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Optical and electrical properties of p-substituted-benzylidenemalononitrile thin films: Optoelectronic applications

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ABSTRACT

A donor-bridge-acceptor type conjugated molecule has been successfully synthesized and characterized. The optical properties such as absorption, photoluminescence and electrical properties such as cyclic-voltammetry and J–V characteristic of p-substituted-benzylidenemalononitrile (BMN) thin films have been investigated. The BMN films shows a wide absorption in visible region, which makes it possible for application in OPV and OLED. The band gap energy of BMN thin film was obtained by experimental calculation from cyclic voltammetry. From the current–voltage characteristics, the electrical bistability in such films can be associated with a memory phenomenon. The obtained results of the materials have promising to be applicable for various optoelectronic applications.

1. Introduction

In the past decades, organic π-conjugated small molecules have attracted much attention for developing high performance organic optoelectronic due to their easily controlled energy levels and absorption. In fact, a huge number of experimental and theoretical studies have demonstrated that small organic molecules such as fullerenes, carbon nanotubes and graphene are of great importance in the development of optoelectronic and photonic devices [1–3]. The conjugation system was the common feature for this kind of materials, thus they had good ability of accepting electron, which made them good application prospects in organic electronic and other fields [4,5]. In particular, donor-acceptor systems receive great attention due to their simple charge trapping/detrapping or charge transfer switching mechanism [6–10]. Moreover, the memory phenomenon and the electrical characteristics of the donor-acceptor systems can be fine-tuned over a wide range via versatile molecular-cum-synthesis strategy [11]. Indeed, given their exceptional chemical and physical properties fullerenes find widely application in diverse fields, such as in photovoltaic, cosmetic and biomedicine [12–14]. The electron affinity for fullerene was proved to be 2.7eV [15], it is a very good ability of electron acceptance; due to its carbon cage structures. The electrical proprieties and transport mechanism in memory structures fabricated using PVK and fullerene are reported in Ref. [16]. Conductance and resistive switching characteristics of organic memory devices with carbon nanotubes have generated

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considerable interest [17–19]. Various types of organic memory materials have been developed by adding carbon nanotubes [20–23]. Indeed, Liu et al. found that the variation of carbon nanotubes ratio in PVK provides various electrical behaviors such as insulator, memory, flash, and conductor behavior [17].

Our current interest is to study the optical and electrical proprieties of p-substituted-benzylidenemalononitrile thin films. BMN is a donor-bridge-acceptor small molecule; it constitutes a useful class of materials due to their importance in biological processes, as well as synthetic organic chemical applications [24–29]. Indeed, some preliminary results of these materials will be given and possible optoelectronic applications are described.

2. Materials and methods

2.1. Synthesis of p-substituted-benzylidenemalononitrile

To a solution of one equivalent of malononitrile and one equivalent of 4-cyanobenzaldehyde in toluene (50 mL), were added a catalytic amount of piperidine (0.05 mL) and of glacial acetic acid (0.1 mL). The mixture was refluxed overnight with a water trap (Dean–Stark), until no further water separated. The solvent was removed under reduced pressure and the residue was taken up in Et_2O. The Et_2O was washed with HCl (50 mL, 5%), then washed several times with water, followed by drying ($MgSO_4$). The solvent was evaporated and the residue was further purified by recrystallization from a pentane/ethyl acetate mixture [30]. We have studied the kinetics of these materials and demonstrated that they possess the character super-electrophile i.e. those materials are deficient in electron [31].

2.2. Experiment and elaboration

BMN was dissolved in ODCB. The ITO substrates was cleaned in an ultrasonic bath with deionized water and then with acetone for 15min. A layer of BMN was spin coated from an ODCB solution at a concentration of 30 mg mL^{-1} on the ITO substrate. The organic layer has been rotated at 3000 rpm for 15s. Finally, aluminum top electrodes were deposited by thermal evaporation through a shadow mask.

3. Results and discussion

3.1. Optical proprieties

Optical absorption and photoluminescence (PL) spectra of BMN in both solution and film are presented in Fig. 1. In solution, the absorption spectra of BMN exhibit a strong absorption band in the range 250–350 nm. The absorption band at 300 nm is assigned to the π-π^* transition. Furthermore, absorption spectrum of the BMN film is substantially expanded and red-shifted in comparison with their solutions suggesting that: the structure is more organized, strong π-π^* piling effect and the existence of the intermolecular interaction. The bands at the range 350–500 nm could be attributed to intramolecular charge transfer transitions in each donor-acceptor molecules [32].

When excited, BMN show a strong PL emission in solution and in film and exhibit a vibronic structure with a maximum at 570 nm and 600 nm, respectively. The two spectra show only one emission peak, indicating that an effective energy transfer from the donor to the acceptor unit occurs. The red-shift in the spectrum of the BMN film is probably due to the reduction of the band gap by more efficient π-piling [33,34]. Then, this material can be used in PVK-based OPV structures or MEH-PPV-

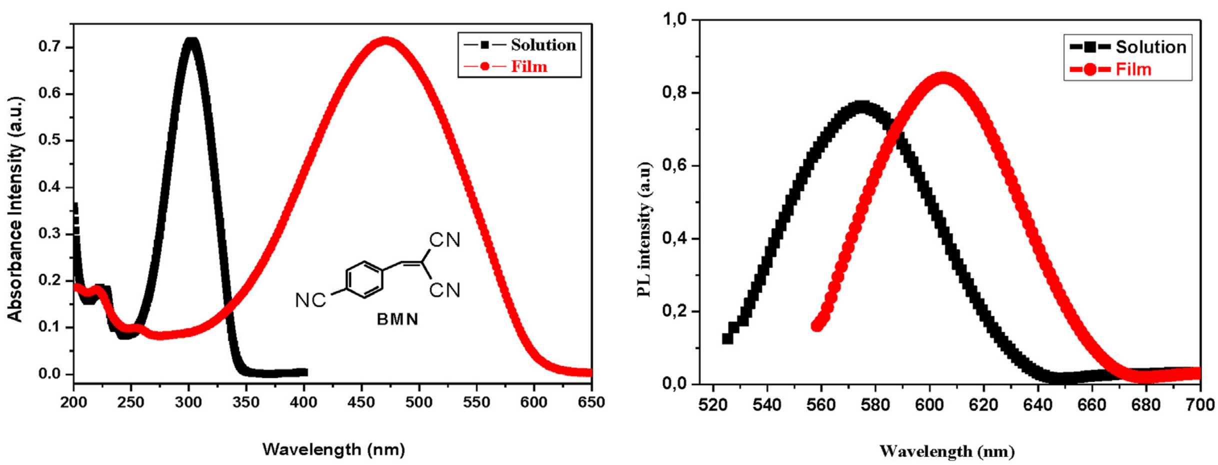

Fig. 1. Absorption (left) and photoluminescence (right) spectra of BMN in solution and in film.