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Enhancement of characteristics of a functionalized oligophenylene by acid hydrolysis modification

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Abstract

New modified oligophenylene was prepared by acid hydrolysis of a functionalized oligophenylene (OMPA).The latter was obtained by (4-methoxy phenyl) acetonitrile electrochemical oxidation. The resulting modified oligomer (OAC) was characterized by various spectroscopic techniques: NMR, FTIR and UV. The thermal study showed that the modified material exhibited a higher thermal stability compared with OMPA. Further, the optical study revealed that in solution, the emission was blue-shifted when compared with the non-modified oligomer emission and that the optical gap changed from 3.1 eV to 2.75eV. In chloroform solution, photoluminescence was again blue-shifted by 90 nm, which is probably due to an interaction between the oligomer chains.

Keywords: oligophenylen, optical gap, cyclic voltammetry, photoluminescence;

1. Introduction

Conjugated polymers have attracted and still attract much attention due to their promising electrochemical, electronic and opto-electronic properties. These kind of polymers are applicable in various technological fields such as electroluminescent displays, field-effect transistors, the elaboration of photovoltaic devices, super capacitors, active thin layer of different sensing devices, etc. [1-4].

In nowadays, compared with inorganic semiconductors, semiconducting polymers have many advantages. In fact, they offer a greater adaptability and flexibility, simple manufacturing techniques and a low cost of production. Moreover, they allow a better and an easier modification polymer's physical and chemical properties when making small structural changes in the monomer [4-12]. Indeed, not only the polymeric backbone influences these properties but also those depend on the nature of the presence of covalently attached functional groups. In fact, the attachment of functional groups onto the polymer backbone or the modification of the monomer repeat unit in a post-polymerization step can be used to achieve molecular level control of the structure and the properties of the polymer. And then, it will be possible to (a) give new functionalities to the polymer (b) enhance the delocalization of electrons through the π-conjugation on the polymer (c) reduce the polymer's band gap by the control of the HOMO-LUMO energy level (d) improve the optical and electrical properties [4-15].

In this frame, one significant design approach towards low band gap polymers is to introduce alternating donor and acceptor units along the polymer backbone [16-19].

In this study, we report the synthesis and the physico-chemical characterization of a new conjugated oligomer prepared by acid hydrolysis modification of a functionalized oligophenylene (OMPA).The obtained material can be described as an oligophenylene backbone with carboxylic pendent chains. Finally, a structural and an optical study of the elaborated material will be described.

2. . Results and Discussion

2.1. Synthesis and characterization

We synthesized the oligomer (OMPA) by the electrolysis of (4-methoxy phenyl) acetonitrile at a controlled potential of 1.8 V as described in the experimental section. The results of gel permeation chromatography analyses and osmometry indicated that the average chain length was about 5 units [20]. Afterward, OMPA was subjected to a chemical modification via acid hydrolysis modification (Scheme 1). The resulting material was analyzed by NMR and FTIR spectroscopy. To analyse the recorded spectra and to assign different signals we prepared the **monomer (AC)** which will serve as a model.
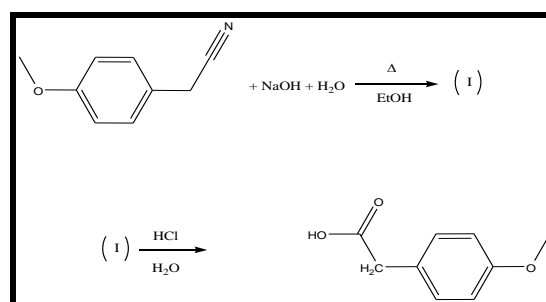
Scheme 1. OAC synthesis

