Synthetic Metals 221 (2016) 75–85

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Synthesis and investigation on optical and electrical properties of a triflato iron porphyrin: Application as an optical BPA sensor

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ARTICLE INFO

Article history:
Received 4 May 2016
Received in revised form 12 July 2016
Accepted 14 July 2016
Available online 5 September 2016

Keywords:
Iron porphyrin
Conduction mode
Charge transport
Hopping

ABSTRACT

In this study, we first describe the synthesis of the triflato(5,10,15,20-tetrakis(4-metoxyphenyl) porphyrinato) iron(III) complex with the formula [Fe^{III}(TMPP)(SO_3CF_3)] (**P1**). This species were characterized by proton NMR and IR. Then optical and electrical properties of **P1** thin films have been investigated. The triflato iron porphyrin film exhibit an absorption spectrum with a resolved electronic structure in the UV–vis range and the energy gap was determined by the Tauc method. Electrical properties of the ITO/**P1**/Al structure have been investigated by I–V characteristics and impedance spectroscopy measurements. The conduction is governed by space-charge-limited current (SCLC) mechanism. The impedance spectroscopy study showed a hopping transport process. Its interaction with Bisphenol A (BPA) was then investigated by UV–vis spectroscopy in a sensing window of 10^{-9}–10^{-4} M. The iron-porphyrin species shows a sensitive response to BPA, which induces an absorbance change to the Soret band. The interaction mechanism of **P1** with BPA involved a coordination interaction.

1. Introduction

Porphyrins dyes, or so called "pigments of life" are a large class of natural occurring intensely colored, red or purple, macrocyclic pigmented compounds. The name (porphyrin) is originated from the ancient Greek word porphyra that was used to describe the color purple (or royal purple) [1] Porphyrins and metalloporphyrins are non static aromatic compounds; where the molecule contains four pyrrole rings linked via methane carbon bridges. The properties of these compounds can be systematically tuned by rational utilization of substituents on meso- and/or ß positions as well as by using different metal atoms in the center of the tetrapyrrole macrocycle. These modifications can change the molecular properties like the geometric, electronic structure and optical properties [2,3]. Because of their inherent stability, strong absorption in the visible part of the solar spectrum and synthetic versatility; substantial work has been done in the areas of solution and gas phase sensing. It is well known that heme binds to a variety of gases, such as nitric oxide, carbon dioxide and oxygen. Other gases detectable with porphyrin based sensors include ammonia, hydrazine, and nitric oxide [4–6]. Porphyrin sensors for solutions species are used to detect anions and cations in solution. The anions commonly detected include nitrite [7], chloride, bromide, and nitrate [8]. Porphyrin compounds absorb visible light and convert photo-energy to electrical and chemical energy; this is because the porphyrin skeleton has an extended π conjugation system, leading to a wide range of wavelengths for light absorption [9]. Owing to its unique optoelectrical property, porphyrins thin films offer the promise of widespread adoption in numerous technology areas, including nanotechnology, biochemistry, non-linear optical material [10,11]. To use these materials in a certain molecular electronic device; it is desirable to study their dynamic properties through the dielectric measurements. The study of their electrical properties, at present is a dynamic field of research since a number of applications can be foreseen, such as photovoltaic devices, light emitting diodes, Schottky diodes, field effect transistors and sensing devices. In all these applications, the transport mechanisms as well as the nature of the contacts between the electrodes and the organic semiconductor are of great importance.

In this paper, we report the synthesis of a new iron porphyrin derivative. In order to develop a BPA optical sensor, we investigated the structural, optical and electrical properties of this compound. Using FTIR and NMR spectroscopy, we have observed the different

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http://dx.doi.org/10.1016/j.synthmet.2016.07.020
0379-6779/

bands characteristics of the triflato iron porphyrin. The optical properties were studied and we have determined the band gap energy of our molecule. The ITO/**P1**/Al structure was characterized using current–voltage I–V measurements in order to predict the predominant operating conduction mechanism. Impedance spectroscopy measurements were done to differentiate among the transport properties of our derivative and to investigate the ac behavior. Using an equivalent electrical circuit, we have modeled the impedance characteristics and extracted some important related parameters.

2. Experimental

2.1. Materials

All reagents and solvents employed were commercially available and were used as received without further purification. The H_2TMPP and [Fe^{III}TMPP(Cl)]were synthesized according to the standard literature method [12,13]. All reactions and manipulations for the preparation of the triflato iron(III) porphyrin derivative were carried out under argon using a double-manifold vacuum line, Schlenkware, and cannula techniques.

2.2. Device elaboration

In our study the devices are composed of a single organic layer sandwiched between two electrodes. ITO-coated glass with a sheet resistance of 20 Ω/cm square was used as an anode in the organic diode fabrication. In this process, the ITO glass was cleaned sequentially in an ultrasonic bath of acetone and isopropanol alcohol; it was then, sonicated in deionized water and finally blown dry with N_2 gas. The ITO coated glass substrates are used as the anode due to its superior properties, such as good transparency, high work function, high efficiency, and high conductivity. A solution of porphyrine derivative was dissolved in a dichlorométhane solvent and then was spin-coated on the cleaned ITO precoated glass substrate at the speed of 2000 rpm for 30 s followed by heating on a hot plate for 30 min. For processing the cathode, samples were put into an evaporator, in which Al metal electrodes (160 nm) were thermally evaporated at 410^{-5} Torr pressure through a shadow mask to produce simultaneously the diode structure. Fig. 1 shows the typical device structure of the diode investigated in this study. The active areas of the diodes were confined within the overlap of the electrodes which is approximately 3.14 mm^2.

