

## Characterization and purification of 1,2,4-triazole-containing phthalocyanines synthesized by microwave method and structure elucidation by spectroscopic techniques

Asiye NAS<sup>1,\*</sup>, Ümit DEMİRBAŞ<sup>2</sup>, Nurhan GÜMRÜKÇÜOĞLU<sup>3</sup>,  
Halit KANTEKİN<sup>2</sup>

<sup>1</sup>Maçka Vocational School, Karadeniz Technical University, Maçka, Trabzon, Turkey

<sup>2</sup>Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey

<sup>3</sup>Vocational School of Health Sciences, Karadeniz Technical University, Trabzon, Turkey

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**Abstract:** The complexes of peripherally tetra-substituted metal-free (**8**), lead(II) (**9**), and zinc(II) (**10**) phthalocyanine derivatives were synthesized for the first time in this work. The structures of these new complex compounds have been elucidated using many spectral methods such as electronic absorption, FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis, and mass spectra. The thermogravimetric behavior of compounds **8–10** was determined by thermogravimetric analysis method in addition to these spectral methods.

**Key words:** Metallophthalocyanine, 1,2,4-triazole, 4-nitrophthalonitrile, thermogravimetric analysis, ethyl 4-methylbenzimidate

### 1. Introduction

The phthalocyanines (Pcs), discovered for the first time in 1907, have a long history of 100 years from their first publication and are widely used in many areas of technology.<sup>1</sup> Because these chemicals have a large  $\pi$ -conjugated system, they absorb strongly in the visible region (about 670 nm), giving a characteristic blue-green color.<sup>2</sup> Pcs are well known for their high stability to heat and light, large extinction coefficient in the near IR region, controllable redox potentials, and, most importantly, semiconductor properties.<sup>3</sup> Pcs have been investigated extensively and used in many fields, including inks,<sup>4</sup> electrochromism,<sup>5,6</sup> optical applications,<sup>7,8</sup> liquid crystals,<sup>9,10</sup> gas sensors,<sup>11,12</sup> semiconductor materials,<sup>13,14</sup> and photodynamic therapy.<sup>15,16</sup>

Since Ben-Hur reported the activity of Pc aluminum chloride anticancer cells in 1985, the metallophthalocyanines, which are used as light-sensitive agents for photodynamic therapy, have received increasing interest.<sup>17</sup>

It is known that in five-membered heterocyclic systems the presence of three nitrogen heteroatoms defines an exciting class of compounds, which are called the triazoles. There are two types of triazoles; one of them is 1,2,3-triazole and the other is 1,2,4-triazole. 1,2,4-Triazoles with molecular formula C<sub>2</sub>H<sub>3</sub>N<sub>3</sub> have a five-membered ring of two carbon atoms and three nitrogen atoms. 1,2,4-Triazoles and their derivatives, which are an essential class of organic compounds, are used in a wide variety of applications, especially as antifungals,<sup>18</sup> such as fluconazole and itraconazole.<sup>19</sup> In recent years, because of their potential biological applications such as antimicrobial, anticancer,<sup>20</sup> antiinflammatory,<sup>21,22</sup> antibacterial,<sup>23,24</sup> antimycobacterial,<sup>25</sup> and anticonvulsant

\*Correspondence: asiyeas@ktu.edu.tr

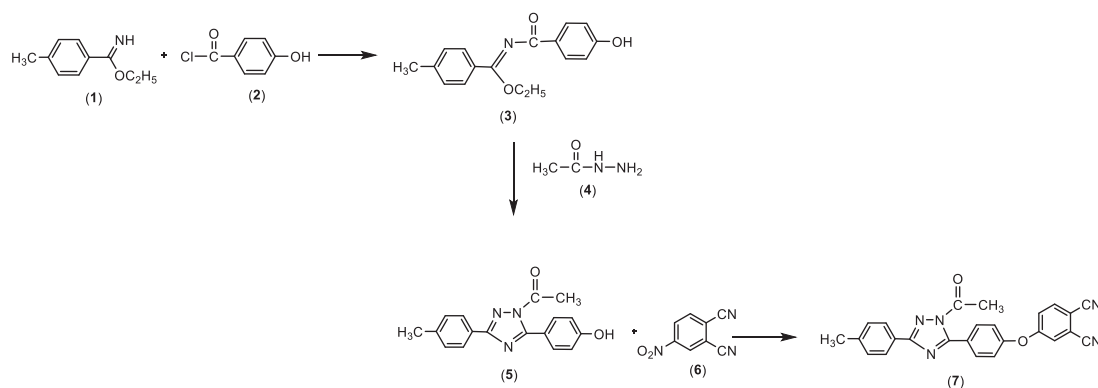
activities,<sup>26,27</sup> triazoles have gained much attention. Therefore, in recent years, there has been a number of papers dealing with triazole-substituted phthalocyanines.<sup>28–30</sup>

