

Optical and electrical study of chromogenic calix[4]arene derivatives

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Abstract

New chromogenic calix[4]arene derivatives proved many applications in optical and electrical fields. Organic diodes formed by sandwiching azo-calix[4]arene layers between indium–tin oxide (ITO) and (Al) contacts have been elaborated and measured. In this paper, studies of devices by current–voltage characteristics $I(V)$ and electrical impedance spectroscopy measurements in a wide frequency range have been reported. The electrical characteristics follow a space charge limited conduction behaviour (SCLC). Therefore, the Cole–Cole plots were modelled by an equivalent circuit. Relaxation processes have been identified too from the impedance spectroscopy. The optical excitation of the organic structure revealed enhancement in electrical properties.

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1. Introduction

The first small molecules based electroluminescent diodes [1] were elaborated in 1987 by the Kodak group. In 1990, it was demonstrated at Cambridge University that organic thin films can find various applications in (opto) electronic devices and sensors [2–4]. Conductive polymeric materials with π -conjugated electronic systems (PPV derivatives, PVK, polypyrrole, polyaniline...) have found growing application in optoelectronics [5,6]. During the last decade, many researches were made to use ionophores (calixarenes, cyclodextrin...) in the electronic components and sensors. Calixarenes, a group of macrocyclic phenol–formaldehyde condensates, are currently the subject of studies in different areas such as chemical sensors [7,8] or selective receptors [9]. They can be used in new photosensitive sensors [10] due to their ease of synthesis and the multiple sites available for structural modification and com-

plexation. Therefore, very little is still known concerning the electrical properties of their interfaces.

It is possible to prepare various derivatives by the functional modification of either the upper and/or lower rims. A new chromogenic calix[4]arene derivative has been proved as an ionophore for potentiometric ion-selective and optical sensor [11]. In the case of chromogenic compounds the most studied are azo-calixarenes, first developed by Shinkai et al. [12]. A novel series of azo-calix[4]arene derivatives have been prepared by functionalization of the lower rim of the chromophore with auxiliary contained oxygen atoms forming ester groups [13,14].

First section of this work was devoted to the study of the optical characteristics of four bis(phenylazo)-substituted calix[4]arene derivatives. In the second section, we have investigated the electrical properties of diode structures (ITO/calix[4]arene derivatives/Al) using indium tin oxide (ITO) as anode and aluminum (Al) as cathode. We used impedance spectroscopy (IS) for the measurement of the electrical impedance Z as function of the input signal over a wide frequency range. A model of the behaviour of real systems by an idealized electrical circuit consisting of discrete electrical components has been deduced. The parameters of the equivalent circuit were optimised to ensure the best fit of the experimental data.

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2. Materials, device elaboration and measurements

2.1. Materials

Our studies have born on new series of chromogenic calix [4]arene derivatives, synthesized at the “Claude Bernard University” by the laboratory LACE according to previously reported synthesis techniques [13,14]. Azo-calix[4]arenes derivatives have been characterised by the presence of chromophores at the upper rim and an ester group at the lower rim. The studied materials (C_1 , C_2 , C_3 and C_4) are represented in Fig. 1.

2.2. Device fabrication

The devices have been fabricated on ITO-coated glass substrates (ITO-thickness 100 nm, sheet resistance 20 Ω /square) used as anodes. The ITO substrates have been supplied by Merck Display Technologies (MDT). Before etching process, the ITO substrates were successively pre-cleaned for 20 min in acetone and isopropyl alcohol in an ultrasonic bath and finally dried by a nitrogen gas flow.

The deposition of the calixarene films was performed by the spin-coating technique from CHCl_3 solution with a controlled speed at about 2300 rpm. Following deposition, films were dried for 30 min at 80 $^\circ\text{C}$. Finally, an electron injecting electrode was deposited by aluminum thermal evaporation (10^{-6} Torr) through a shadow mask.

2.3. Measurements

2.3.1. Optical UV-Vis absorption

The UV-Visible absorption spectra were recorded with a Perkin-Elmer UV-Vis spectrophotometer (Lambda 35). For UV-Vis study, azo-calixarenes thin films were spin coated on spectroil glass substrates to avoid the strong absorption of ITO in the UV.

