

Microwave-assisted and conventional synthesis of new phthalocyanines containing 4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one moieties

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Abstract

New metal-free and metal (Zn, Ni, Cu and Co) phthalocyanines containing 4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one moiety have been prepared from 1-(3,4-dicyanophenyl)-4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one by both conventional and microwave-assisted methods. All of these compounds are soluble in CHCl₃, DMF and DMSO. The new compounds have been characterized by elemental analysis, IR, NMR, UV–Vis spectroscopies. The crystal structures of compounds **I** and **II** were also determined by the single crystal diffraction technique.

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1. Introduction

Phthalocyanines are known as excellent functional materials. They have been studied in detail for many years, especially with regard to their properties as pigments for printing inks and for plastics and in paints and coatings. In the coming decade, their commercial utility is expected to have significant ramification.

Thus future potential uses of metal phthalocyanines, currently under study, include sensing elements in chemical sensors, electrochromic display devices, photodynamic reagents for cancer therapy and other medical applications, applications to optical computer read/write discs and related information storage systems, laser dyes, and molecular metals and conducting polymers [1]. Bulky substitu-

ents on the periphery enhance the solubility and the donor atoms such as N and O of the substituents are capable of solving the phthalocyanines [2–5].

1,2,4-Triazols and 4,5-dihydro-1*H*-1,2,4-triazol-5-ones have been found to be associated with diverse pharmacological activities [6,7].

High-speed synthesis by microwaves has attracted a considerable amount of attention in recent years. Using a microwave oven in microwave-assisted organic synthesis (MAOS), not only reduces chemical reactions times from hours to minutes, but also reduces side reactions, increases the yield, and improves reproducibility. Therefore, many academic and industrial research groups are already using MAOS as a forefront technology for rapid optimization of reactions, for the efficient synthesis of new chemical entities, and for discovering and probing new chemical reactivity [8]. We have previously synthesized phthalocyanines containing macrocyclic substituents by using the microwave irradiation method [9–12].

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The present paper reports both microwave-assisted and conventional synthesis methods of starting compound (**II**), metal-free and metal (Zn, Ni, Cu and Co) phthalocyanines containing four 4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one moieties.

2. Results and discussion

4-Nitrophthalonitrile has been recently used to prepare monosubstituted phthalonitrile derivatives through base catalysed electrophilic aromatic substitution reaction [13]. 1-(3,4-Dicyanophenyl)-4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**II**) was synthesized by treating 1,2-dicyanobenzene with 4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**I**) by using both microwave and conventional methods (Scheme 1). The reaction conditions for conventional method were at room temperature in dimethylformamide (DMF) with K_2CO_3 as the base for 24 h [14], for microwave method were at 350 W for 5 min in DMF [9–12] and the yields were more than conventional method. The metal-free phthalocyanine was obtained by treating a mixture of the dicyano derivative with hydroquinone by both conventional and microwave methods. The reaction times are 24 h under N_2 for conventional method and at 350 W for 8 min for the microwave method. Also the metallo phthalocyanines were prepared from the dicyano derivative and the corresponding metal salts in dimethylaminoethanol (DMAE) by both conventional and microwave methods. The yields for microwave irradiation were more than the conventional method. In the conventional method for the NiPc, the phthalonitrile and $NiCl_2$ were heated for 24 h under N_2 ; for the ZnPc, the phthalonitrile and $Zn(CH_3COO)_2$ were heated for 24 h under N_2 ; for the CuPc, the phthalonitrile, CuCl and urea was heated for 24 h under N_2 and; for the CoPc, the phthalonitrile, $CoCl_2$ and ammonium molybdate were heated for 24 h under N_2 . In the microwave-assisted synthesis, for all of these complexes the mixtures were irradiated at 350 W for 8 min in the microwave oven. The new synthesized compounds were soluble in common organic solvents such as chloroform, DMF and DMSO.