In this paper, we have studied the synthesis and characterization of organosoluble metal-free (**8**), lead(II) (**9**), and zinc(II) (**10**) Pcs containing very biologically essential triazole groups. We also clarify the structures of these new compounds using many spectral methods.

## 2. Results and discussion

### 2.1. Synthesis and characterization

We synthesized new 1-acyl-3,5-disubstituted 1,2,4-triazole (**5**) by starting from N-acyl imidate (**3**) that was incorporated from the known reaction of imidoester (**1**) with acyl chloride (**2**).<sup>31,32</sup> In this study, (Z)-ethyl N-4-hydroxybenzoyl-4-methylbenzimidate (**3**) was synthesized from the reaction of ethyl 4-methylbenzimidate (**1**) with 4-hydroxybenzoyl chloride (**2**) (Scheme 1). Compound **3** was refluxed with acetohydrazide (**4**) in ethanol to give 1-(5-(4-hydroxyphenyl)-3-p-tolyl-1H-1,2,4-triazol-1-yl)ethanone (**5**) (Scheme 1). These novel compounds (**3**, **5**) were obtained in yields of 44% and 74%, respectively.

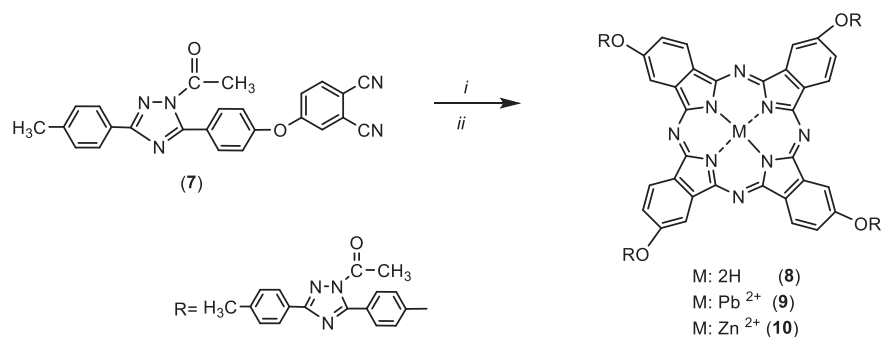


**Scheme 1.** Synthetic pathways of novel dinitrile compound (**7**).

4-(4-(1-Acetyl-3-p-tolyl-1H-1,2,4-triazol-5-yl)phenoxy)phthalonitrile (**7**) was prepared by  $K_2CO_3$ -catalyzed nucleophilic aromatic nitro displacement of 1-(5-(4-hydroxyphenyl)-3-p-tolyl-1H-1,2,4-triazol-1-yl)ethanone (**5**) and 4-nitro phthalonitrile (**6**) in dry dimethylformamide at 50 °C for 120 h under a nitrogen atmosphere with yield of 63%.

Cyclotetramerization of the phthalonitrile derivative (**7**) to the metal-free phthalocyanine (**8**) was accomplished in *n*-pentanol and in the presence of a strong nonnucleophilic base such as DBU at 160 °C for 24 h under a nitrogen atmosphere. The tetra-substituted metal-free phthalocyanine (**8**) was purified on silica gel by column chromatography using a chloroform:methanol (90:10) solvent system as eluent. This compound was obtained in 27% yield. Tetra-substituted metallophthalocyanines (**9**, **10**) were obtained by cyclotetramerization of compound **7** in 2-(dimethylamino)ethanol (DMAE) in the presence of related metal salts ( $PbO$  and  $Zn(CH_3COO)_2$ ) by microwave processing (Scheme 2). The obtained new compounds (**9** and **10**) were purified on silica gel by column chromatography using a chloroform:methanol solvent system ((97:3) for compound **9**, (93:7) for compound **10**) as eluent. These compounds (**9**, **10**) were obtained in 13% and 24 % yields, respectively.

