Electrical properties of ITO/benzylated cyclodextrins (β-CDs (Bz))/Al diode structures

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Abstract

Investigations of the electrical characteristics of benzylated cyclodextrins (β-CDs (Bz)) diodes are reported. We present current–voltage characteristics and impedance spectroscopy measurements performed on partially benzylated cyclodextrins β-CDs (Bz) thin films in sandwich structures ITO/β-CDs (Bz)/Al. The static electrical characterizations show a space charge limited conduction (SCLC) and a conductivity with power low frequency behavior characteristic of a hopping transport in disordered materials. The impedance spectra can be discussed in terms of an equivalent circuit model designed as a parallel resistor $R_P$ and capacitor $C_P$ network in series with resistor $R_S$. We extract numerical values of these parameters by fitting experimental data. Their evolution with bias voltages has shown that the SCLC mechanism is characterized by an exponential trap distribution. We estimated from the capacitance voltage characteristic an acceptor concentration of about $10^{11}$ cm$^{-3}$ due to trap states.

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1. Introduction

Organic materials have recently attracted a great interest as semi conducting materials [1–3] and have been successfully applied to electroluminescent devices [3,4], field-effect transistors [5,6], solar cells [7,8] and chemical sensors [9,10], in particular, molecular host–guest recognition systems such as calixarenes and cyclodextrins [10–16]. The latter have good physical and chemical stability, compatibility with large field applications and lead to low-cost devices. Among synthetic host molecules, cyclodextrins (CDs) have emerged as an ideal candidate for this pursuit due to its well-defined molecular cavity and its ability to accommodate a variety of guest molecules [17]. Nevertheless, the strong solubility of CDs in water makes their use difficult in the development of chemical sensors working in aqueous media. In our group, different immobilization methods have been used to overcome this problem: the β-CDs molecules were fixed to silica insulator surfaces; either by chemically grafting polymethyl-hydrosiloxanes (PMHS) chains as a coupling agent [18] or by physically incorporating CDs in plasticized poly(vinyl chloride) (PVC) [19]. In previous work, we have chemically modified β-CDs (β-CDs (Bz)) and used them as sensitive membranes for heavy metal cations detection (such as Pb$^{2+}$ and Cd$^{2+}$) [20]. This has given us a great stimulus to the deeper study of their electrical and dielectric properties. Impedance spectroscopy (IS) has proved to be a powerful tool for studying the transport mechanisms and relaxation processes in organic devices [21,22]. The objective is to establish a correlation between chemical structure, in terms of number of benzyl moieties, and electrical performances toward an ion sensor with optimized sensitivity. Indeed, we present in another work [23] a comparison between CD grafted with 5 and 10 benzyl moieties in terms of heavy metal detection.

In this paper, we have investigated the electrical properties of this partially benzylated β-cyclodextrin whose synthesis was presented in the previous work [20]. We investigated charge-carrier injection and transport...
processes of β-CDs (Bz) diodes via $I$–$V$ characteristics as well as impedance spectroscopy. The diode structure studied is a metal/polymer/metal consisting of indium tin oxide as positive contact and an aluminum electrode as the negative contact as shown in Fig. 1. The IS measurements at different bias voltages have given a deeper insight into transport mechanism of the device. Moreover, the obtained results were fitted to an electrical equivalent circuit in order to extract the relaxation time in these materials.

2. Experimental details

Thin films were obtained by spin-coating β-CDs(Bz)/chloroform solutions on ITO glass substrates which were precleaned by successive ultrasonic treatment for 20 min in acetone and methanol followed by drying with nitrogen gas (ITO-thickness 100 nm, sheet resistance $20\ \Omega/cm^2$). Following the spin-coating process, the films were annealed for 30 min in an oven at $80^\circ C$ under ambient atmosphere. The indium tin oxide (ITO) thin films have been used, due to their good efficiency as a hole injecting material into organic thin film. The aluminum top electrode was deposited on β-CDs (Bz) thin film by thermal evaporation through appropriately shadow masks in high vacuum conditions ($10^{-6}$ Torr). The current–voltage characteristics of the ITO/β-CDs (Bz)/Al devices were measured from an applied bias of $0–5$ V by using a Keithley 236 source measure unit. In general, the excitation potential for AC measurements is given by:

$$V = V_0 + V_{\text{mod}} \cos(\omega t),$$

with $V_0$ is the DC bias and $V_{\text{mod}}$ is the oscillation level and $\omega/2\pi$ is the frequency. In our case, the measurements were performed in the following conditions $V_0: 0–3.5$ V and $V_{\text{mod}}$ of $50$ mV over a frequency range of $500$ Hz–$13$ MHz using a computer controlled HP 4192A LF. All electrical measurements were performed in dark and at room temperature.