Elemental analysis, IR, 1H NMR, ^{13}C NMR, UV–Vis spectra, and X-ray (for **I** and **II**) confirm the proposed structures of the compounds. These products were obtained in sufficient purity after successive washing with different solvents and by column chromatography (silica gel, chloroform–methanol (80:1)).

2.1. IR spectra

Spectral investigations of the newly synthesized intermediates and phthalocyanines are in accordance with the proposed structures. By comparing the IR spectra of each step some information as to the nature of the products were obtained. In this context, comparison of the IR spectral data clearly indicated the formation of compound **I** by

the appearance of a new Aromatic band at 1600–1450 cm^{-1} , and the formation of compound **II** by the disappearance of the NH band at 3204 cm^{-1} in **I** and the appearance of a new CN band at 2226 cm^{-1} , and the formation of the metal-free **I** and metal phthalocyanines **2–5** by the disappearance of the CN band at 2226 cm^{-1} in **II**. The IR spectra of metal-free **I** and metal phthalocyanines **2–5** (M = Ni, Zn, Cu or Co) were very similar. The only difference was the presence of $\nu(NH)$ vibration assigned to the band at 3429 cm^{-1} in the free phthalocyanine. This band was absent in the spectra of the metal complexes. The M–N vibrations were expected to appear at 400–100 cm^{-1} but they were not observed in KBr pellets [15].

2.2. NMR spectra

In the 1H NMR spectrum of **I**, the NH proton as a singlet at 11.63 ppm, CH_3 protons as a singlet at 2.01 ppm and the aromatic protons as a multiplet were assigned on the basis of the results of a previous work on macrocyclic ligands. The ^{13}C NMR spectrum of **I** shows one signal for the C=O carbon at 163.89 ppm, one signals for the CH_3 at 12.14 ppm and multiple signal for the aromatic carbons at 154.16–115.89 ppm.