Figures 1 and 2 give us the ^{13}C NMR spectra of AC and OAC, respectively. They revealed that OMPA was partially modified by acidic hydrolysis reaction. In fact, the signal appearing at 40 ppm in the OAC spectrum corresponds to the deblinded benzylic carbons resulting from the chemical modification. On the other hand, the presence of a signal at 180 ppm (Fig.2), corresponding to the new carboxylic carbons, evidenced the complete modification. It should be noted that signals located around 111 ppm and 130 ppm, were assigned to the quaternary carbons resulting from the C-C inter-ring bond in the oligophenylene structure.
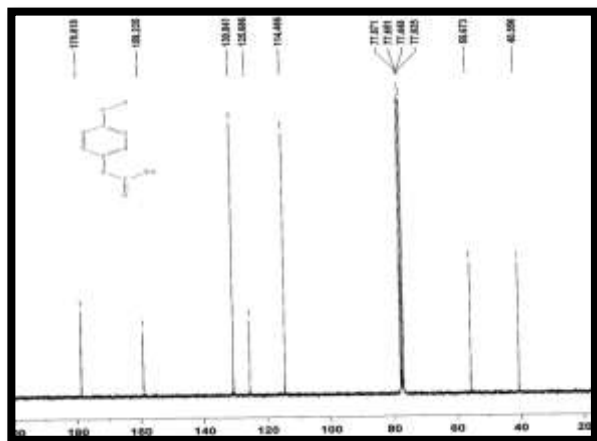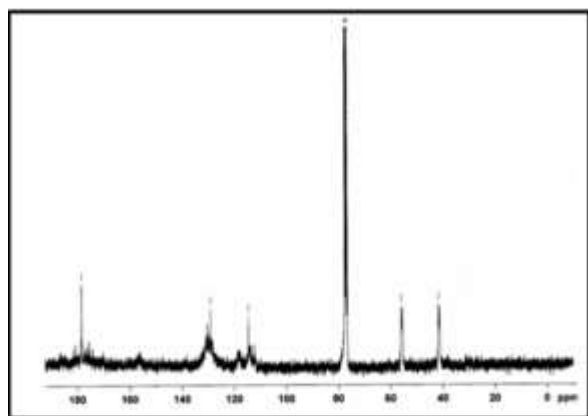

Figure 1.^{13}C NMR spectra of AC.

Figure 2.^{13}C NMR spectra of OAC.

In the ^{1}H NMR spectra of OAC, given in figure 3, we detected three broad signals. The first appeared around 3.8 ppm and corresponded to methoxylic and benzylic protons, the second signal, recorded between 6.8 and 8 ppm, was assigned to aromatic protons and the third, having a low intensity, appears at 12 ppm and corresponds to the mobile hydrogen of carboxylic function.
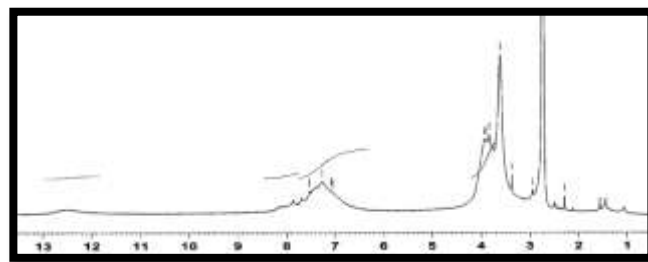

Figure 3.^{1}H NMR spectra of OAC.

The recorded FTIR spectra for OMPA, AC and OAC are illustrated in figure 4. It can be noted that both spectra possess almost the same absorption bands. The most important bands are grouped in Table 1.
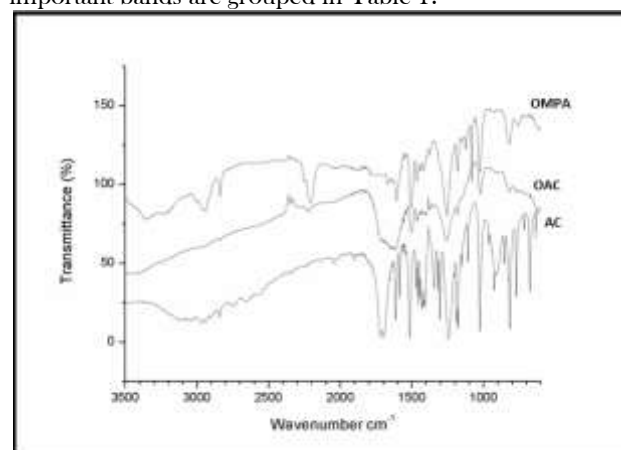

Figure 4. FTIR spectra of OMPA **(top),** OAC**(middle)** and AC **(bottom).**

Table 1. Group frequency assignment for the main infrared band observed in OMPA, AC and OAC spectra.

