



# Synthesis of Ni(II) porphyrazine peripherally octa-substituted with the 4-*tert*-butylbenzylthio moiety and electronic properties of the Al/Ni(II)Pz/p-Si Schottky barrier diode

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## ABSTRACT

Magnesium porphyrinate substituted with eight 4-*tert*-butylphenylthio-groups on the peripheral positions has been synthesized by cyclotramerization of 1,2-bis(4-*tert*-butylphenylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid, and further reaction of this product with nickel(II) acetate led to the metal porphyrinate (M = Ni). These new compounds have been characterized by elemental analysis, together with FT-IR, <sup>1</sup>H NMR and UV-Vis spectral data. The electronic properties of a spin coated film of NiPz have been studied by fabricating metal-insulator-semiconductor (MIS) capacitors. Current-voltage (*I*-*V*) and capacitance-voltage (*C*-*V*) measurements were carried out. It was observed that the Al/NiPz/p-Si structure exhibits rectifying behavior with a barrier height value of 0.89 eV and with an ideality factor value of 1.81. It was seen that this value of the obtained barrier height is remarkably higher than those given for metal/Si semiconductor contacts in the literature. The Lien, So and Nicolet method, combined with conventional forward *I*-*V*, was used to extract the series resistance value and it was found to be 26 kΩ. High frequency *C*-*V* measurements were used to determine the mobile oxide charge in the NiPz layer and this was found to be  $1.6 \times 10^{11} \text{ cm}^{-2}$ .

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## 1. Introduction

Porphyrazine macrocycles afford a skillful platform to build up detailed molecular superstructures and this property, coupled with a full and well-improved synthetic chemistry, has surpassed the synthesis of different catalytically essential metallo porphyrazines and original model compounds of various functions [1–3]. In contrast to the structural similarity between phthalocyanines and porphyrazines, the latter have been relatively less studied compared to the phthalocyanines [4–6]. The diffuse nature of porphyrazines  $\pi$  electronic structure would help us understand there are long-range interactions between different parts of the molecule. The presence of soft S donor atoms play an important role in affecting the solid-state interactions, and an extensive series of derivatives with physical and chemical properties comparable to those of phthalocyanines have been reported [7–9]. Derivatization of porphyrazines has generally been accomplished by the addition of various substituents to the peripheral positions. These substituents enhance the solubility of the products (e.g., *tert*-butyl) and provide

additional functionalities for interaction with alkali or transition metal ions, mesophase formation, etc. [10–12]. Nickel porphyrazine (NiPz), compared with other metal-centered tetrapyrroles, e.g., metal phthalocyanines (Pc), offers new ways to induce, modify and to control molecular properties and has a high metal/ligand stability [4,13,14].

Schottky barrier diodes (SBDs) play a crucial role in modern semiconductor technology as the basis of a large number of electronic devices such as field-effect transistors (FETs), solar cells and photodetectors [15,16]. Recently there has been extensive investigation of organic materials for their use in SB diodes to improve the fundamental SB diode parameters such as the Schottky barrier height  $\Phi_B$  and the ideality factor *n*. A SB diode with the desired electronic properties can be obtained by means of the choice of a suitable interlayer. With that regard, phthalocyanines, porphyrins and porphyrazines have been considered to be one of the most stable organic semiconductors for various electronic and optoelectronic applications. Considerable attention has been given in recent years to the fabrication and characterization of SB diodes using some phthalocyanine compounds [17]. Although porphyrazines are of interest because of their potential applications, such as molecular electronics [18], sensors [19–21], organic solar cells

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[22], photodynamic therapy [23] and organic field effect transistors [24,25], unlike some phthalocyanine compounds, the electronic and interface properties of porphyrazines have not been widely studied. Furthermore, although there are a lot of works on heterojunctions with phthalocyanines and some other organic compounds, as yet there are no reports on porphyrazine plus a p-Si type junction.

The purpose of the present work is to synthesize nickel(II) inserted peripherally *tert*-butylbenzylthio substituted porphyrazine (NiPz) and to investigate the electronic properties of the Al/NiPz/p-Si SB diode by the insertion of the NiPz organic layer between the Si semiconductor and Al metal.

## 2. Experimental

### 2.1. Reagents, instruments and measurements

[Octakis(4-*tert*-butylbenzylthio)porphyrazinato]Mg(II) (**1**) (MgPz) and [2,3,7,8,12,13,17,18-octakis(4-*tert*-butylbenzylthio)<sup>21</sup>H,<sup>23</sup>H porphyrazine] (**2**) (H<sub>2</sub>Pz) were prepared according to the previously reported procedures and characterized by comparing their spectral data to those reported earlier [26]. The Mg(II) complex and the metal free porphyrazine (H<sub>2</sub>Pz) were stable at room temperature, non-hygroscopic, insoluble in water, but soluble many common organic solvents. *Reagents*: Chemicals employed were of the highest grade available. Unless specified otherwise, reagent grade reactants and solvents were used as received from the chemical suppliers.

The FT-IR spectra were recorded in the 4000–400 cm<sup>-1</sup> range on a Perkin Elmer Spectrum One spectrometer using KBr pellets. The electronic spectra and absorbance measurements were recorded on an Agilent 8453 UV-Vis spectroscopy system. Proton NMR spectra were recorded on Bruker 250 MHz and 500 MHz Varian Inova spectrometers. Elemental analyses were recorded on Thermo Flash EA 1112 series equipment.

