



# Synthesis, characterization, spectral and electrical properties of peripherally tetra-triazole-substituted phthalocyanines and its metal complexes

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## ABSTRACT

The substituted [1,2,4]triazole **3** was obtained from the reaction between compound **1** and compound **2**. Novel substituted phthalonitrile **5** was prepared by the substitution of the nitro group of 4-nitrophthalonitrile **4** with triazole moiety **3**. The synthesis of metal-free, zinc, nickel, cobalt and copper phthalocyanines with four substituted [1,2,4]triazole groups on peripheral position were performed from cyclotetramerization of novel substituted dinitrile compound **5**. Metal-free phthalocyanine **6** and its Zn-, Ni-, Co- and Cu- complexes **7–10** were prepared in DMAE at reflux temperature. All new compounds were characterized by a combination of elemental analyses, IR, <sup>1</sup>H/<sup>13</sup>C NMR, MS and UV–vis spectroscopy. Aggregation behaviors of NiPc **8** and CuPc **10** were also investigated. While NiPc **8** was aggregated in acetone, DMF, DMSO, THF, ethylacetate and toluene and non-aggregated in dichloromethane and pyridine at  $10 \times 10^{-6}$  mol dm<sup>-3</sup> concentration, CuPc **10** showed monomeric behavior in dichloromethane, DMSO, DMF, pyridine, THF and showed aggregation in acetone, ethylacetate and toluene at  $14 \times 10^{-6}$  mol dm<sup>-3</sup> concentration. On the other hand, substituted NiPc **8** and CuPc **10** did not show aggregation behavior between  $4 \times 10^{-6}$ – $14 \times 10^{-6}$  mol dm<sup>-3</sup> concentration range in chloroform. Dc and ac conductivity and Impedance Spectroscopy (IS) studies were also done on thin films of compounds **6**, **7**, **8**, **9** and **10** as a function of temperature (295–523 K) and frequency (40–10<sup>5</sup> Hz) under vacuum ( $\sim 2 \times 10^{-3}$  mbar) in dark. The compounds **7**, **8**, **9** and **10** showed nearly same dc conductivity values in the measured temperature range. Variation of dc conductivity of **6**, **7**, **8**, **9** and **10** with temperature exhibited the semiconducting behavior. Variation of ac conductivity of the films with frequency represented by the function  $\sigma_{ac} = A\omega^5$ . The results indicated that charge transport mechanism of the films can be explained by hopping and small polaron tunneling model for **6**, **7**, **8**, **9** and **10** depending on temperature and frequency region. Results of the impedance spectra measurements showed that, at high temperatures, depressed semicircles with different radius indicate deviation from Debye dispersion relation.

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## 1. Introduction

After accidental synthesis of phthalocyanine (Pc) by Braun and Tcherniac in 1907, many advances have been made in phthalocyanine (Pc) chemistry [1–4]. Pc and its transition metal complexes have been used in numerous technological applications such as chemical sensors [3], electrochromic displaying systems [4], non-linear optics [5], solar cells [6], photo-voltaic optics, molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10].

Because of the above mentioned importance of Pcs, preparing novel Pc molecules are important. Unsubstituted Pc is insoluble in common organic solvents and water because of the intermolecular interaction of the Pc molecules. This interaction results in aggregation that decreases their solubility and minimizes their applications. For this reason, one of the important goal of this investigation is to enhance the solubility. Pc derivatives having high solubility have been obtained by peripheral substitution with bulky or long alkyl/alkoxy chains [11–15].

[1,2,4] triazoles, a five membered ring having two carbon and three nitrogen atoms, have been reported as pharmacologically active compounds [16] and some used as anti-inflammatory [17],

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antiviral/anti-HIV and anti-tuberculosis [18], antibacterial agents [19] in medicine. On the other hand, Pcs having substituents including bulky groups and donor atoms may increase the solubility them [20,21]. To the best of our knowledge, there are many Pcs that have triazole moiety on the periphery, however aggregation and electrical properties investigation have been made for only a few of them [22–24], so we have preferred triazole moiety as substituent on Pc ring.

In the present paper, metal-free, Zn-, Ni-, Co- and Cu- phthalocyanines having [1,2,4]triazole peripheral substituents were prepared by conventional methods. In addition aggregation behavior of Ni- and Cu- phthalocyanines in different solvents and at different concentrations were studied. Furthermore, electrical properties of metal-free, Zn-, Ni-, Co- and Cu- phthalocyanines were also investigated.