Vibration	Aromatic ring C-H stretching	Methyl group C-H stretching	Aromatic ring C=C stretching	Methoxy C-O-C
$\nu(cm^{-1})$	3100	2900	1609, 1512 ,1470	1250, 1029

However, we detected the most important modifications in OA and OAC spectrum. In fact, the band appearing at 2258 cm^{-1}, typical of the nitrile stretching disappears both spectra of AC and OAC and we note a formation of a new and intense band at 1700 cm^{-1} characteristic of C=O carboxylic.

2.2. Electrochemical Study

Measurements of cyclic voltammetry were performed using a three-electrode cell setup, the supporting electrolyte, tetrabutylammonium tetrafluoroborate (Bu₄NBF₄), has a concentration of 0.1M in degassed acetonitrile. The electrochemical behaviour of the oligomers was studied to understand their electrochemical stability in p and n-doped states. Figures 5 and 6 illustrate the cyclic voltammograms of AC and OAC, respectively. During the first anodic scan

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(fig.5), AC exhibits an irreversible oxidation peak at around 1.7 V which is almost the same than that of MPA [20], clearly indicating that both of MPA and AC have the same donor unit. In the other hand, we note that, like the MPA [20], there isn't a reduction peak. The peaks irreversibility, indicate the short lifetime of the formed radical ions during electrochemical processes. The cyclic voltammogram of OAC exhibits irreversible anodic and, unlike AC, a cathodic responses. However, no clear peaks were recorded. This result could be explained by a slow electron transfer processes and by the presence of oligomer chains with different lengths. Nevertheless, the electrochemical gap, related to the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, can be estimated by calculating the difference between the onset of electron and hole injections under the experimental conditions. We note that both anodic and cathodic processes occur at lower potentials than for AC. In fact, the extension of the electronic delocalization, over the molecular structure of the modified oligomer, stabilizes the electrogenerated radical ions. The calculated electrochemical band gap of OAC was found to be 2.41eV.
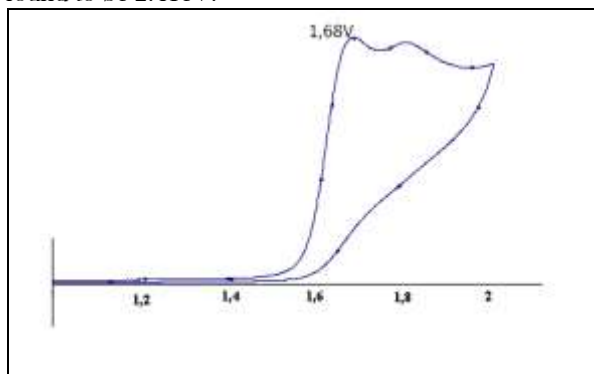

Figure 5. Oxidation voltammogram of AC performed in acetonitrile, NBu₄BF₄ 0.1 M; $C=10^{-3}$ M; $v=$ 100mVs⁻¹ on platinum disc (d = 2mm).
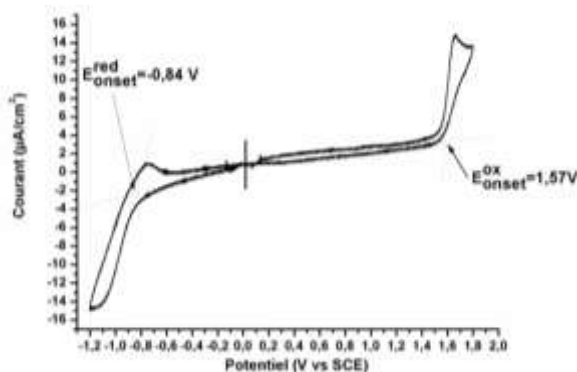

Figure 6. Oxidation and reduction voltammogram of OAC performed in acetonitrile, NBu4BF4 0.1 M; $C=10^{-3}$ M; $v=$ 20mVs⁻¹ on platinum disc (d = 2mm).

