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ß-Aldol Condensation as a new Synthetic Approach for the Preparation of Luminescent Oligomers

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Summary

In this paper, we report the crossed aldol condensation between the acetone and the 2,5-bis(octyloxy)-terephthalaldehyde (OTP) to obtain new photoluminescent oligomers as potential candidates for the construction of organic luminescent diodes (OLED's). The reaction is carried out in ethanol as solvent, but when THF is added to the reaction medium as co-solvent, a higher molecular weight can be obtained. The analysis of the structure of the product obtained when THF is added was elucidated by ^{1}H NMR, infrared, ultraviolet-visible (UV-Vis) and fluorescence spectroscopy and the results indicate that the number of repetitive units corresponds with that of a tetramer with an excellent solubility in common organic solvents and intense fluorescence in the green region. Moreover it can be processed by self-assembly in homogeneous thin films with controlled thickness. These results are promising in view of the possible application of this oligomer in electroluminescent diodes.

Introduction

Since the pioneering work of Heeger, Shirakawa and McDiarmid on polyacetylene, an enormous effort has been realized by organic scientists to obtain new processable, stable and well defined conjugated molecules for biosensoring, lasers, light emitting diodes, etc [1]. So far, conjugated systems based on acetylene, diacetylene, phenylene, phenylene-vinylene, pyrrol, aniline, tiophene and many other π electrons moieties have been synthesized by condensation reactions, oxidative coupling, solid state reactions, electrochemical and enzymatic polymerization, soluble precursor methods [2] etc. In this work, we report a new synthetic approach, which consists in the aldol condensation between a ketone with a hydrogen and an aromatic dihaldehyde. In details, this paper reports the results obtained by the reaction between acetone and 2,5-bis(octyloxy)terephthalaldehyde (OTP), and its characterization in nanofilms.

Theoretical basis

Aldol condensation [3,4] is a reaction in which a carbonylic compound, after removal of the α–hydrogen under basic conditions, reacts as a nucleophile and attacks the electrophilic carbonyl carbon of another molecule of a carbonyl compound. Ketones and aldehydes are two different carbonyl compounds that can be used in an aldol condensation and by this route they can form β-hydroxyaldehydes and β-hydroxyketones that are dehydrated when they are heated in acid or base conditions. When the aldehyde or ketone presents p electrons moiety such as aromatic rings and the stoichiometric reaction conditions are appropriate, a conjugated system with a sequence of carbon-carbon double and single bonds can be obtained.

Experimental

Materials

The next reactive grade products: TPA, OTP, $CHCl_3$, acetone, EtOH, THF, were purchased from Aldrich and T.J. Baker and used without further purification. THF was from Fisher Scientific. The thin films were prepared on Corning glass substrates.

Instruments

^1H NMR spectra were recorded on a JEOL 300 MHz spectrometer using $CDCl_3$ as solvent. FTIR was performed on a Nicolet Magna-550 spectrometer as thin films on KBr pellet. The UV-Vis and fluorescence spectra were carried out on a Shimadzu 2401PC spectrophotometer and a Perkin Elmer LS50B spectrofluorimeter, respectively. Size exclusion chromatography (SEC) was realized on a Waters chromatograph for 1 mg/ml THF solutions using polystyrene as standard and HPLC grade THF as effluent (1ml/min speed). AFM analysis was carried out in tapping mode with a Dimension 3100 Digital Instruments microscope at a speed of 0.3 Hz.

Polymerization General Procedure

A solution containing (1 mmol) of NaOH and (0,5 mmol) of 2,5-bis(octyloxy)-terephthalaldehyde (OTP) in 20 ml of EtOH/H2O (1:1) is heated at 60 °C and gently stirred. Then acetone (0,5 mmol) dissolved in EtOH/H2O (at 16,6 % v) was drop wise added. After 20 min of reaction, a first red precipitate (POTPsoln) is formed and adhered to the magnetic stirrer from which it is recovered after decantation. The remained solution is let to reach the room temperature and a second yellow precipitate (POTPppdo) is obtained and recovered by filtration.

Polymerization General Procedure Using THF as Co-solvant

A second reaction was carried out with the same reactive concentrations, but adding 5 ml of THF to the initial solution of OTP. The first reddish precipitate adhered to the magnetic stirrer was identified as POTPsoln/THF and the second yellow-orange precipitate after cooling was classified as POTPppt/THF. All samples (POTPs) were successively filtered and washed with distilled water and dried in vacuum.