## 2. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [25]. Ethyl (1*Z*)-*N*-benzoylethanehydrazonoate **1** [26], 4-(3-methyl-5-phenyl-4*H*-1,2,4-triazol-4-yl)phenol **3** [26] and 4-nitrophthalonitrile **4** [27] was prepared according to the literature and 4-aminophenol **2** was purchased from Merck. <sup>1</sup>H-NMR/<sup>13</sup>C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>, and chemical shifts were reported ( $\delta$ ) relative to Me<sub>4</sub>Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum one FT–IR spectrometer in KBr pellets. The MS spectra were measured with a Micromass Quattro LC/ULTIMA LC–MS/MS spectrometer equipped with chloroform–methanol as solvent. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument; the obtained values agreed with the calculated ones. UV–vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Melting points were measured on an electrothermal apparatus and are uncorrected.

### 2.1. Synthesis

#### 2.1.1. 4-[4-(3-methyl-5-phenyl-4*H*-1,2,4-triazol-4-yl)phenoxy]phthalonitrile (**5**)

4-nitrophthalonitrile **4** (1 g, 5.78 mmol) and compound **3** (1.45 g, 5.78 mmol) were dissolved in dry DMF, under N<sub>2</sub> atmosphere and the temperature was increased up to 60 °C. Thereafter, finely ground dry K<sub>2</sub>CO<sub>3</sub> (0.797, 5.78 mmol) was added portion-wise over a period of 2 h and the reaction mixture left to stir for 5 days at this temperature. The completeness of the reaction was controlled by thin layer chromatography (TLC) (chloroform:methanol (1:1)). The mixture was added to ice-water and mixed overnight. The resulting precipitate was filtered and dried in vacuum over P<sub>2</sub>O<sub>5</sub> and recrystallized from ethanol. The pure tawny product was obtained by column chromatography with silica gel using chloroform as eluent. Yield: 1.43 g (65.6%), mp.: 233–234 °C.

Anal. Calc. for C<sub>23</sub>H<sub>15</sub>N<sub>5</sub>O: C, 73.20; H, 4.01; N, 18.56.

Found: C, 73.27; H, 3.95; N, 18.62.

IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3060  $\nu(\text{Ar}-\text{CH})$ , 2917  $\nu(\text{aliph. CH})$ , 2231 (C≡N), 1638–1590  $\nu(\text{CH}=\text{N})$ , 1509  $\nu(\text{C}=\text{C})$ , 1273–1246  $\nu(\text{C}-\text{O}-\text{C})/(\text{C}-\text{N})$ , 1170  $\delta(\text{C}-\text{N})$ , 1015  $\delta(\text{C}-\text{O}-\text{C})$ , 979  $\delta(\text{CH})$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>) ( $\delta$ : ppm): 7.81–7.79 (d, 1H/Ar–H), 7.32–7.16 (m, 11H/Ar–H), 2.35 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) ( $\delta$ : ppm): 160.65, 154.56, 149.66, 145.78 (C=N<sub>methyl</sub>), 143.13 (C=N<sub>phenyl</sub>), 139.86, 135.42, 129.64, 128.19,

125.42, 125.12, 124.97, 124.20, 123.83, 122.02, 117.76 (C≡N), 115.27 (C≡N), 109.57, 13.04 (CH<sub>3</sub>).

MS (ESI) (*m/z*): Calculated: 377.40; Found: 377.52 [M]<sup>+</sup>.

#### 2.1.2. Metal-free phthalocyanine (**6**)

Substituted phthalonitrile **5** (0.1 g, 2.65 × 10<sup>−4</sup> mol) was dissolved in 10 ml of dry N,N-dimethylaminoethanol (DMAE). After increasing the temperature to 90 °C, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3.79 × 10<sup>−5</sup> L, 2.65 × 10<sup>−5</sup> mol) was added to the media. Thereafter the temperature was raised to 160 °C and stirred for 24 h under nitrogen. After cooling, the solution was dropped to ethyl alcohol (40 ml). The solid product was filtrated and washed with hot ethanol, hot methanol, n-hexane and diethyl ether. The yellowish green crude product was purified by passing through a silica gel column with chloroform and then chloroform:methanol (10:1) elution. Yield: 0.027 g (27%), mp. > 300 °C (decomposition).

Anal. Calc. for C<sub>92</sub>H<sub>62</sub>N<sub>20</sub>O<sub>4</sub>: C, 73.10; H, 4.13; N, 18.53.

Found: C, 73.45; H, 4.03; N, 18.38.

IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3280 (–NH), 3060  $\nu(\text{Ar}-\text{CH})$ , 2922–2852  $\nu(\text{aliph. CH})$ , 1617  $\nu(\text{CH}=\text{N})$ , 1507  $\nu(\text{C}=\text{C})$ , 1234  $\nu(\text{C}-\text{O}-\text{C})/(\text{C}-\text{N})$ , 1165  $\delta(\text{C}-\text{N})$ , 1010  $\delta(\text{C}-\text{O}-\text{C})$ , 929  $\delta(\text{CH})$ .

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) ( $\delta$ : ppm): 7.54–7.21 (m, 48H/Ar–H), 2.27 (s, 12H, CH<sub>3</sub>).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) ( $\delta$ : ppm): 161.44, 155.61, 151.87, 148.24, 144.21 (C=N<sub>methyl</sub>), 142.76 (C=N<sub>phenyl</sub>), 138.54, 134.60, 127.68, 126.93, 125.56, 124.03, 123.84, 122.67, 121.15, 121.02, 119.89, 108.42, 12.95 (CH<sub>3</sub>).

UV–vis (chloroform):  $\lambda_{\max}/\text{nm}$  [(4 × 10<sup>−5</sup> log  $\epsilon$  dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>): 700 (4.88), 664 (4.80), 644 (4.37), 602 (4.15), 344 (4.58).

MS (ESI) (*m/z*): Calculated: 1511.61; Found: 1512.86 [M + H]<sup>+</sup>.

#### 2.1.3. The general procedure for synthesis of metallophthalocyanines **7–10**

Substituted phthalonitrile **5** (0.1 g, 2.65 × 10<sup>−4</sup> mol) and corresponding dry metal salts (Zn(OAc)<sub>2</sub> (0.0122 g, 6.63 × 10<sup>−5</sup> mol); Ni(OAc)<sub>2</sub> (0.0117 g, 6.63 × 10<sup>−5</sup> mol); CoCl<sub>2</sub> (0.0086 g, 6.63 × 10<sup>−5</sup> mol); CuCl<sub>2</sub> (0.0089 g, 6.63 × 10<sup>−5</sup> mol) were dissolved in 4 ml of dry DMAE. After increasing the temperature to 90 °C, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3.79 × 10<sup>−5</sup> L, 2.65 × 10<sup>−5</sup> mol) was added to the media. Thereafter the temperature was raised to 160 °C and stirred for 24 h under nitrogen. After cooling, the solutions were dropped to ethyl alcohol (40 ml). The solid products were filtrated and washed with hot ethanol, hot methanol, n-hexane and diethyl ether. The yellowish green crude products were purified by passing through a silica gel column with chloroform:methanol (((10:1) for ZnPc) ((9:1) for NiPc) ((11:1) for CoPc and CuPc)) elution.

2.1.3.1. Zn(II) phthalocyanine (**7**). Yield: 0.032 g (31%), mp.: > 300 °C (decomposition).

Anal. Calc. for C<sub>92</sub>H<sub>60</sub>N<sub>20</sub>O<sub>4</sub>Zn: C, 70.16; H, 3.84; N, 17.79. Found: C, 70.56; H, 3.39; N, 17.62.

IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3060  $\nu(\text{Ar}-\text{CH})$ , 2917–2854  $\nu(\text{aliph. CH})$ , 1640–1600  $\nu(\text{CH}=\text{N})$ , 1506–1471  $\nu(\text{C}=\text{C})$ , 1231  $\nu(\text{C}-\text{O}-\text{C})/(\text{C}-\text{N})$ , 1160  $\delta(\text{C}-\text{N})$ , 1043  $\delta(\text{C}-\text{O}-\text{C})$ , 942  $\delta(\text{CH})$ .

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) ( $\delta$ : ppm): 7.76–7.73 (d, 4H/Ar–H), 7.63–7.58 (d, 22H/Ar–H), 7.50–7.37 (m, 22H/Ar–H), 2.34 (s, 12H, CH<sub>3</sub>).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) ( $\delta$ : ppm): 160.12, 154.76, 152.78, 148.21, 144.76 (C=N<sub>methyl</sub>), 142.43 (C=N<sub>phenyl</sub>), 139.96, 135.53, 126.87, 125.46, 124.85, 123.72, 122.36, 121.52, 121.01, 120.46, 118.26, 109.83, 13.32 (CH<sub>3</sub>).

UV–vis (chloroform):  $\lambda_{\max}/\text{nm}$  [(4 × 10<sup>−5</sup> log  $\epsilon$  dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>): 678 (4.90), 610 (4.14), 354 (4.66).

MS (ESI) (*m/z*): Calculated: 1575.00; Found: 1575.65 [M]<sup>+</sup>.

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