The UV–Visible absorption spectra were recorded with a Perkin-Elmer UV–Vis spectrophotometer (Lambda 35) on β-CDs (Bz) thin films spin-coated on spectrosil glass substrates to avoid the strong absorption of ITO in the UV.

3. Results and discussion

3.1. Surface morphology

The produced films are smooth and homogeneous in surface topography as shown in the AFM image in Fig. 2. The surface shows a very low roughness (RMS) of $0.5$ nm measured over a $500 \times 500$ nm$^2$ area. The thickness was estimated by the AFM-scratching technique to be about 20 nm.

3.2. UV–Vis study

UV–Vis spectra of β-CDs (Bz) performed in solution and on thin film samples, exhibit one significant absorption band ($\lambda_{\text{max}} = 260$ nm) as shown in Fig. 3a. The estimated optical band gap is about $4.4$ eV giving a device electronic structure shown in Fig. 3b.

3.3. Current–voltage characteristics

The measured $I$–$V$ characteristics show typical diode behavior with a threshold bias voltage of $2.5$ V. As it can be seen in Fig. 4a, the current was observed in both forward and reverse bias voltage. The electrically symmetric $I$–$V$ characteristic, for low voltages, can be explained by the localized-state theory with defects providing the localized gap states [24]. Indeed, if the defects are amphoteric, it is possible to observe electrically symmetric behavior at low voltages. The asymmetric $I$–$V$ characteristic at higher voltages is attributed to the difference of injection barriers to electron and hole due to different work functions for the ITO anode ($4.7$ eV) and the Al cathode ($4.3$ eV). The $I$–$V$ characteristic in log–log plots of ITO/β-CDs (Bz)/Al is shown in Fig. 4b. The current dependence of applied voltage appears to follow power law behavior $J \propto V^\prime$ with two regimes corresponding to:

$$(1) \quad \text{An ohmic region with } J \propto V \text{ at low voltage. Indeed, for the case of existence of a single set of shallow traps in}$$

![Fig. 1. ITO/β-CD(Bz)/Al diode heterostructure.](image)

![Fig. 2. AFM topography of a spin-coated partially benzylated cyclodextrins (β-CDs (Bz)), image at 3D.](image)
solids, at low voltages, electrical conduction is Ohmic and the current density is described by

\[ J = q \mu n_0 V \frac{V}{d}, \]  

(2)

where \( q \) is the electronic charge, \( \mu \): the charge carrier mobility, \( n_0 \): the free carrier density, \( V \): the applied voltage and \( d \): the film thickness.

(2) A trapped charge limited region with \( J \propto V^2 \). As the voltage increases, the current is controlled by space charge and follow the relation \([25,26]\):

\[ J = \frac{8\varepsilon \theta \mu}{9} \frac{V^2}{d^3}, \]  

(3)

where \( \varepsilon \) is the organic material permittivity, \( \theta \) relating the proportion of trapped charges \((n, p)\) to free charges \((n', p')\) then \( \theta = n/(n + n') = p/(p + p') \) where \( n \) and \( n' \) are the density of free and trapped electron respectively, \( p \) and \( p' \) the density of free and trapped hole respectively.

These two regimes show clearly a space charge limited current (SCLC) process \([27,28]\). This is a similar behavior as observed in previous works for several ITO/organic film/Al diode structures \([29–36]\). The organic layers used were a conjugated polymer (PPV), a small molecule (Alq3), an alternating block copolymer and other different macro-molecules (diazooamino glyoxime (DAG) and anthylvinyl benzene (AVB)) \([29–36]\). These reports have considered that this SCLC mechanism is attributed to a bulk-limited conduction process. However, de Boer and Morpurgo \([37]\) have shown recently; that surface traps cause a large change in the electrostatic profile of the bulk material thereby profoundly affecting the behavior of SCLC. Their calculations illustrate how the combined effect of surface and bulk traps results in features in the \( I-V \) curves that have been so far attributed to different physical mechanisms. The crucial point is that in high-purity samples, the total amount of surface traps can dominate over the total amount of bulk traps, even for sizable contact separations \([37]\).