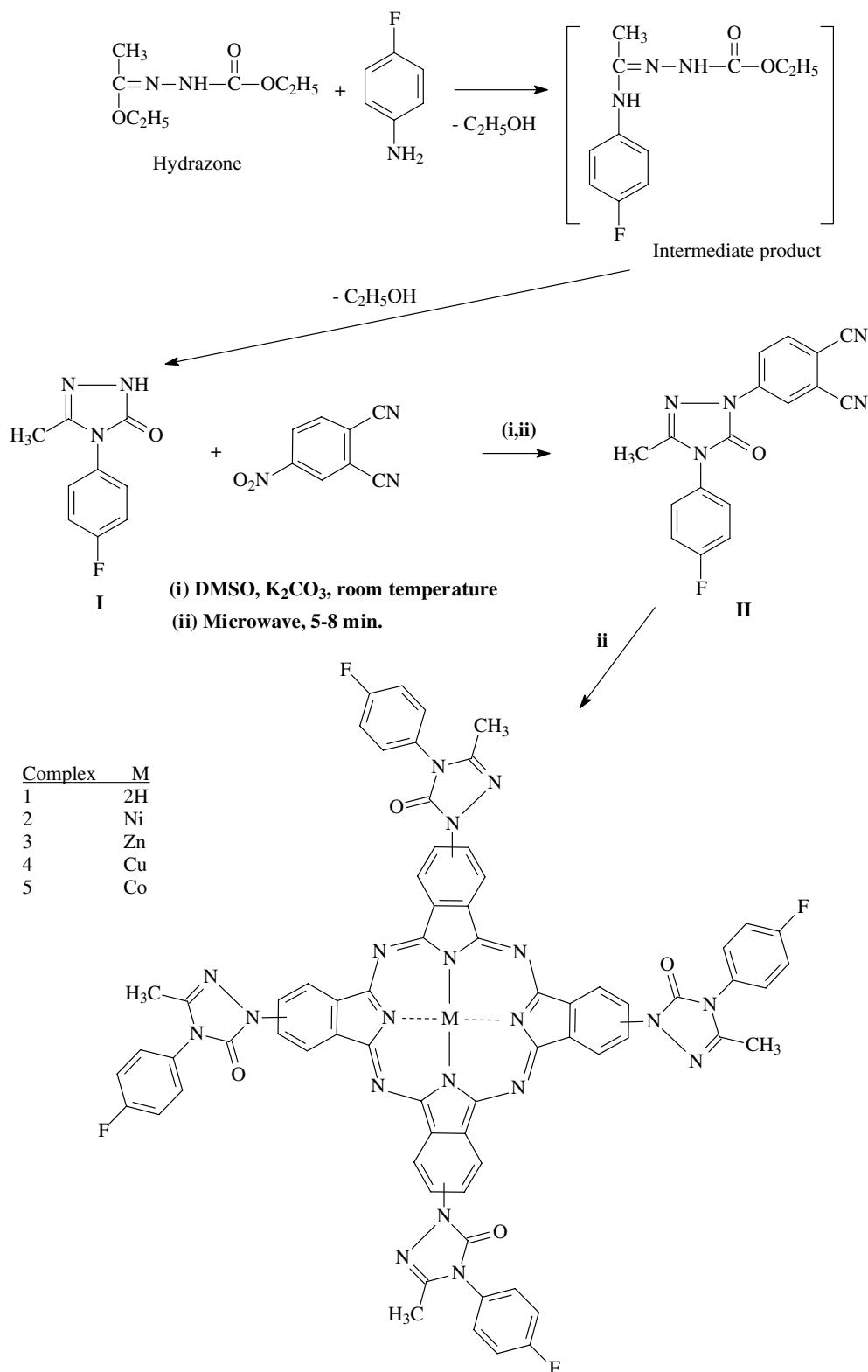
Comparison of the 1H NMR and ^{13}C NMR spectral data clearly indicated the formation of **II** by the disappearance of the NH band at 11.63 ppm and the appearance of a new aromatic band as a multiplet at 8.50–7.40 ppm. The other 1H NMR data of **II** were the CH_3 band as a singlet at 2.19 ppm. The ^{13}C NMR spectrum of **II** shows signals at 164.52 (C=O), 159.61, 150.97, 146.87, 140.96, 135.44, 129.94, 129.76, 128.18, 121.06, 120.97, 116.73, 116.27, 115.84, 115.49, 109.46 and 12.15 (CH_3).

The 1H NMR spectrum of **I** (metal-free Pc) shows the aromatic protons at 8.56–7.26 ppm and the CH_3 protons at 2.25 ppm. A common feature of the spectra of the metal-free phthalocyanines is the broad absorptions probably caused by aggregation of the phthalocyanine. The NH protons of compound **I** could not be observed, due to this phenomenon. Because of the ring current of the 18 π electron system of the inner phthalocyanine core, the protons are shifted to low or high field [16]. In the 1H NMR spectra of **I** (metal-free), **2** (Ni) and **3** (Zn), the chemical shifts for aromatic systems are at 7.26 ppm and 8.56 ppm, and for the CH_3 protons at 2.10 ppm and 2.25 ppm, respectively. 1H NMR measurement was precluded owing to the paramagnetic nature of the copper phthalocyanine **4** and cobalt phthalocyanine **5** [1].

^{13}C NMR spectra of the complexes were similar to the metal-free phthalocyanine.

2.3. UV–Vis spectra

The phthalocyanines **1–5** showed typical electronic spectra with two strong absorption regions. One of them was in the UV region at about 351 nm (B band) and the other in



Scheme 1. Synthesis of the ligand and the complexes.

the visible region at 706 nm (Q band), respectively. Although the symmetry of the phthalocyanines is lowered by the heteroatom substituent on each phenyl group, compound **1** still shows Q band absorption of D_{2h} symmetry in

$CHCl_3$ [1]. These complexes showed an intense absorption at 706 nm and a shoulder band of lower intensity at 638 nm (Fig. 5). The thermal decomposition temperatures of these complexes were higher than 200 °C.