Multilayer films formation

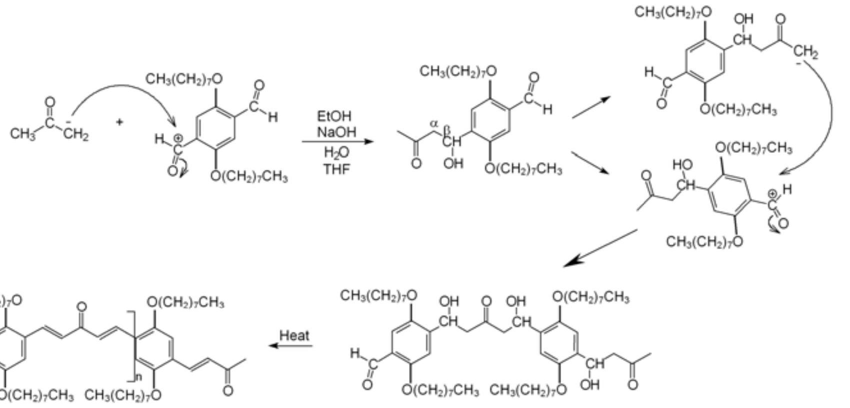
The films were prepared on previously treated hydrophilic glass slides by the self-assembling technique. The substrates were dipped in 0.47 mg/ml solutions of POTPs in spectroscopic $CHCl_3$.

The monolayer film for devices were prepared with a 3 mg/ml solution of POTPppt in spectroscopic $CHCl_3$ spin-coated on Indium tin oxide (ITO) coated glass slide. The I-V curves were recorded simultaneously using a Keithley 2400 current source measurement unit.

Results and discussion

The mechanism of the reaction between acetone and 2,5-bis(octyloxy)-terephthalaldehyde to yield the conjugated oligomer (POTPs) is reported in Scheme 1. In a first step, the typical nucleophylic mechanism of the aldolic reaction is predicted to occur between the carbanion of the acetone and the carbocation of the terephthalaldehyde to form a β alcohol intermediate. Due to the basic conditions of the reaction, the acid H of the terminal CH_3 group of the intermediate can give rise to another nucleophyle, which permits to continue the condensation forming dimers, trimers and higher conjugated molecules. In the last step, the heating causes the loss of two molecules of water in the β alcohol yielding the enone aromatic systems. In a first attempt, terephthalaldehyde was used as reactive and two parallel reactions were performed, the first one using pure EtOH/NaOH/water solution as reaction medium and in the second THF was added as co-solvent. The addition of a co-solvent is expected to maintain in solution the growing molecules increasing the molecular weight [5]. Both reactions gave a very insoluble product that could not be characterized. With the aim to increase the solubility without affecting the electronic and optical properties of the products, a terephthalaldehyde substituted with two octyloxy chains was also studied, using the two conditions reactions already described above. In both cases, a pasty red precipitate was firstly separated from the solution after few minutes of the acetone addition, hereafter named POTPppt and POTPppt/THF. The remaining solution was still left reacting longer time (around 30 minutes) and a yellow-orange precipitate was then recollected, the two fractions are hereafter named POTPsoln and POTPsoln/THF. The four products turned out to be soluble in $CHCl_3$ and THF. Table 1 gives the determination by SEC using PS standards; the average molecular weights for the four fractions as well as their corresponding properties in $CHCl_3$.

The ^1H NMR spectra of the four reactions which are reported on table 1 are identical, indicating that they correspond to the same chemical structure. As an example, Fig. 1 shows the ^1H NMR spectrum of POTPppt/THF. In agreement with the molecular structure (inserted in the same figure), the triplet at 0.88 ppm is assigned to the methylene protons (a) of the lateral aliphatic chains, the ethylenes $–CH_2-$ (b) are centered at 1.29 ppm and the $–CH_2$-g-O (c) appears at 1.48 ppm, while those of the CH_2-b-O (d) and $–CH_2$-a-O (e) are centered at 1.84 and 4.02 ppm, respectively. Notice, the appearance of one intense peak at 2.38 (f) and other one less intense at 10.47 (g) ppm, that are ascribed to the CH_3 of the acetone and the aldehyde proton, respectively. Their integration rate suggests that the molecules are rather terminated by CH_3- of the acetone groups, this characteristic makes that the aromatic protons next to the aldehyde are chemically different and appear at 7.17 (i) and 7.23 (j) ppm, while the central ring protons (j) as well as those of the phenyl bearing the CH_3-acetone terminal groups appear as a singlet at 7.05 ppm. Finally it is worth noting that the vinyl protons -CH=CH- give also different resonant doublets: the protons of double bonds of the central part of the structure (between two aromatic rings, k and l) appear at 7.09 and 7.98 ppm which are chemically different to those of the extreme parts of the molecule (bonded to only one aromatic ring, m and n) that appear at 6.71 and 7.84 ppm. The chemical structure was also confirmed by FTIR spectroscopy, where the main characteristics are the carbonyl vibration at 1665 cm^{-1}, the CH=CH vinyl and aromatic stretching bands are found at 1597 cm^{-1} and the C-O- stretching of the phenyl-octyloxy appears at 1257 cm^{-1}.



