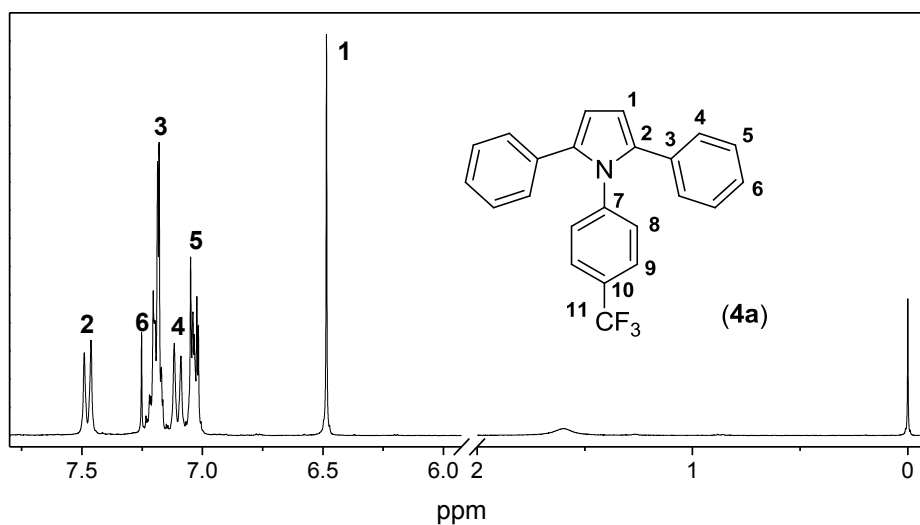


Figure 3. ^1H NMR spectrum of the compound **4a**.

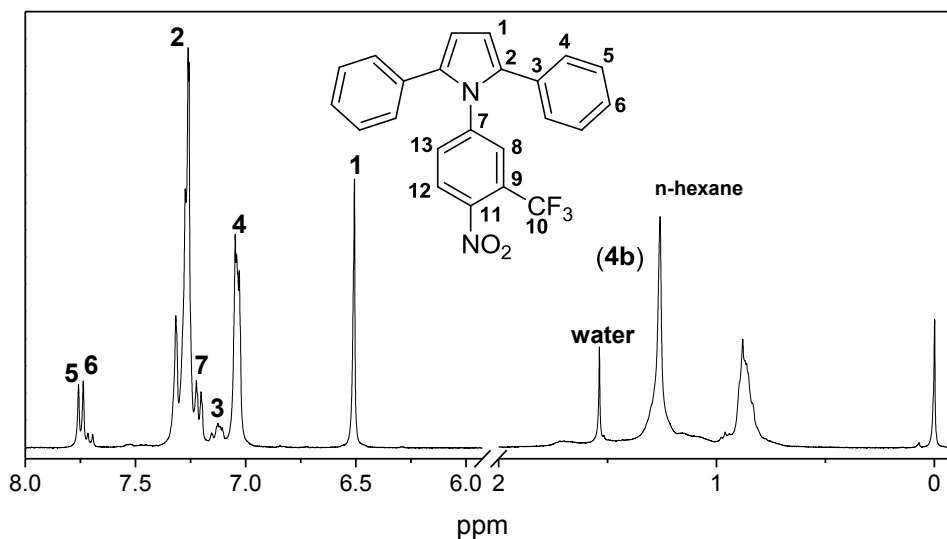


Figure 4. ^1H NMR spectrum of the compound **4b**.

In **figures 5 and 6** ^{13}C NMR spectra of compounds **4a** and **4b** are shown, where we can see the signal corresponding to C1 atom (**4a**: 110.68ppm and **4b**: 111.70ppm), which is characteristic of the pyrrole ring.