3. X-ray spectra

The title compounds, $C_9H_8FN_3O$ (**I**) and $C_{15}H_{10}FN_5O$ (**II**), containing the triazole ring display the characteristic features of 1,2,4-triazole derivatives (Figs. 1 and 3). In a three-dimensional network, molecules (**I** and **II**) are linked by van der Waals interaction (Figs. 2 and 4). From an analysis of the values there in, it can be concluded that for both structures $C8=N2$ (**I**) and $C8=N3$ (**II**) are well defined double bonds, and are the shortest bonds in the heterocycle ring (Tables 1 and 3).

For both compounds the triazole system is essentially planar. The maximum deviation from the plane of the five membered ring is, C7 atom for **I** and **II**. The triple $C\equiv N$ bond distance in the cyano groups is in good agreement with our previous report, 4-(4-benzyloxyphenoxy)phthalonitrile [17].

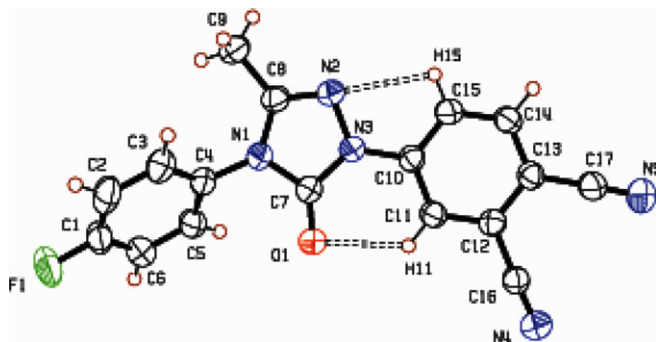


Fig. 3. Crystal structure for **II**.

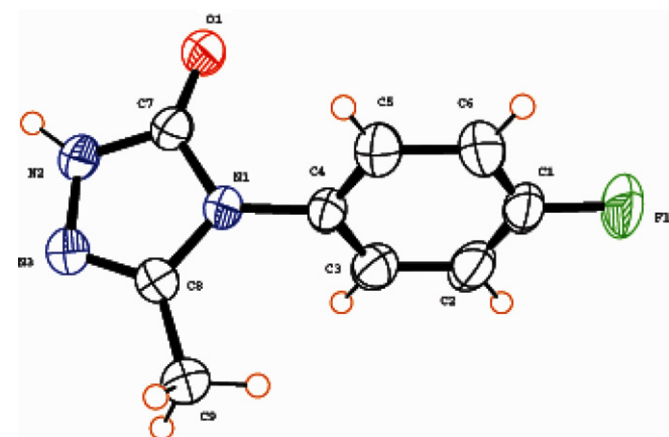


Fig. 1. Crystal structure for **I**.

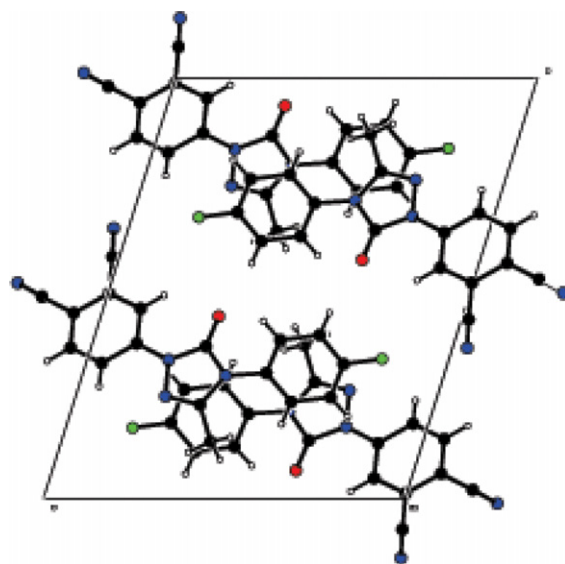


Fig. 4. The packing diagram for **II**.