Generally, Pc complexes have low solubility in most organic solvents. Adding some substituents on the



**Scheme 2.** Syntheses of metal-free Pc (**8**) and metallophthalocyanines (**9**, **10**). *i*: *n* pentanol, DBU; *ii*: DMAE, MW, anhydrous PbO, Zn (CH<sub>3</sub>COO)<sub>2</sub>.

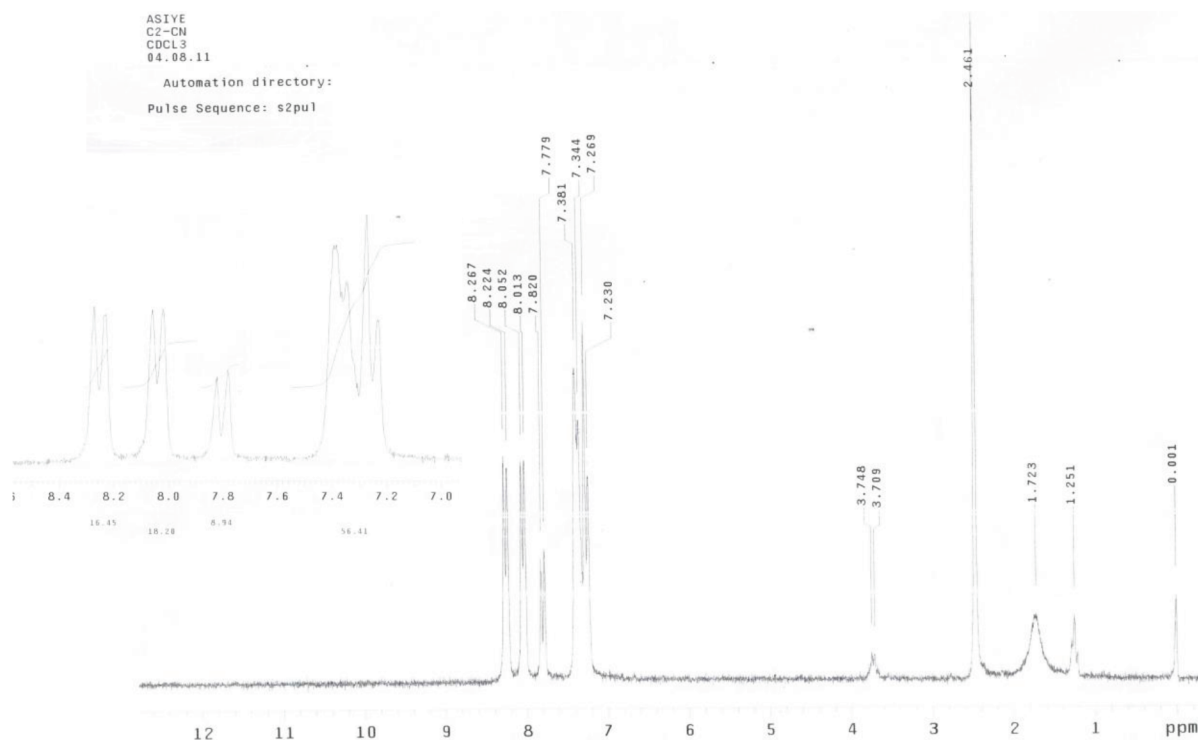
Pc ring increased the solubility of the newly synthesized compounds (**8–10**). All integrated novel Pc complexes have excellent solubility in some organic solvents such as chloroform, dichloromethane, THF, DMSO, and DMF.

All novel compounds (**3**, **5**, **7–10**) were characterized by spectroscopic methods (<sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-Vis, elemental analysis, FT-IR, mass spectrometry, and thermogravimetric analysis). Spectral data of the novel synthesized compounds (**3**, **5**, **7–10**) are consistent with the proposed structures.

The FT-IR spectrum of (*Z*)-ethyl *N*-4-hydroxybenzoyl-4-methylbenzimidate (**3**) showed an absorption band at 1674 cm<sup>-1</sup> due to a carbonyl group, and the characteristic C=N absorption band appeared at 1644 cm<sup>-1</sup>. The carbonyl group of compound **5** showed an absorption band at 1748 cm<sup>-1</sup>. The FT-IR spectrum of compound **7** exhibits a distinctive sharp absorption band at 2231 cm<sup>-1</sup> assignable to C≡N vibration. After the cyclotetramerization of the dinitrile derivative (**7**), this sharp band for the C≡N vibration around 2231 cm<sup>-1</sup> disappeared for compounds **8–10**. The rest of the FT-IR spectra of compounds **8–10** were very similar to those of precursor dinitrile compound **7**.