Scheme 1. Synthetic route for the aldol condensation.

Table 1. Average molecular weights and polydispersity indexes obtained by SEC relative to PS standards in THF solutions and optical absorption and emission wavelengths for the four fractions of the reaction in $CHCl_3$.

	Fraction	M_n	M_w	P.I.	Number of repetitive units	λ(nm) absorption	λ(nm) emission
Reaction without THF	$POTP_{soln}$	887	1090	1.23	1.4	318, 393	480
	$POTP_{ppt}$	1260	1867	1.48	2.4	327, 423	511
Reaction adding THF	$POTP_{soln/THF}$	1018	1398	1.37	1.8	320, 405	488
	$POTP_{ppt/THF}$	1680	2864	1.70	3.8	330, 427	525

According to the SEC analysis and optical characterization, the red pasty products correspond to fractions with higher molecular weight and to more conjugated systems. It can be noted that the molecular weight of all the fractions is modest suggesting that they correspond rather to oligomers with a polydispersity index relatively sharp. Nevertheless, it is well known that determination of the molecular weight of rigid rod molecules by SEC using polystyrene standards is not reliable because values are usually overestimated [5] thus these results must be confirmed by other techniques such as MALDI-TOF.

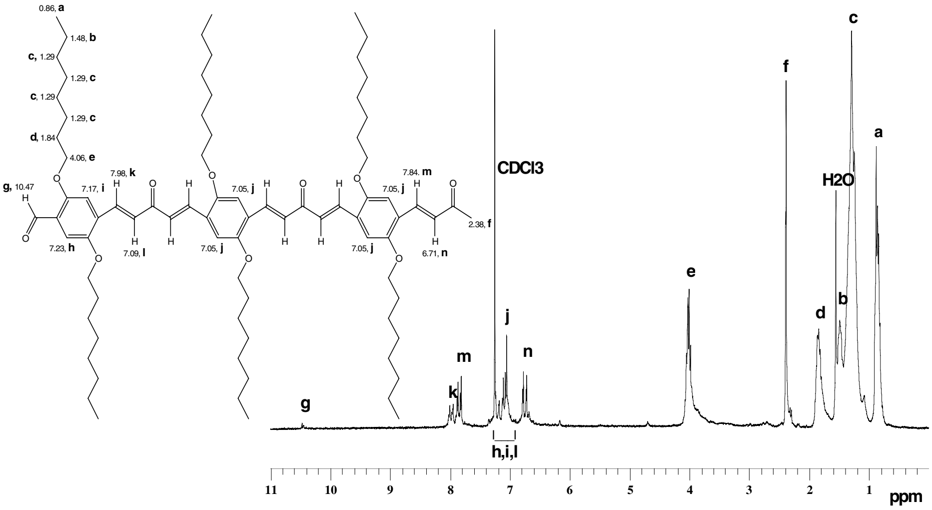


Figure 1. ^{1}H NMR spectrum of fraction POTP$_{ppt/THF}$ and the proposed chemical structure.

The UV-Vis and fluorescence spectra of POPTs in solution are shown in Fig. 2. The higher energy band can be assigned to the substituted aromatic ring while the peak at higher wavelength is due to the electronic transitions of the conjugated chain. This latter peak exhibits a batochromic shift along with the increase in the molecular weight as found for other conjugated systems [6, 7]. The most relevant point is that according to the reaction conditions, the emission wavelength can be modulated from 480 to 525 nm. In particular the fraction POTPppt/THF emits high bright green light. Furthermore, POTPppt/THF is the oligomer, which presents the higher solubility of all POTPs allowing the elaboration of multilayer films. The UV-Vis spectra of 1-6 multilayer structured filmsb by self-assembly of POTPppt/THF are presented in Fig. 3.

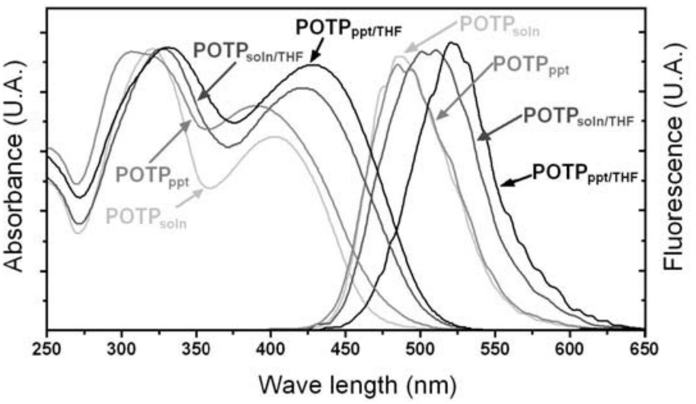


Figure 2. UV-Vis and fluorescence spectra for POTPs showing the batochromic shift from POTPsoln to POTPppt/THF.