### 3.4. Impedance spectroscopy

#### 3.4.1. \( G(\omega) \) and \( C(\omega) \) measurements

Impedance spectroscopy was applied to understand the dielectric behavior of the ITO/\( \beta \)-CDs (Bz)/Al device. 

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**Fig. 3.** (a) UV–Vis spectra of \( \beta \)-CDs (Bz) and (b) energy levels diagram of ITO/\( \beta \)-CDs (Bz)/Al.

**Fig. 4.** (a) Current–voltage characteristics of the ITO/\( \beta \)-CD (Bz)/Al and (b) log–log plot of the \( I-V \) curve of Fig. 4a. The slopes of AB and BC lines indicate two regions ohmic and SCLC with exponents 1.22 and 2.04, respectively.
The variation of conductance and capacitance, of β-CDs (Bz) derivative based diodes versus frequency at different bias voltages are plotted as shown in Figs. 5 and 6, respectively.

The conductance characteristic remains constant at low frequencies and power-law behavior was observed at higher ones. Indeed, a hopping transport mechanism can be postulated. In general, the trend of the conductance with frequency, in disordered materials, obeys the following relation [38]:

\[ G(\omega) = G_{dc} + G_{ac}(\omega) \quad \text{where} \quad G_{ac}(\omega) = A\omega^s, \]

where \( G_{dc} \) is the dc conductance, \( \omega \) the angular frequency of the applied excitation, \( A \) constant, \( s \) the critical exponent \( 0 < s < 1 \).

As shown in Fig. 6 the capacitance decreases as the frequency increases (capacitance curves are off-set by 1 pF for clarity). This effect can be ascribed to traps inside the device [39] as observed also in polymer light emitting diodes by Blom and coworkers [40]. In our case, it appears that the capacitance \( C \) exhibits distinct frequency dependence:

- At low frequencies \( C \) decreases and the frequency at which this decrease stops is about 10–100 kHz depending on the applied bias. Indeed, since the device is space charge limited, the ac frequency modulates the number of charge carriers in the device. Nevertheless, the time scale for the built-up of charge carriers is given by the transit time \( \tau_i \) of the injected carriers. At low frequencies the built-up of the space charge is fast enough to follow the ac modulation. Given that \( \tau_i \) is finite the corresponding current lags behind the ac modulation excitation and this result in an additional inductive (negative) contribution to the capacitance.

- For higher frequencies the space charge cannot be redistributed in a period of the applied voltage and the measured capacitance equals to the geometrical value, \( C_0 = \varepsilon_0 \varepsilon_r A/d \).

Moreover, the slow decrease of \( C \) and strong increase of \( G \) with frequency reflect the relaxation of permanent dipoles present in the material. The disordered nature of the organic material gives rise to a distribution of dipolar relaxation times, (the evolution of the latter with bias voltage will be discussed in Section 3.4.3) and the dielectric response can be accurately described by the Cole–Cole representation [41].

3.4.2. Cole–cole representation

The IS technique consists in the measurement of the electrical impedance \( Z \) as a function of the frequency of the input signal over a wide frequency range. The collected data may be visualized as a Nyquist diagram or cole–cole plot, represented by the imaginary component \( Z' \) of the impedance as a function of \( Z'' \) the real component. The Cole–Cole plots of ITO/β-CDs (Bz)/Al device at several dc bias voltages as seen in Fig. 7, display a single semicircle and a net decrease in diameter with increasing applied dc bias. The strong dependence of the impedance with the bias indicates the presence of a depletion layer in the sample with a resistance decreasing with increasing bias. Capacitance voltage measurements (see Section 3.5) confirm the presence of a depletion layer in forward bias before the injection becomes significant. In this case two semicircles should be obtained on the plot of \( \text{Im}(Z) \) vs \( \text{Re}(Z) \), one representing junction and the other representing the bulk behaviour. In our case, only one semicircle is observed because the bulk and the junction capacitances are not sufficiently different. Thus, the semicircle diameter corresponds to the sum of bulk and junction resistances. Analog results has been obtained for PPV [42] and AVB [36] based devices.

A single semicircle in a Nyquist plot suggests an equivalent electrical circuit, shown in Fig. 8, composed of a single parallel resistor \( R_P \) and a capacitor \( C_P \) network placed in series with resistance \( R_S \) [21]. We plotted the
data in log–log scale (Fig. 9). The slope of 0.5 means the curvature is a semicircle [21,41]. The obtained slopes are in the range of 0.46–0.68 for high and low bias voltages. It suggests a single characteristic relaxation time.

