



# Synthesis, characterization and ethanol sensing properties of carboxylic acid-terminated naphthoxy substituted phthalocyanines

Seher Neccaroğlu Işık<sup>a</sup>, Gülnur Keser Karaoğlan<sup>a</sup>, Birsal Can Ömür<sup>b</sup>, Ahmet Altındal<sup>b</sup>,  
Gülşah Gümrükçü Köse<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Yıldız Technical University, 34220 Esenler, Istanbul, Turkey

<sup>b</sup> Department of Physics, Yıldız Technical University, 34220 Esenler, Istanbul, Turkey



## ARTICLE INFO

### Keywords:

Phthalocyanine  
Carboxylic acid  
Naphthol  
Ethanol sensing  
Response time  
Sensitivity

## ABSTRACT

A new mono substituted phthalonitrile derivative of 4-(6-carboxy-2-naphthoxy)phthalonitrile was prepared by a nucleophilic displacement reaction of 4-nitrophthalonitrile with 6-hydroxy-2-naphthoic acid. Metallophthalocyanines of [2,9,16,23-tetra-(4-(6-carboxy-2-naphthoxy)-phthalocyaninato-zinc(II)), cobalt(II), copper(II), nickel (II), and metal free phthalocyanines bearing carboxylic acid groups at the peripheral positions have been designed and synthesized by cyclotramerisation of the phthalonitrile to investigate the influence of the central metal atom on the ethanol vapor sensing properties. All newly synthesized compounds were characterized by UV–Vis, FTIR, <sup>1</sup>H-NMR, MALDI-TOF MS and elemental analysis spectral data. The influence of COOH group on the organic vapor sensing performance towards 5 different groups of analytes (alkanes, chlorinated hydrocarbons, amines, alcohols and aromatics) were examined. Ethanol adsorption onto the thin films of these compounds and the effects of operating temperature on the sensing properties were also studied. The sensing data show that all the films of phthalocyanine compounds show response to ethanol, among which, [2,9,16,23-tetra-(4-(6-carboxy-2-naphthoxy)-phthalocyaninato-nickel (II)] based sensor show the highest response, demonstrating central metal atom dependence of ethanol sensitivity. Surface topography of the sensing films were analyzed by atomic force microscopy.

## 1. Introduction

Phthalocyanines (Pcs) and their derivatives, fully-aromatic eight nitrogen containing planar 18 $\pi$ -electron heterocyclic conjugated compounds, have been the subject of intense research because of their unique chemical, physical, biological and spectral properties they possess with the binding of a simple functional unit (e.g., catalytic, photo-active, redox-active) to the periphery of the phthalocyanine core or the exchange of central metal ions [1–3]. Phthalocyanines are extremely important substances in different fields outside of their traditional use as pigments and dyes and also can be functionalized to allow for various technological applications [4] including in organic field-effect transistors (OFETs) [5], photodynamic therapy (PDT) [6,7], sensors [8], photovoltaics [9], nonlinear optics [10,11] and solar cells [12].

Dyestuffs containing carboxylic group are advantageous because they can be anchored onto the hydroxyl-bearing oxide surface [13,14]. Carboxyl-bearing metallophthalocyanines have been studied in terms of photophysical and photochemical properties in homogeneous solutions

and in micellar systems [15,16]. Condensed multicyclic aromatic compounds (e.g., naphthalene derivatives) are functional groups effective in photoemission studies [17]. As bulky electron rich units, the presence of naphthalenyl groups on the periphery phthalocyanines is also expected to change the ordering of molecules in the solid state and an intense absorption due to the  $\pi \rightarrow \pi^*$  transition of naphthalene groups appeared in these phthalocyanine derivative in the UV region at about 290 nm. However, in the case of naphthalocyanines, the physical and chemical identity of naphthalene units is no longer distinct [18,19].

The development of sensing material for low level detection of ethanol vapor at low temperatures has been an important issue to researchers because of wide range of application of ethanol in various fields including medicine, fermentation processes, and food industry and can also be fixed on vehicle steering wheels to monitor drunken driving [20–23]. A number of metal-oxide films and nano structures including W/TiO<sub>2</sub> thin film [24], lance-shaped CuO nanostructures [25], copper oxide [26], SnO<sub>2</sub> nanobelt [27]. The water adsorption effects on room temperature ethanol sensitivity of a SnO<sub>2</sub> single crystal nanobelt was studied by Qiao et al. [27]. It was reported that the

\* Corresponding author.