In the <sup>1</sup>H NMR spectrum of compound **3**, CH<sub>3</sub> and CH<sub>2</sub> protons were observed at δ: 1.46 and 4.26 ppm, and CH<sub>3</sub> protons attached to the aromatic ring appeared at δ: 2.20 ppm. In the <sup>1</sup>H NMR spectrum of compound **5**, a COCH<sub>3</sub> methyl proton was seen at δ: 2.71 and a CH<sub>3</sub> proton was seen at δ: 2.19 ppm. The <sup>1</sup>H NMR spectrum of compound **7** exhibited the characteristic chemical shifts, as expected (Figure 1). For compound **7**, the resonances belonging to the methyl groups were observed at δ: 2.46 and 1.72 ppm. The phenyl protons were observed at δ: 8.27–7.23 ppm for compound **7**. For the peripherally tetra-substituted metal-free Pc (**8**), the resonances belonging to the methyl groups were observed at δ: 2.29 and 1.65 ppm. The resonances of the phenyl protons for compound **8** were observed in the range of δ: 8.00–7.14 ppm in the <sup>1</sup>H NMR spectrum. The typical shielding of inner core protons belonging to the metal-free Pc (**8**), which are generally located in the negative ppm region,<sup>33</sup> were not observed because of strong aggregation.<sup>34</sup> In the <sup>1</sup>H NMR spectra of lead(II) (**9**) and zinc(II) (**10**) Pcs, the resonances belonging to the methyl groups were observed at δ: 2.46 and 1.58 ppm for compound **9** and at δ: 2.45 and 1.69 ppm for compound **10**. The aromatic protons were observed in the range of δ: 7.89–7.18 ppm for compound **9** and δ: 8.00–7.16 ppm for compound **10**.

In the <sup>13</sup>C NMR spectrum of compound **3** the signals due to C=O and C=N were seen at δ: 170.90 and δ: 164.12 ppm, respectively. The triazole carbons of compound **5** were observed at δ: 160.74 and 157.30 ppm. The COCH<sub>3</sub> carbonyl signal was observed at δ: 163.88 ppm. The COCH<sub>3</sub> signal was recorded at δ: 30.09 ppm and the CH<sub>3</sub> signal was seen at δ: 20.46 ppm. In the <sup>13</sup>C NMR spectrum of compound **7**, the



**Figure 1.**  $^1\text{H}$  NMR spectrum of compound **7** in  $\text{CDCl}_3$ .

characteristic peaks belonging to dicyano carbons were exhibited at  $\delta$ : 115.39 and 114.97 ppm, as expected. The  $^{13}\text{C}$  NMR spectrum was almost identical for compounds **8–10** with disappearance of the peaks belonging to dicyano carbons at  $\delta$ : 115.39 and 114.97 ppm. The rest of the  $^{13}\text{C}$  NMR spectra of compounds **8–10** were very similar to those of precursor dinitrile compound **7**.

In addition to elemental analysis results, mass spectra of the newly synthesized compounds (**3**, **5**, **7–10**) confirmed the proposed structures. In the mass spectra of compounds **3** and **5**, the molecular ion peaks were observed at  $m/z$ : 284.15  $[\text{M}+\text{H}]^+$  and 294.13  $[\text{M}+\text{H}]^+$ , respectively. In the mass spectrum of compound **7**, the molecular ion peak, which was observed at  $m/z$ : 443.54  $[\text{M}+\text{Na}+\text{H}]^+$ , supported the desired structure. Similarly, the molecular ion peaks were observed at  $m/z$ : 1680.81  $[\text{M}+\text{H}]^+$  for compound **8**, at  $m/z$ : 1884.18  $[\text{M}]^+$  for compound **9**, and at  $m/z$ : 1767.52  $[\text{M}+\text{Na}+\text{H}]^+$  for compound **10**.

## 2.2. Thermal analysis of the Pcs

Metal-free, lead(II), and zinc(II) Pcs (**8–10**) were studied using thermogravimetry/differential thermal analysis (DTA). The thermogravimetric data for the newly synthesized compounds (**8–10**) showed exceptional thermal stability. The minimum decomposition temperatures were observed at 175 °C, 194 °C, and 176 °C for compounds **8–10**, and the maximum decomposition temperatures were observed at 212 °C, 215 °C, and 178 °C for compounds **8–10**, respectively. The fact that Pcs generally sublime at 550–600 °C without decomposition signifies their extreme thermal stability,<sup>35</sup> but not all of them.  $\text{H}_2\text{Pc}$  (**8**),  $\text{PbPc}$  (**9**), and  $\text{ZnPc}$  (**10**) show similar thermal patterns with a slightly lower decomposition temperature. It seems that binding of the 1,2,4-triazol group to the Pc ring decreases thermal stability. The maximum and minimum decomposition temperatures are given in Table 1. The thermal stability of these compounds was found to be in the order of **9** > **10** > **8**.