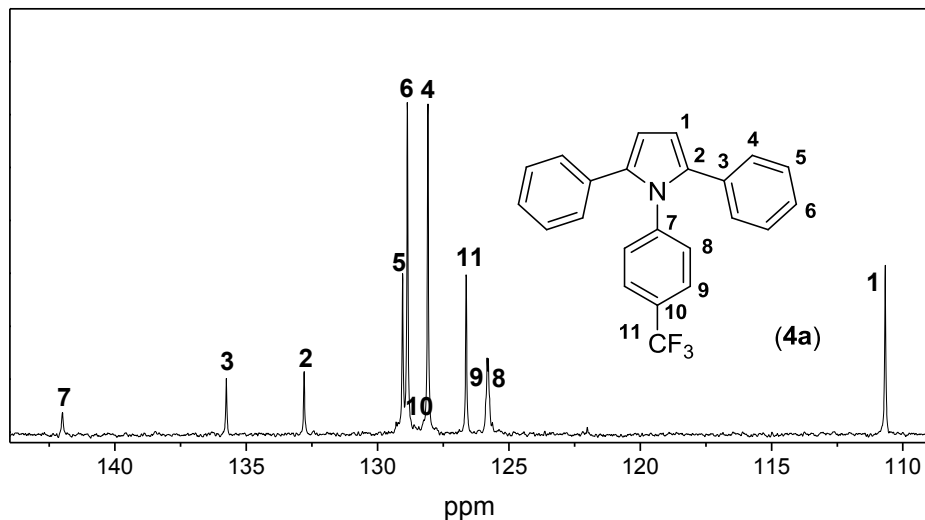


Figure 5. ^{13}C NMR spectrum of the compound **4a**.

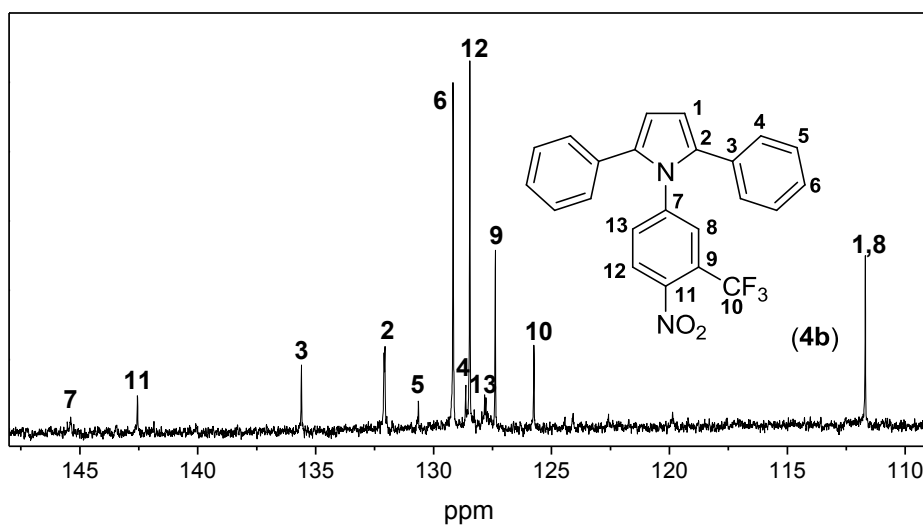
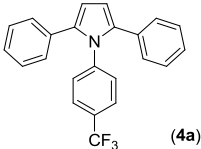
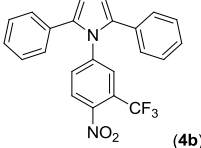


Figure 6. ^{13}C NMR spectrum of the compound **4b**.

Finally, in **Table 1** are shown the energies of the HOMO and LUMO orbitals of molecules **4a** and **4b** as well as the Band Gap energies calculated using the Gaussian 09 program.

Table 1 shows that the band gap of the compound **4b** smaller than the one of the compound **4a** due to the compound **4b** contains two electron withdrawing groups which cause a greater decrease in the electron density of the system.

Table 1. Energies of HOMO and LUMO orbitals and Band Gap energies of the compounds **4a** and **4b**.

Material	Name	HOMO (eV)	LUMO (eV)	Band Gap (eV)
 (4a)	2,5-diphenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrrole	5.442	1.442	4.0
 (4b)	1-(4-nitro-3-(trifluoromethyl)phenyl)-2,5-diphenyl-1H-pyrrole	5.714	3.374	2.34

CONCLUSIONS

It was carried out the synthesis and characterization of 2,5-diphenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrrole (**4a**) and 1-(4-nitro-3-(trifluoromethyl)phenyl)-2,5-diphenyl-1H-pyrrole (**4b**) as well as the calculation of energies of the HOMO and LUMO orbitals and Band Gap energies of these compounds. The compound **4b** has a greater tendency to be a semiconductor material because its band gap is among the typical values of organic semiconductors.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Gerardo Cedillo, Miguel Angel Canseco, Ruben Gaviño for the technical assistance.

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