E-mail address: [ggumruk@yildiz.edu.tr](mailto:ggumruk@yildiz.edu.tr) (G. Gümrükçü Köse).

current response of the SnO<sub>2</sub> nanobelt to ethanol gas increased substantially when water was pre-adsorbed. On the other hand it was also reported that no change was observed without water pre-adsorption. The effect of the ZnO on ethanol sensing performance of the electrospun SnO<sub>2</sub> sensor in the presence of CH<sub>4</sub> have been investigated in temperature interval of 200–400 °C by Khodadadi et al. Authors reported that an optimum amount of 1.0 wt% ZnO significantly enhances the sensor responses to ethanol [28]. The main drawback in the use of metal-oxide semiconductor as sensing element is their high operating temperature [29].

On the other hand, organic compounds, such as phthalocyanines, offers new possibilities for the application of gas sensing because of their open coordination sites for axial ligation, low operating temperature and easy processing [30]. The potential of the phthalocyanine thin films as sensing material for detection of various gases has been demonstrated previously [31–33]. Methanol, ethanol and propanal sensing properties of drop casting thin films of copper phthalocyanine tetrasulfonated tetrasodium salt have been investigated by Tripathi et al. [34] These films exhibit maximum sensing response to methanol while low sensitivities towards ethanol and propanol have been observed. The changes in sensitivities have been correlated with the presence of carbon groups in the chemical vapours. The sensing response of thin films of chloroaluminium phthalocyanine, fluoroaluminium phthalocyanine and fluorochromium phthalocyanine towards various alcohols including ethanol have been investigated using surface plasmon resonance as the sensing method [35]. It was reported that the diffusion coefficients and the swelling characteristics of the films are dependent on the functional group of the phthalocyanine molecule and the molecular size of the analyte. Solvothermally grown iron phthalocyanine nanorods were applied as gas sensor to detect the ethanol. The results demonstrated that iron phthalocyanine nanorods were excellent candidates for gas sensor to ethanol [36]. Ni(II) and Zn (II) phthalocyanines (Pcs) having fluorinated and non-fluorinated alkyl and aryl oxy substituents were characterized as sensitive coatings for chemical gas sensors. It was reported that the responses of Zn centered materials did not increase in parallel to the increasing number of fluorinated substituents, whereas the responses of Ni centered materials increased going from tetra to octa [37]. The sensor response of MPCFx (M = Cu, Co, Zn; x = 0, 4, 16) films towards ammonia was studied by a chemiresistive method and compared to that of unsubstituted MPc films to reveal the effects of central metals and F-substituents on the sensing properties. It has been observed that the response of MPcF4 films to ammonia is noticeably higher than that of MPc films [38].

In this work, a systematic investigation was performed on the VOC vapor sensing performance of mononuclear symmetrically substituted metal-free and metallophthalocyanines in order to clarify the effect of COOH group and central metal atom. For this purpose, a series of carboxylic acid-terminated naphthoxy substituted metallophthalocyanines 4–7 (Zn, Co, Cu, Ni, respectively) and metal free phthalocyanine 8 have been synthesized and characterized.

## 2. Experimental section

### 2.1. Instruments and chemicals

All chemicals and solvents which were purchased in high purity and all solvents were dried on molecular sieves (4Å). 4-Nitrophthalonitrile (1) was synthesized and purified according to the procedure published in the literature [39]. 6-hydroxy-2-naphthoic acid (2) was used as supplied commercially. All reactions were carried out in an argon atmosphere in dried solvents. The synthesis steps were monitored by thin layer chromatography. Infrared spectra were obtained by using a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. A Varian Unity Inova 500 MHz spectrophotometer was used for <sup>1</sup>H NMR spectra and an Agilent 8453 UV/Vis spectrophotometer was used for Electronic spectra in the UV–vis region.

Agilent 6530 Q-TOF LC–MS was used for high resolution mass spectra of the synthesized ligand. Mass spectra of the synthesized substances were obtained by using a Bruker microflex LT MALDI-TOF MS. Melting points of the substances were determined using an Electrothermal Gallenkamp device. Elemental analyses were assigned with a Thermo Flash EA 1112.