2.3. Instrumentations and measurements

UV–vis spectra were recorded with a Win ASPECT PLUS (validation for SPECORD PLUS version 4.2) spectrometer. The ^{1}H NMR spectra were recorded at room temperature on a Bruker 300 Ultrashield spectrometer. IR spectra were registered on a FT-IR Nexus (Nicolet) spectrometer with a micro-ATR accessory (Pike). Perkin–Elmer UV–VIS spectrophotometer (Lambda 35) was used to characterize the optical properties of these thin films. Films of iron porphyrins were deposited on a glass substrate to prevent the absorption of ITO substrate in the UV region. The surface morphology of **P1** layer deposited on top of ITO was performed by atomic force microscopy (AFM) using a Nanoscope III in tapping mode.

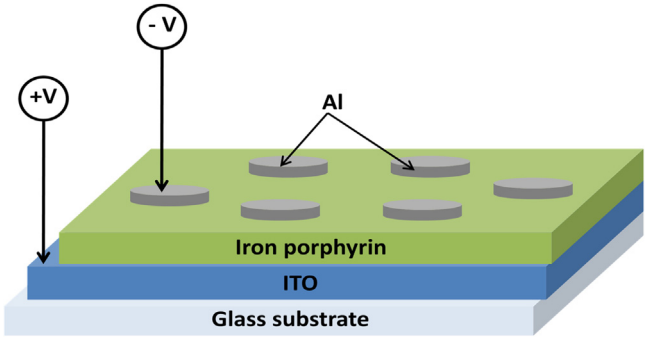

Fig. 1. ITO/**P1**/Al diode strucrure.

The current–voltage measurements were determined with an applied bias of −6 to 6 V by using a Keithley 236 measure unit and the impedance measurements were conducted using an impedance analyzer (Hewlett Packard 4192ALF) controlled by a computer acquisition. In general, the excitation potential for dynamic measurements is given by:

$$V = V_0 + V_{mod}\cos(wt) \quad (1)$$

With V_0 is the dc bias and V_{mod} is the oscillation level, whereas $\frac{w}{2\pi}$ is the frequency.

In our case, the measurements were performed in the following conditions: $V_0 = 0 - 6$ V and $V_{mod} = 50$ mV over a frequency range of 100 Hz to 13 MHz. All these electrical measurements were performed in dark and at room temperature.

The interaction between metalloporphyrin [Fe^{III}(TMPP)(SO_3CF_3)] and BPA was investigated by UV–vis spectrophotometer. A stock solution of the guest BPA and host metalloporphyrin [Fe^{III}(TMPP)(SO_3CF_3)] were prepared in dichloromethane (DCM). DCM can fully dissolve the iron porphyrin species, as well as BPA. As a non-coordinating solvent, DCM will not bond to the iron(III) porphyrin derivative and interfere with the coordination [14]. Various amounts of BPA were added to the solution of host metalloporphyrin in a quartz cell with a path length of 3 cm. The spectrum was recorded, then to obtain the metalloporphyrin UV–vis spectrum.

2.4. Synthesis of the triflato (5,10,15,20-tetrakis(4-metoxyphenyl) porphyrinato) iron(III)([Fe^{III}TMPP(SO_3CF_3)])

In a Schlenk tube, 400 mg (0.48 mmol) of [Fe^{III}(TMPP)Cl] and 135.627 mg (0.52 mmol) of silver triflate ($AgSO_3CF_3$) was dried under vacuum for 2 h. Then 100 ml of dry and degassed THF was added under argon. The color of the solution rapidly changes from brown to red and silver chloride (white solid) starts to precipitate (Scheme 1). The solution is kept under magnetic stirring, at room temperature and under argon for 12 h. After filtration of the red solution, the obtained filtrate is subjected to evaporation to dryness and then 10 ml of hexanes was added. The solution was concentrated by slow evaporation until crystallization. The resulting mass was 0.54 g (yield ∼90%). UV–vis ($CHCl_3$: λ_{max} in nm (log ε)): 411(4.99), 512(4.53). FT-IR [KBr disk, cm^{-1}]: ν(CH) porph.: 2934-2831, ν(O—CH_3)porph.: 1606, ν(C=C)(C=N)porph.: 1509, ν(CN)porph.: 1248, δ(CCH): 990, triflato-ligand: 1339-1282-1173-794.MS (MALDI-TOF) *m/z*: 788.1 [Fe^{III}(TMPP)]$^+$, 735.2 [Fe^{III}(TMPP-2Ph-OCH_3)(CF_3SO_3)]$^+$.^{1}H NMR [300 MHz, $CDCl_3$]: δ (ppm) 35.04 (s, 8H, H β-pyrr.), 11.66 (s, 8H, H-ortho), 8.46 (s, 8H, H-metha), 4.06 (s, 12H, O—CH_3).

3. Results and discussion

3.1. IR

The IR spectrum of the [Fe^{III}(TMPP)(SO_3CF_3)] (**P1**) complex shows an absorption band at 2934 cm^{-1} attributed to ν(C—H) of the porphyrin (Fig. 2). The C—O stretches of the coordinated O-CH_3