2.3.2. Current–Voltage measurements

The electrical characteristics of the devices was carried out in a dark chamber and performed using a Keithly 236.

2.3.3. Impedance spectroscopy

Impedance measurements were carried out in the same conditions with an impedance analyser (Hewlett Packard 4192A LF) controlled by a computer acquisition system. All the measurements were performed in the frequency range (50 Hz–6 MHz) for different values of bias. Study of the bias voltages effect has been carried out with an optimised oscillation level of about 50 mV.

3. Results and discussion

3.1. Optical study

The UV-vis spectra of different ligands performed in solution exhibited different absorption bands. Their absorption

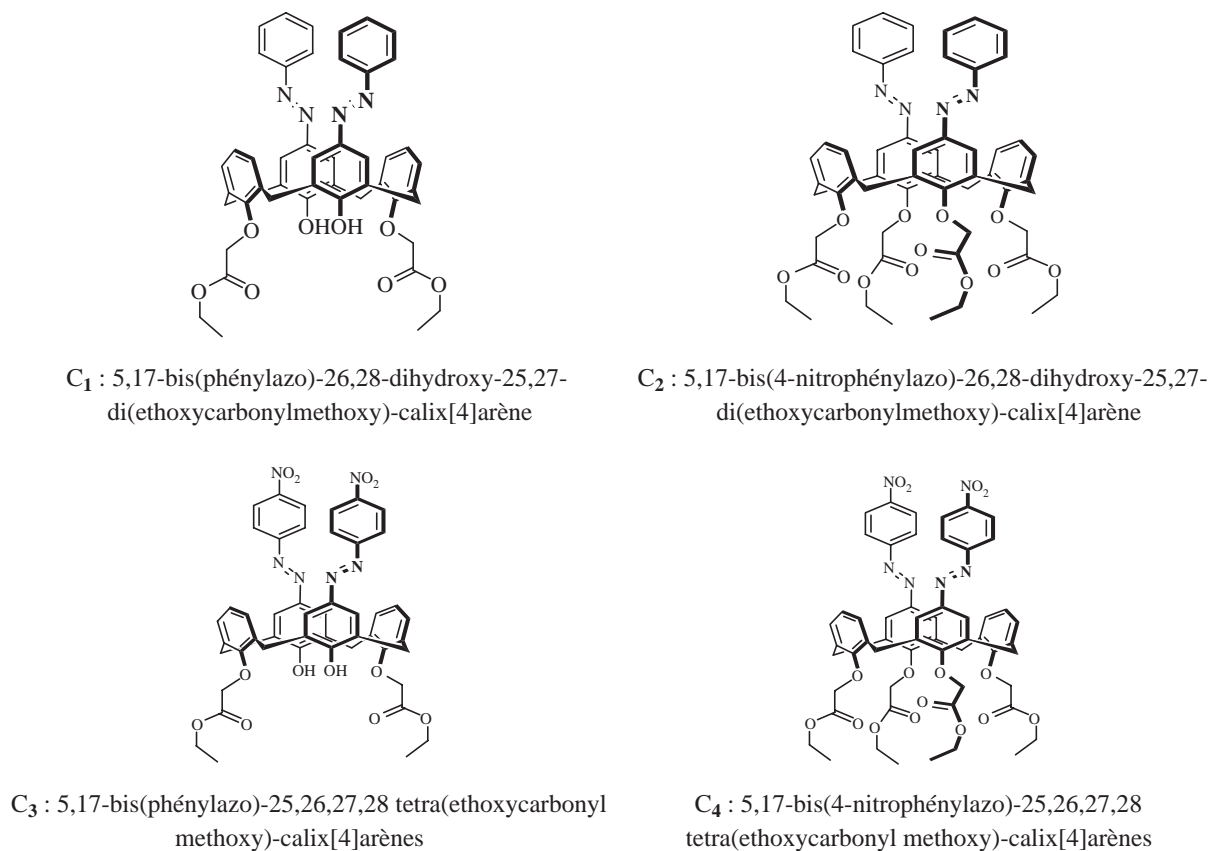


Fig. 1. Chemical structures of the materials used in the work.

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