### 2.2. Synthesis of [2,3,7,8,12,13,17,18-octakis(4-*tert*-butylbenzylthio)porphyrazinato]Ni(II) (**3**)

To a solution of anhydrous Ni(CH<sub>3</sub>COO)<sub>2</sub> (173 mg, 0.094 mmol) in 10 ml of absolute ethanol was added a solution of **2** (80 mg, 0.046 mmol) in 10 ml of THF, and the resulting mixture was refluxed under Ar for about 18 h. The precipitate that formed, composed of the crude product and the excess metal salt, was filtered then washed with hot THF. After evaporation of the solvent, the remaining product was treated with hot water to remove the unreacted metal salt, washed with methanol and dried. The pure dark blue porphyrazine was obtained. The product was very soluble in chloroform, THF and dichloromethane.

Yield: 71 mg (84%). FT-IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3028 (H-Ar), 2956 C-(CH<sub>3</sub>)<sub>3</sub>, 1636, 1513, 1461, 1263, 1191, 1105, 1018, 834. <sup>1</sup>H NMR (CDCl<sub>3</sub>) ( $\delta$ , ppm): 7.34–7.27 (d, m, 4H, Ar-H), 4.59 (m, s, 2H, CH<sub>2</sub>-S), 1.33 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>-C). *Anal. Calc.* for C<sub>104</sub>H<sub>120</sub>NiN<sub>8</sub>S<sub>8</sub>: C, 69.50; H, 6.73; N, 6.23; Ni, 3.27; S, 14.27. *Found*: C, 68.35; H, 6.57; N, 5.84; S, 12.73%.

### 2.3. MIS diode fabrication

For the MIS diode fabrication, p-type single crystal silicon (100) with resistivity in the 8–10  $\Omega$  cm range was used. Prior to the deposition, the silicon substrates were cleaned by ultrasonic treatment in acetone, propanol and water for 10 min each, and subsequently etched in diluted HF solution, to remove the native SiO<sub>2</sub> layer. An Ohmic back contact was established by the thermal evaporation of 200 nm high purity (99.999%) Al followed by annealing

at 400 °C for 20 min in ambient nitrogen. The film of the Pz compound was prepared by the spin coating method. The ellipsometric technique was used to measure the thickness of the NiPz film and it was found to be 110 nm. After the film deposition process, the substrate was immediately placed in a vacuum system for the processes. Al metal contacts were formed on a NiPz layer by vacuum thermal evaporation of Al at pressure of approximately 3.0  $\times$  10<sup>-6</sup> mbar using an Edwards Auto 500 thermal evaporator system. The current-voltage (*I*-*V*) measurements were performed using a KEITHLEY 6517A electrometer and data of current-voltage measurements were recorded on a PC using a GPIB data transfer card. The capacitance-voltage (*C*-*V*) measurements on the prepared Schottky diodes were also carried out using an Agilent 4284A LCR meter. All the measurements were performed under 10<sup>-3</sup> mbar.

## 3. Results and discussions

### 3.1. Synthesis and characterization

The starting point of this new nickel(II) porphyrazine structure with eight (4-*tert*-butylbenzylthio) groups bound to the periphery is 1,2-bis-(4-*tert*-butylbenzylthio) maleonitrile (TBBTMnt), which was synthesized as a solid product in relatively high yield according a previous report (Scheme 1) [26]. The presence of electron donating S-groups is expected to shift the absorption range of the porphyrazine Q-band to higher wavelength and the *tert*-butyl groups are expected to enhance the solubility [4,13,14,27].

The cyclotetramerization process of the dinitrile derivative (TBBTMnt) by the template effect of magnesium butanolate in butanol resulted in the blue-green octakis(4-*tert*-butylbenzylthio)porphyrazinato magnesium **1** in very good yield (Fig. 1). The metal-free derivative **2** was obtained in a reasonable yield of 30–40% by treatment of **1** with trifluoroacetic acid at room temperature for 8 h. The change of color from dark blue-green to purplish blue and the lowering of the solubility are apparent differences between the magnesium and metal-free products. Insertion of metal ions into **2** with nickel(II) acetate was performed in THF and ethanol at reflux temperature for 18 h and afforded derivative **3** in approximately quantitative yield (84%). The elemental analysis results closely follow the values calculated for **3**.

Spectroscopic investigations on the newly synthesized intermediates and porphyrazine are in accordance with the proposed structures. In the FT-IR spectrum of TBBTMnt, the stretching vibration of C $\equiv$ N is observed at 2213 cm<sup>-1</sup>, the *tert*-butyl peak around 2978 cm<sup>-1</sup>, the S-CH<sub>2</sub> peak around 680 cm<sup>-1</sup> and the aromatic C-H peaks around 3028 cm<sup>-1</sup>. These values comply with those reported in the literature for similar compounds and with the previous report for TBBTMnt [26,28]. The sharp C $\equiv$ N vibration around 2213 cm<sup>-1</sup> disappeared after the formation of porphyrazine **1**. The N-H stretching vibration of the inner core of the metal-free porphyrazine **2** was observed around 3289 cm<sup>-1</sup> after demetallation of **1** [25,29,30]. The FT-IR spectrum of the NiPz (**3**) derivative showed a stretching vibration of the *tert*-butyl peak around 2863–2956 cm<sup>-1</sup> and aromatic C-H peaks around 3028 cm<sup>-1</sup>, which are very similar with the literature (M = Cu, Co, Zn) as expected [4,26].

In the <sup>1</sup>H NMR spectra of **1**, **2** and **3**, chemical shifts corresponding to the *tert*-butyl protons came out at the expected values: a singlet at 1.3 ppm in the ligand TBBTMnt, 1.14 ppm in **1**, 1.17 ppm in **2** and 1.33 ppm in **3** [5,26,29,31,32].

To identify the structure of the porphyrazines (**1**–**3**), electronic spectra are especially useful. The electronic absorption spectra of the metallo-porphyrazines (**1** and **3**) exhibit a strong absorption between 648 and 674 nm which is due to a  $\pi \rightarrow \pi^*$  transition and

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