**Table 1.** Thermal behaviors of the novel Pcs.

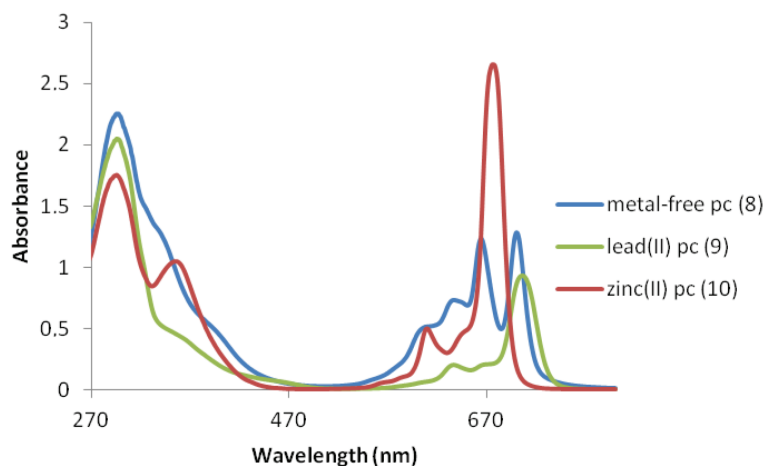
Compound	M	Minimum decomposition temperature in °C	Maximum decomposition temperature in °C
<b>8</b>	2H	175.7	212.9
<b>9</b>	Pb	194.8	215.1
<b>10</b>	Zn	176.8	178.6

### 2.3. Ground state electronic absorption

The absorption spectra of the metallated Pc complexes consist of an intense absorption band in the visible region of about 670 nm, which is called the Q-band, and a weaker band of about 340 nm, which is called the B-band.<sup>36</sup> The ground state electronic absorption spectra showed monomeric behavior evidenced by a single (narrow) Q-band, typical of metallated Pc complexes.<sup>37</sup>

In contrast, unmetallated Pc compounds show a split in the Q-band because of the degeneracy of the LUMO (eg) level. However, the Q-band splitting of unmetallated Pc compounds becomes smaller in longer wavelengths,<sup>38</sup> resulting in redshifted metal-free compounds that do not exhibit the typical split Q-band. The presence of the narrow Q-band of the unmetallated Pc complex exhibits random degeneration of molecular orbitals.<sup>39</sup>

In the electronic absorption spectrum of unmetallated Pc (**8**) in DMF, it was seen that in the Q-band, there was a split near  $\lambda_{\max}$ : 701 and 664 nm with shoulders at 634 and 602 nm. A weaker band near  $\lambda_{\max}$ : 343 nm corresponding to the B-band was observed. The electronic spectra of lead(II) (**9**) and zinc(II) (**10**) Pcs in DMF showed a single Q-band at  $\lambda_{\max}$ : 705 and 676 nm with weaker absorptions at  $\lambda_{\max}$ : 634 and 610 nm, corresponding to the Q-band in the visible region. B-bands of compounds **9** and **10** were observed at  $\lambda_{\max}$ : 360 nm for compound **9** and 357 and 297 nm for compound **10** (Figure 2; Table 2).



**Figure 2.** Electronic spectra of compounds **8** (—), **9** (—), and **10** (—) in DMF.

The Pc complexes can be hosts to over 70 different metal ions in their central cavity,<sup>1</sup> but not all of the metallated Pcs showed similar absorption spectra. In the absorption spectrum, the Q-band of the lead Pc complex (**9**) has shifted to red compared to other related Pc complexes (H<sub>2</sub>Pc (**8**) and ZnPc (**10**)). For