We presented in Fig. 10(a) the real part of the impedance of ITO/β-CD(bZ)/Al device as a function of frequency at 0, 1.5 and 3.5 bias voltages. The maximum Re(Z) value corresponds to the sum of the device resistance and the resistance of the ITO substrate. At higher frequencies, Re(Z) (Fig. 10a) and Im(Z) (Fig. 10b) are more frequency-independent.

### 3.4.3. Simulation of impedance spectroscopy results

The impedance of the equivalent circuit is given by

\[
Z(\omega) = \left[ R_S + \frac{R_P}{1 + (\omega/\omega_0)^2} \right] - j \left[ \frac{R_P\omega/\omega_0}{1 + (\omega/\omega_0)^2} \right] = \text{Re}(Z) / \text{Im}(Z),
\]

where \( \omega \) is the angular frequency of the ac excitation and \( \omega_0 = 1/R_P C_P \) the proper angular frequency of the circuit. Eliminating the angular frequency we obtain the following equation relation:

\[
\left[ \text{Re}(Z) - \left( \frac{R_S + R_P}{2} \right) \right]^2 + \text{Im}(Z)^2 = \frac{R_P^2}{4}.
\]

The minimum \( \text{Re}(Z) \) value observed at high frequencies corresponds to the \( R_S \) value which is bias and frequency independent and should be attributed to the hole injecting interface ITO/β-CDs (Bz) which can be regarded as ohmic. In this device \( R_S \) is about 289.5 \( \Omega \) (for 0 V bias). The maximum \( \text{Re}(Z) \) value at low frequencies corresponds to the sum of \( R_S \) and the β-CDs (Bz) resistance \( R_P \) which is strongly bias dependent. Fig. 11 shows the measured real and imaginary parts of the impedance as a function of the frequency for the diode ITO/β-CDs (Bz)/Al at dc bias voltage of 0 V. Symbols are measured data and the solid lines are the fitting results using the correspondent equivalent circuit of Fig. 8. The fit of experimental results by Eq. (5) give the parameters \( R_P \) and \( C_P \) of the circuit which are summarized in Table 1. The interfacial capacitance is negligible, which suggests that there are negligible insulating barriers such as oxide or air gap formed between the β-CDs (Bz) thin film and the top and/or bottom electrodes.

The variation of the fitting parameters of the ITO/β-CDs (Bz)/Al device are shown in Fig. 12. The \( R_P \) decreases as the dc bias voltage increases while \( C_P \) is almost independent of bias voltage. The independence of \( C_P \) with applied bias is exactly the behavior expected for the SCLC mechanism, where the total charge in the device is equal to \( C_P V \).
From the SCLC with an exponential trap distribution theory, voltage dependent current for one carrier dominated transport, hole in this case, is given by

$$J = \frac{KV_m}{d^2} + \frac{1}{\Omega^2}, \quad (7)$$

where $d$ and $K$ are the thickness of the film and a constant, respectively.

The voltage dependence of $R_P$ is thus described by

$$R_P = \frac{J}{V_m^m}, \quad (8)$$

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$$R_P = \frac{J}{V_m^m}. \quad (8)$$

The plot of log $R_P$ vs log $V$ is shown in the inset of Fig. 12. The linear behavior of log $R_P$ vs log $V$ implies that conductance of the hole in $\beta$-CDs (Bz) thin film is consistent with a SCLC mechanism with exponential trap distribution where the corresponding $m$ is about 1.9. The carriers may be trapped by chemical impurities and/or structural defects.

The range of relaxation times, for different bias voltage, is indicative of dipolar relaxation.

### 3.5. Capacitance–voltage characteristics

More quantitative information about trap concentration in our device can be obtained from capacitance–voltage
trap distribution and relaxation time can be extracted from the space charge limited current theory with traps and the impedance spectroscopy formalism. Moreover, the slow decrease of $C$ and strong increase of $G$ with frequency reflect the relaxation of permanent dipoles present in the material. The disordered nature of the organic material gives rise to a distribution of dipolar relaxation times. From the plot of $1/C^2$ vs bias voltage of ITO/β-CDs (Bz)/Al diode we deduce the acceptor concentration $N_A$.

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