Besides, we calculated the HOMO and the LUMO energies as described in the experimental section. We estimated E_{HOMO} and E_{LUMO} to be -5.8 and -3.39 eV, respectively.

2.3. Thermal study

OAC thermal stability was investigated by TGA and DTA. The obtained results are shown in Fig. 7. It should be noted that a small weight loss (<10%), most probably related to evaporation of the residual solvents used during the oligomer preparation and purification, was observed from 80 °C to 120 °C. The results of differential thermal analysis showed that a slow exothermic phenomenon took place from 150°C to 250°C when an accentuated peak was observed. The corresponding weight loss exceeded 30%. This phenomenon could be attributed to the degradation of carboxylic pendant chains. This assumption was supported by the higher thermal stability of the modified oligomer relatively to OMPA [20]. Finally, a faster degradation was observed from 370 °C corresponding to the polyphenylene backbone degradation as previously described [21].
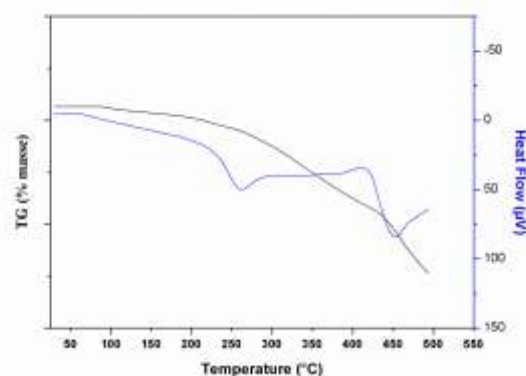

Figure 7. TGA and TDA thermograms of OAC under Nitrogen.

2.4. Optical properties

The optical absorption spectroscopy enables us to provide fundamental information on the properties of absorption, especially in the case of molecules very absorbing in the UV-Visible as well as in conjugated polymers.

2.4.1. Optical absorption

The optical absorption spectrum performed on OAC in chloroform solution is shown in Figure 8. From this spectrum we can immediately deduce that the solution of OAC absorbs in UV and near UV ranges with a strong absorption band located at 290 nm.
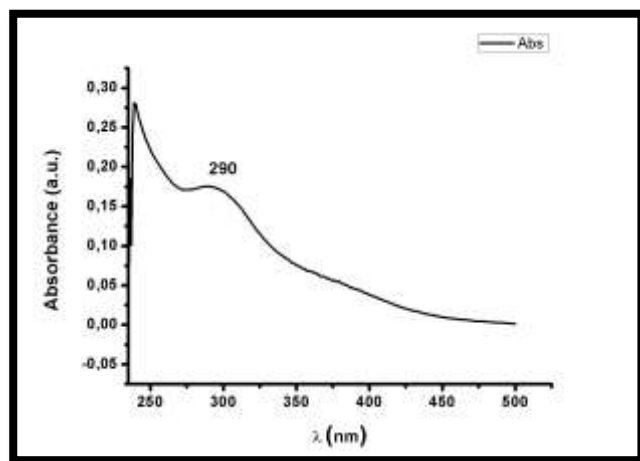
Figure 8. UV-vis absorption spectra of OAC in chloroform solution

When compared to the OMPA spectrum, band is blue-shifted at 290 nm. This displacement can be explained by the extension of the electronic delocalization over the oligomer after the chemical modification. The onset λ_{onset} of the OAC optical absorption spectrum (Figure 8) is estimated to be at 450 nm (2.75 eV). This indicates the band gap of OAC is smaller compared to that reported for the unmodified oligomer (400 nm; 3.1 eV) [20]. Note that this value is different from the electrochemical gap previously obtained. This result could be explained by the fact that the optical electron transition leads to the formation of excited states whereas electrochemical reduction/oxidation are reactions generating species in a ground states. Indeed, the electro-generation of radical anion or radical cation in solution involves other kinetic and affects thermodynanic (salvation...). In fact, it is expected that the onsets potential will be lowered owing to fast chemical reactions following electron transfer inducing kinetic instability of the primarily generated radical ions.