### 2.2. Synthesis and characterization

#### 2.2.1. Synthesis of 4-(6-carboxy-2-naphthoxy)phthalonitrile (3)

4-Nitrophthalonitrile (0.98 g, 5.66 mmol) (1), 6-hydroxy-2-naphthoic acid (1.06 g, 5.66 mmol) (2) and K<sub>2</sub>CO<sub>3</sub> (2.35 g, 16.98 mmol) were dissolved in DMF (40 mL). The reaction mixture was stirred at 60 °C for 76 h under argon stream. The progress of the reaction was monitored by TLC. The reaction mixture was poured into 200 mL of cold water and the pH of the solution was adjusted to 1 by addition of 1:1 concentrated hydrochloric acid (v/v). After the mixture was left for 1 h, the precipitate was filtered and washed with water until the filtrate was neutral. Finally, the cream colored product was crystallized from methanol–water. This compound is soluble in chloroform, THF, dichloromethane (DCM), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and acetone. Yield: 75% (1.33 g); m.p. 248 °C. FTIR  $\nu_{\max}/\text{cm}^{-1}$ : 3103, 3072, 3042 (CH arom.), 2234 (C≡N), 1698 (C=O), 1657, 1590, 1577, 1568, 1490, 1473 (Ar C=C), 1405, 1386, 1298, 1280, 1245 (Ar–O–Ar), 1142, 1122, 1097, 969, 834, 821, 765, 633; <sup>1</sup>H-NMR (d<sub>6</sub>-DMSO)  $\delta$ , ppm: 13.15 (s, 1H, carboxylic acid OH), 8.67 (s, 1H, Ar-H), 8.27 (d, 1H, Ar-H), 8.13 (d, 1H, Ar-H), 8.01 (d, 1H, Ar-H), 7.98 (s, 1H, Ar-H), 7.77 (d, 1H, Ar-H), 7.56 (d, 1H, Ar-H), 7.49 (d, 1H, Ar-H), 7.45 (s, 1H, Ar-H); Anal. Calc. for C<sub>19</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub> (314.294 g/mol): C, 72.61; H, 3.21; N, 8.91; found: C, 72.30; H, 3.11; N, 8.60%; MS  $m/z$  (100%) Calc.: 314, Found: 315 [M+H]<sup>+</sup>.

#### 2.2.2. Synthesis of [2,9,16,23-tetra-(4-(6-carboxy-2-naphthoxy)-phthalocyaninato-zinc(II))] (4)

A mixture of compound 3 (100 mg, 0.318 mmol), anhydrous Zn (CH<sub>3</sub>COO)<sub>2</sub> (15 mg 0.079 mmol), a catalytic amount of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) and dry DMF (1 mL) in a sealed glass tube was heated and with efficient stirring at 170 °C under argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was precipitated by adding methanol. The product was separated by filtration as a green solid. The product was separated by filtration as a green solid which was washed several times with methanol and ethanol to remove any unreacted precursor and by products and dried in vacuo. This compound is soluble in DMF and DMSO. Yield: 47 mg (45%); m.p. > 200 °C. FTIR  $\nu_{\max}/\text{cm}^{-1}$ : 3600–2500 (carboxylic acid OH), 3063 (CH, arom.), 1707 (C=O), 1601, 1468 (Ar C=C), 1216 (Ar–O–Ar), 1146, 1129, 1089, 1044, 970, 947, 914, 881, 830; <sup>1</sup>H NMR (d<sub>6</sub>-DMSO)  $\delta$ , ppm: 13.10 (s, 4H, carboxylic acid OH), 8.71–6.96 (m, 36H, Ar-H); UV–vis (DMSO):  $\lambda_{\max}/\text{nm}$  ( $10^{-5} \log \epsilon$ , Lmol<sup>-1</sup> cm<sup>-1</sup>): 680 (5.05), 618 (4.54), 357 (4.85); Anal. Calc. for C<sub>76</sub>H<sub>40</sub>N<sub>8</sub>O<sub>12</sub>Zn: C, 69.02; H, 3.05; N, 8.47; found: C, 69.56; H, 3.61; N, 8.09%; MS (MALDI-TOF):  $m/z$  Calc.: 1322, Found: 1322 [M]<sup>+</sup>.

#### 2.2.3. Synthesis of [2,9,16,23-tetra-(4-(6-carboxy-2-naphthoxy)-phthalocyaninato-cobalt(II))] (5)

A mixture of compound 3 (100 mg, 0.318 mmol), dry CoCl<sub>2</sub> (10.3 mg, 0.079 mmol) and a catalytic amount of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) in 1 mL dry DMF was heated and stirred at 170 °C in a sealed glass tube under argon atmosphere for 24 h. After cooling to room temperature, the crude product was precipitated by the addition of methanol. The green reaction product was purified by washing several times with methanol and ethanol to remove any unreacted precursor and by products and dried in vacuo. This compound is soluble in DMF and DMSO. Yield: 40 mg (38%); m.p. > 200 °C. FTIR  $\nu_{\max}/\text{cm}^{-1}$ : 3600–2500 (carboxylic acid OH), 3060 (CH, arom.), 1682 (C=O), 1601, 1464 (Ar C=C), 1216 (Ar–O–Ar), 1146, 1129, 1089,

Download English Version:

<https://daneshyari.com/en/article/11020120>

Download Persian Version:

<https://daneshyari.com/article/11020120>

[Daneshyari.com](https://daneshyari.com)