**Table 2.** Electronic spectra of novel Pcs.

Compound	$\lambda_{\text{max}}/\text{nm}$ ( $\varepsilon \times 10^{-5}$ )	
	Q-band	B (Soret)-band
<b>8</b>	701 (5.11), 664 (5.09), 634 (4.86), 602 (4.68)	343 (5.09)
<b>9</b>	705 (4.97), 634 (4.30)	360 (4.64)
<b>10</b>	676 (5.42), 610 (4.70)	357 (5.02), 297 (5.24)

compound **9**, the large redshift was attributed to the highly deformed Pc skeleton due to the central metal ion ( $\text{Pb}^{2+}$ ), which was not fitting into the cavity of the Pc molecule because of the large atomic size of the lead atom. Namely, Pc ligand deformation causes the red-shifting of the Q-band.<sup>36</sup>

### 3. Experimental

#### 3.1. Materials

All reagents and solvents used during the process are dried and purified as indicated in the relevant literature.<sup>40</sup> Compounds **1** and **6** were synthesized according to the given literature.<sup>31,32,41</sup> All other reagents and solvents in reactive quality were obtained from commercial sources.

#### 3.2. Used equipment

Elemental analyses were obtained from a LECO Elemental Analyzer (CHNS O932) and Unicam 929 AA spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer using TMS as an internal reference in DMSO- $d_6$  or  $\text{CDCl}_3$  solution. Infrared spectra were recorded using KBr pellets on a PerkinElmer 1600 FT-IR spectrophotometer. Mass spectra were obtained on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Optical spectra in the UV-Vis region were recorded with a Unicam spectrophotometer operating in the range of 200–800 nm with quartz cells. Melting points were measured on an electrothermal melting point apparatus. A domestic microwave oven was used for carrying out all syntheses of metallophthalocyanines. A Seiko II Exstar 6000 thermal analyzer was used to record the DTA curves under a nitrogen atmosphere with a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  in the temperature range of 30–900  $^\circ\text{C}$  using platinum crucibles.

#### 3.3. Synthesis

##### 3.3.1. (Z)-Ethyl N-4-hydroxybenzoyl-4-methylbenzimidate (3)

Ethyl 4-methylbenzimidate (**1**) (8.2 g, 0.05 mol) was dissolved in freshly distilled triethylamine (7 mL, 0.05 mol) and  $\text{CH}_2\text{Cl}_2$  (1000 mL). A solution of 4-hydroxybenzoyl chloride (**2**) (5.7 mL, 0.05 mol) in  $\text{CH}_2\text{Cl}_2$  (500 mL) was added dropwise over 30 min and cooled in an ice/salt bath. The mixture was allowed to cool to a temperature of 0  $^\circ\text{C}$  or less for 2 h and then left to sit for another 16 h. The mixture was filtered to remove triethylammonium chloride and evaporated. The residue was extracted with anhydrous diethyl ether to remove triethylammonium chloride. The resulting solution was evaporated and the residue was dried in vacuo; the desired compound (**3**) was recrystallized from ethanol. Yield: 6.2 g (44%), mp: 76–77  $^\circ\text{C}$ . Anal. Calc.  $\text{C}_{17}\text{H}_{17}\text{NO}_3$ : C 72.07%, H 6.05%, N 4.94%. Found: C 72.19%, H 6.04%, N 4.94%. FT-IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr pellet): 3300–3200 (OH), 1674 (C=O), 1644 (C=N), 831, 820.  $^1\text{H}$  NMR (DMSO- $d_6$ ) ( $\delta$ : ppm): 1.46 ( $\text{CH}_3$ ,

3H, t), 2.20 (CH<sub>3</sub>, 3H, s), 4.26 (CH<sub>2</sub>, 2H, q), 6.90 (Ar-H, 2H, d), 7.60–7.85 (Ar-H, 2H, m), 7.94–8.01 (Ar-H, 4H, m), 10.38 (OH, 1H, s). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) (δ: ppm): 170.90, 164.12, 158.43, 138.75, 133.14, 131.40, 131.22, 130.84, 128.16, 127.45, 60.89, 20.86, 14.41. MS (ES<sup>+</sup>), *m/z*: Calc.: 283.33; Found: 284.15 [M+H]<sup>+</sup>.