2.4.2. Photoluminescence

The steady state PL is widely used to provide fundamental information on the photophysical properties. Figure 9 displays the steady state PL spectra carried out on an OAC in chloroform solution. When compared with spectrum of OMPA in chloroform solution [20], the PL spectrum of OAC in solution (Figure 9) presents two maxima emission at 380 and 485 nm. It presents a maximum emission blue shifted of 90 nm with respect to OMPA in solution because of the presence 4-metoxy cyanostyryl pendant chains in OMPA. These groups increase the degree of delocalization of π-electrons on the carbon atoms of the oligomer backbone which are responsible for the conjugation. This case shows how the chemical nature of the substituent group can impact the conjugation of polymer.
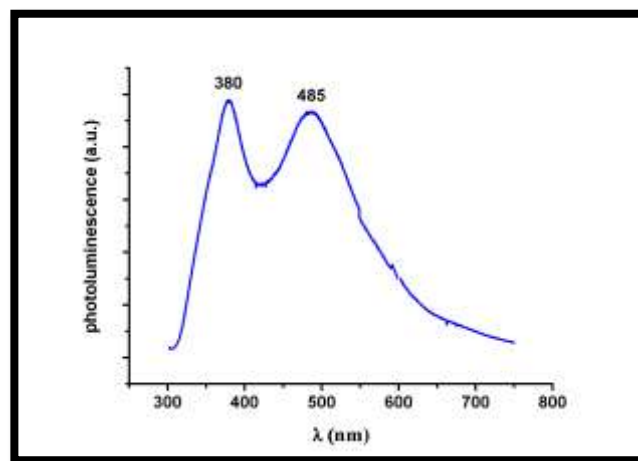

Figure 9. Steady state PL spectra of OAC in $CHCl_2$ solution; (excitation wavelength 320 nm).

3. Experimental Section

3.1. Chemicals

4-Methoxyphenyl acetonitrile, 4-methoxybezaldehyde and tetraethyl ammonium tetrafluoroborate were from ACROS. Chloroform and dichloromethane were from PROLABO. Diethyl ether, ethanol, petroleum ether and acetonitrile were from PANREAC. Chemicals were used as received.

3.2. Analysis

3.2.1 Spectroscopic Analysis

FTIR analysis was performed with a Bruker Vector 22. The spectra were obtained with KBr pressed pellets. ^{1}H NMR and ^{13}C NMR spectral data were obtained on a Bruker AV 300 spectrometer in $CDCl_3$ as solvent. UV-Vis spectrophotometric measurements were performed with a Shimadzu spectrophotometer.

3.2. 2. Gel permeation chromatography (GPC) and osmometry analysis.

The oligomer's chain length was determined by Gel permeation chromatography (GPC) and osmometry. A μ styragel 500 A–15 μm column (length300 nm and diameter7.8 mm) was used in GPC. The temperature was 30°C. The solvent was tetrahydrofuran with a flow rate of 0.85 nL/min. Polystyrene was used as a standard for the column calibration. For the osmometry study, a Knauer thermoelectric apparatus was used with the (4-methoxy phenyl) acetonitrile as standard.

3.2.3. Thermal Study

A METTLER DSC was used for the thermal study. The samples were analyzed between ambient temperature and 500°C with a heating rate of 10 °C/min. The dynamic thermogravimetric analysis was carried out in a Perkin-Elmer TGS-1 thermal balance with a Perkin-Elmer UV-1 temperature program control. The samples were placed in a platinum sample holder and the thermal degradation measurements were carried out between 30 and 550°C at a speed rate of 10°C/min under Nitrogen atmospheres.

3.2.4. Photoluminescence Study

Optical density measurements were carried out at room temperature (RT) using a Cary 2300 spectrophotometer, in the range 200 to 2200 nm. Steady-state photoluminescence emission (PL) was carried out on a Jobin-Yvon Fluorolog 3 spectrometer using a Xenon lamp (500 W) at RT and sample degradation.

The transient PL was spectrally dispersed into an ORIEL MS260i imaging spectrograph (150 grooves/mm, f=1/4) designed to minimize stray light with high spectral resolution.