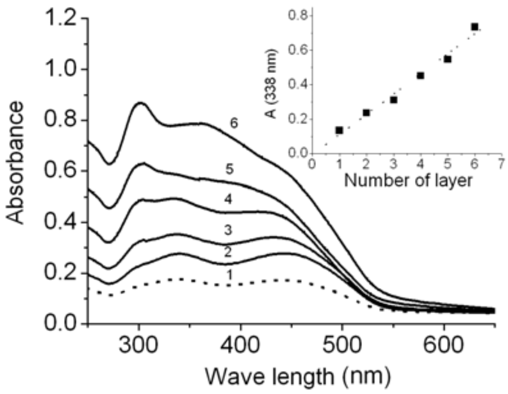


Figure 3. UV-Vis spectra of POTPppt/THF multilayers showing the batochromic shift. The Insert shows the graphic of the absorbance vs. the number of layers.

The spectrum of the first layer shows the same spectral features previously discussed for solutions, with peaks at 338 and 444 nm. The slight red-shift with respect to solution is expected due to solid state effects. Along with the deposition process, the lower λ band splits in two peaks at 300 nm and 330 nm, while the band at 444 nm becomes broader. A possible explanation to this spectral change could be to the formation of aggregates as the film thickness increases [8]. An important result is however that the absorption at the maximum wavelength increases linearly with the number of layers, suggesting a regular build-up of the multilayer by self-assembly (insert of Fig. 3).

The AFM analysis (Fig. 4) reveals that the morphology of the film is of columnar type analogously to what found for other conjugated molecules [9], with an homogeneous distribution of columns along with the substrate surface, and a typical rugosity of 0.894 nm (in surface area of 4 µm^2).

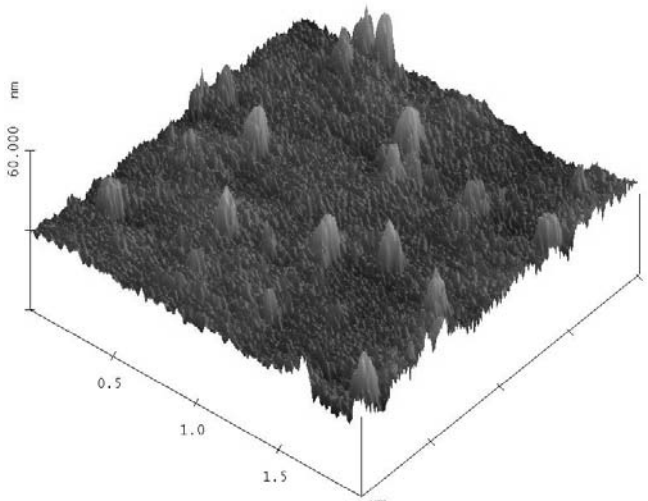


Figure 4. AFM image of a POTPppt monolayer film by self-assembly.

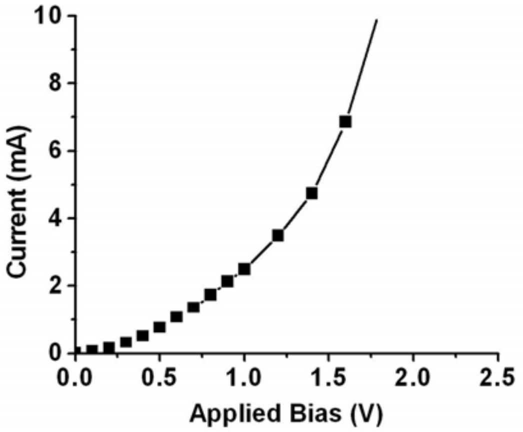


Figure 5. Current–voltage characteristics for a diode with configuration of ITO/ POTPppt/Al.

We examined the behavior of a monolayer device with the typical configuration ITO/POTPppt/THF/Al.

The device shows the same behavior and this results obtained are comparable with experimental I-V curves of ITO/PPV/Al device [10].

Conclusion

In this work we have demonstrated that a β-aldol condensation of acetone with a terephthalaldehyde derivative allows the preparation of conjugated oligomers with interesting optical properties and good processability in self assembled films. The cross-coupling of acid H ketone with different bifunctional aromatic aldehydes opens the possibility to use the aldol condensation for the preparation of several series of conjugated materials.

The detailed investigation of how the reaction conditions could affect the molecular weight of the condensation products and their optical and optoelectronic properties is in progress. These preliminary results indicate that this synthetic approach does permit to obtain conjugated systems with possible application in OLED devices.

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