### 3.3.2. 1-(5-(4-Hydroxyphenyl)-3-p-tolyl-1H-1,2,4-triazol-1-yl)ethanone (5)

Compound **3** (5.66 g, 0.02 mol) was mixed with acetohydrazide (**4**) (1.48 g, 0.02 mol) in ethanol (100 mL) and refluxed for 8 h. The resulting solution was evaporated under reduced pressure at 40–45 °C and the residue was dried in vacuo, which was recrystallized from ethanol to the desired product. Yield: 4.32 g (74%), mp: 118–119 °C. Anal. Calc. C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C 69.61%, H 5.15%, N 14.33%. Found: C 69.64%, H 5.14%, N 14.36%. FT-IR  $\nu_{\max}/\text{cm}^{-1}$  (KBr pellet): 3300–3200 (OH), 1748 (C=O), 1610–1562 (C=N), 816, 833 (arom. ring). <sup>1</sup>H NMR (DMSO- d<sub>6</sub>) (δ: ppm): 2.19 (CH<sub>3</sub>, 3H, s), 2.71 (COCH<sub>3</sub>, 3H, s), 6.98 (Ar-H, 2H, d), 7.20 (Ar-H, 2H, d), 7.94–8.01 (Ar-H, 4H, m), 10.39 (OH, 1H, s). <sup>13</sup>C NMR (DMSO- d<sub>6</sub>) (δ: ppm): 163.88, 160.74, 157.30, 158.86, 141.84, 129.86, 128.56, 126.36, 120.71, 116.09, 114.05, 30.09, 20.46. MS (ES<sup>+</sup>), *m/z*: Calc.: 293.33; Found: 294.13 [M+H]<sup>+</sup>.

### 3.3.3. 4-(4-(1-Acetyl-3-p-tolyl-1H-1,2,4-triazol-5-yl)phenoxy)phthalonitrile (7)

1-(5-(4-Hydroxyphenyl)-3-p-tolyl-1H-1,2,4-triazol-1-yl)ethanone (**5**) (0.9 g, 3.07 mmol) was dissolved in dry DMF (15 mL) under a nitrogen atmosphere and 4-nitrophthalonitrile (**6**) (0.53 g, 3.07 mmol) was added to the solution. After stirring for 30 min finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> (1.69 g, 12.28 mmol) was added portion-wise over 2 h. The reaction mixture was stirred under a nitrogen atmosphere at 50 °C for 4 days. The mixture was monitored by thin-layer chromatography using a chloroform solvent system. At the end of the last period, the mixture was poured into ice water (150 g) and the dark yellow product was precipitated. The product was filtered off and washed with distilled water. Finally, the solid product obtained was crystallized from ethanol. Yield: 0.8 g (63%), mp: 187–191 °C. Anal. Calc. C<sub>25</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>: C 71.59%, H 4.09%, N 16.70%. Found: C 71.52%, H 4.07%, N 16.74%. FT-IR  $\nu_{\max}/\text{cm}^{-1}$  (KBr pellet): 3069 (Ar-H), 2920–2870 (aliph. C-H), 2231 (C≡N), 1685 (C=O), 1588, 1490, 1313, 1245, 1072, 949, 857, 825, 725. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ: ppm): 8.27–8.22 (ArH, 2H, d), 8.05–8.01 (ArH, 2H, d), 7.82–7.78 (ArH, 1H, d), 7.38–7.23 (ArH, 6H, m), 2.46 (CH<sub>3</sub>, 3H, s), 1.72 (CH<sub>3</sub>, 3H, t). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (δ: ppm): 163.56, 160.87, 156.66, 144.13, 142.88, 135.89, 130.12, 129.70, 127.18, 122.60, 122.33, 122.11, 121.15, 118.20, 115.39, 114.97, 110.18, 23.47, 21.96. MS (ES<sup>+</sup>), *m/z*: Calc.: 419.44; Found: 443.54 [M+Na+H]<sup>+</sup>.

### 3.3.4. Metal-free Pc (8)

A mixture of 4-(4-(1-acetyl-3-p-tolyl-1H-1,2,4-triazol-5-yl)phenoxy)phthalonitrile (**7**) (0.2 g, 0.48 mmol), 3 mL anhydrous *n*-pentanol, and 3 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was placed in a standard Schlenk tube. The reaction mixture was then stirred at 160 °C for 12 h. After cooling to room temperature, the mixture was stirred with ethanol (20 mL) to precipitate the product. The dark-green product was filtered off and refluxed with ethanol for 3 h. The product was finally filtered and dried in a vacuum. Finally, the solid product was purified by column chromatography on silica gel, eluting with chloroform:methanol (90:10). Yield: 53 mg (27%), mp: 175–212 °C (decomposition). Anal. Calc. C<sub>100</sub>H<sub>70</sub>N<sub>20</sub>O<sub>8</sub>: C 71.50%, H 4.20%, N 16.68%. Found: C 71.55%, H 4.20%, N 16.66%. FT-IR  $\nu_{\max}/\text{cm}^{-1}$  (KBr pellet): 3061 (Ar-H), 2920–2854 (aliph. C-H),