3.2.5. Electrochemical Techniques

The voltammetric study was performed with a Voltalab10 apparatus from Radiometer driven by the Volta Master software. The working electrode was a 2mm diameter platinum disk; the reference electrode was a SCE (Tacussel SR110) and the counter electrode was a platinum wire. The preparative electrolyses were carried out in a two-compartment cell, under nitrogen, at a controlled potential versus a SCE (Tacussel C12). The potentiostat and the current integrator were Tacussel (PRT 1-100 and IG 5 respectively). The working electrode and the counter electrode were a 4 cm^2 and a 0.25 cm^2 platinum gaze, respectively. The separation between cell compartments was realized by a number 4 glass frit.

The E_{HOMO} and the E_{LUMO} were calculated according the empirical method [22, 23] where:

E_{HOMO} (eV) = $-(E_{onset}^{oxi} + 4,4)$ and E_{LUMO} (eV) = $-(E_{onset}^{red} + 4,4)$ with the onset potentials were measured vs an ECS electrode.

3.3. Synthesis

3.3.1. OMPA synthesis

OMPA was prepared by preparative electrolyses carried out at a constant potential of 1.8 V. The supporting electrolyte used was tetraethyl ammonium tetrafluoroborate (NEt_4BF_4) and the (4-methoxy phenyl) acetonitrile (MPA) concentration was about 0.1M. Homogenization of the solution was assured by a mechanical stirring. The electrolyses were stopped after consumption of 2 F/mole of the starting material. The electrolysis solutions were evaporated under vacuum until elimination of the major part of acetonitrile, then 50 ml of water was added and an extraction with dichloromethane was performed to eliminate the supporting salt. The organic phase, containing the electrolysis products, was concentrated and then precipitated in diethyl ether. OMPA was collected by filtration as a brown powder. The weight ratio of the powder to the starting material (m_p/m_b) was around 0.3.

3.3.2. Synthesis of monomer (AC)

A 50 ml reaction vessel was equipped with a magnetic stirrer, reflux condenser, gas inlet and a rubber septum. It was charged with 1mmol of MPA dissolved in 20 ml of anhydrous ethanol. To this mixture was added drop-wise, with stirring, **2** ml of a solution of sodium hydroxide (**2M**) and heated to reflux for twenty-four hours. The reaction was controlled by thin layer chromatography. Then the medium is acidified with a concentrated HCl solution , that 's when it appears a white precipitate that will be filtered through a sintered porosity 4. The reaction yield is 65%. mp 77 ° C

^{1}H NMR (300 Hz, CDCl$_3$) **3.58 (2H, s), 3.79 (3H, s), 6.85– 7.25 (4H, m), ^{13}C NMR (300 MHz, CDCl$_3$) 40.55, 55.67, 114.46, 125.68, 130.84, 159.23 and 179.** GC-MS-m/z: [M$^+$] 152.

3.3.3. Oligo AC (OAC) Synthesis

A 50 ml reaction vessel was equipped with a magnetic stirrer, reflux condenser, gas inlet and a rubber septum. It was charged with 145 mg of OMPA dissolved in 20 ml of anhydrous ethanol. To this mixture was added drop-wise, with stirring, 2 ml of a solution of sodium hydroxide (2M). The mixture was refluxed and stirred under Argon atmosphere for 24 h. The OAC was precipitated in diethyl ether. The yield was about 65 %. The obtained oligomer exhibits a good solubility in commonly used solvents (CHCl$_3$, CH$_2$Cl$_2$, THF...)

4. Conclusions

In this study we showed that the acidic hydrolysis of a functionalized oligophenylene (OMPA) can be used for controlling the optical properties of the resulting material. The OMPA was obtained by the electrochemical oxidation of (4-methoxy phenyl) acetonitrile. The chemical modification, performed on its oligomer, led to a highly modified oligophenylene processing a carboxylic moiety as a pendant chain. The obtained material was characterized by various spectroscopic techniques: photoluminescence, NMR, FTIR, and UV. The optical study revealed that, in solution, the modified oligomer exhibited two emissions at 380 and 485 nm, taking place 90 nm lower than the non-modified material and that the optical gap changed from 3.1 eV to 2.75 eV.

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