1604, 1489, 1419, 1312, 1226, 1164, 1010, 927, 820, 740.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 8.00–7.96 (ArH, 8H, m), 7.90–7.76 (ArH, 8H, d), 7.24–7.14 (ArH, 28H, m), 2.29 ( $\text{CH}_3$ , 12H, s), 1.65 ( $\text{CH}_3$ , 12H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 164.42, 162.44, 153.81, 145.93, 139.29, 135.55, 130.71, 129.12, 125.05, 123.48, 121.47, 121.33, 121.09, 119.46, 105.00, 23.49, 21.80. UV-Vis (DMF):  $\lambda$ , nm ( $\log \epsilon$ ): 701 (5.11), 664 (5.09), 634 (4.86), 602 (4.68), 343 (5.09). MS ( $\text{ES}^+$ ),  $m/z$ : Calc.: 1679.79; Found: 1680.81  $[\text{M}+\text{H}]^+$ .

### 3.3.5. Pb(II) and Zn(II) metallophthalocyanines (9, 10)

4-(4-(1-Acetyl-3-p-tolyl-1H-1,2,4-triazol-5-yl)phenoxy)phthalonitrile (0.2 g, 0.48 mmol) (**7**) reacted with 27 mg of anhydrous PbO or 22 mg of  $\text{Zn}(\text{CH}_3\text{COO})_2$  in the presence of 2-(dimethylamino)ethanol (DMAE) (2 mL) was irradiated in a microwave at 175 °C for 6 min at 350 W. After cooling to room temperature, the mixture was stirred with ethanol (20 mL) to precipitate the product. The dark-green product was filtered off and refluxed with ethanol for 3 h. Finally, the solid products were purified with column chromatography on silica gel with chloroform:methanol at 97:3 for **9** and 93:7 for **10** as eluent.

#### 3.3.5.1. Pb(II) Pc (9)

Yield: 30 mg (13%), mp: 194–215 °C (decomposition). Anal. Calc.  $\text{C}_{100}\text{H}_{68}\text{N}_{20}\text{O}_8\text{Pb}$ : C 63.72%, H 3.64%, N 14.86%. Found: C 63.70%, H 3.64%, N 14.85%. FT-IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr pellet): 3061 (Ar-H), 2918–2849 (aliph. C-H), 1603, 1470, 1326, 1229, 1166, 1075, 940, 821, 725.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 7.89–7.18 (ArH, 44H, m), 2.46 ( $\text{CH}_3$ , 12H, m), 1.58 ( $\text{CH}_3$ , 12H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 165.23, 161.58, 156.88, 144.69, 141.41, 134.93, 130.47, 129.11, 125.58, 122.99, 120.32, 120.26, 116.36, 107.69, 25.28, 20.21. UV-Vis (DMF):  $\lambda$ , nm ( $\log \epsilon$ ): 705 (4.97), 634 (4.30), 360 (4.64). MS ( $\text{ES}^+$ ),  $m/z$ : Calc.: 1884.98; Found: 1884.18  $[\text{M}]^+$ .

#### 3.3.5.2. Zn(II) Pc (10)

Yield: 50 mg (24%), mp: 176–178 °C (decomposition). Anal. Calc.  $\text{C}_{100}\text{H}_{68}\text{N}_{20}\text{O}_8\text{Zn}$ : C 68.90%, H 3.93%, N 16.07%. Found: C 68.96%, H 3.93%, N 16.04%. FT-IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr pellet): 3060 (Ar-H), 2919–2845 (aliph. C-H), 1603, 1487, 1392, 1228, 1086, 941, 820, 726.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 8.00–7.16 (ArH, 44H, m), 2.45 ( $\text{CH}_3$ , 12H, m), 1.69 ( $\text{CH}_3$ , 12H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ : ppm): 163.16, 162.73, 155.57, 146.03, 140.60, 136.98, 131.58, 128.70, 123.83, 122.44, 121.02, 120.49, 119.63, 105.91, 24.12, 21.66. UV-Vis (DMF):  $\lambda$ , nm ( $\log \epsilon$ ): 676 (5.42), 610 (4.70), 357 (5.02), 297 (5.24). MS ( $\text{ES}^+$ ),  $m/z$ : Calc.: 1743.16; Found: 1767.52  $[\text{M}+\text{Na}+\text{H}]^+$ .

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