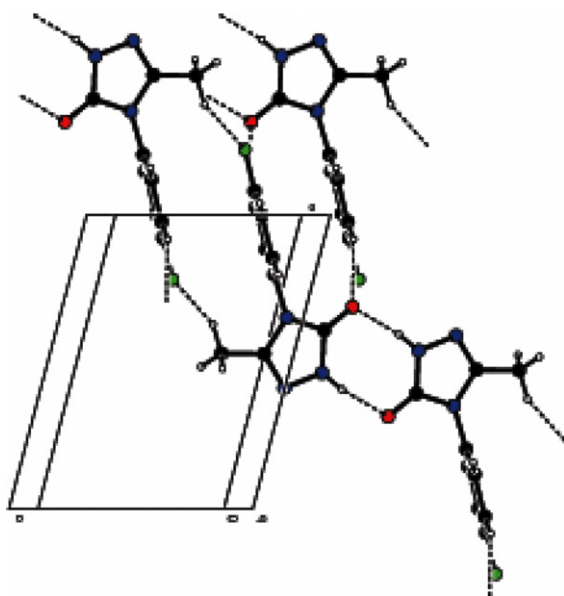


Fig. 2. The packing diagram for **I**.

The structure of the title compound **I** contains weak $C-H\cdots O$ and $C-H\cdots N$ type contacts namely $C11-H11\cdots O1$ and $C15-H15\cdots N2$ (Table 2). In addition to, it does exhibit weak $C-H\cdots\pi$ interaction [$C9-H9B\cdots Cg1$, $Cg1$ is the centroid of the $C1-C6$ ring]. The structure of the title compound **II** contains medium strength, $N2-H2N\cdots O1$, $C6-H6\cdots O1$ and $C9-H9C\cdots F1$ type hydrogen bonds (Table 4), where $O1$ atom, added to triazole ring, accepts hydrogen bonds from $C-H$ donors.

4. Experimental

Routine IR spectra were recorded on a Mattion Fourier-transform spectrometer as KBr pellets, UV-Vis spectra on a Unicam UV-Vis spectrometer and 1H NMR and ^{13}C NMR spectra on a Bruker AC-200 Fourier-transform spectrometer. Elemental analysis was performed by the Instrumental analysis Laboratory of TÜBİTAK Gebze Research Center. 4-Nitrophthalonitrile was synthesized according to the reported procedure [18]. Domestic microwave oven was used for all synthesis of phthalocyanines and dinitrile compounds. For the X-ray study, X-ray data collection:

Table 1
Bond distances (Å) for **I**

C(13)–C(14)	1.3835(17)	C(13)–C(12)	1.4033(16)	C(13)–C(17)	1.4381(16)
C(10)–C(15)	1.3892(16)	C(10)–C(11)	1.3912(16)	C(10)–N(3)	1.4074(14)
N(2)–C(8)	1.2924(15)	N(2)–N(3)	1.3940(13)	C(8)–N(1)	1.3810(15)
C(8)–C(9)	1.4823(17)	O(1)–C(7)	1.2109(14)	N(1)–C(7)	1.3900(15)
N(1)–C(4)	1.4327(14)	N(3)–C(7)	1.3778(14)	C(17)–N(5)	1.1401(17)
C(11)–C(12)	1.3826(15)	C(11)–H(11)	0.9300	C(4)–C(5)	1.3795(18)
C(4)–C(3)	1.3816(17)	C(14)–C(15)	1.3806(16)	C(14)–H(14)	0.9300
C(12)–C(16)	1.4336(16)	C(16)–N(4)	1.1402(16)	C(15)–H(15)	0.9300
C(3)–C(2)	1.3854(19)	C(3)–H(3)	0.9300	C(5)–C(6)	1.3822(17)
C(5)–H(5)	0.9300	F(1)–C(1)	1.3520(14)	C(1)–C(2)	1.363(2)
C(1)–C(6)	1.370(2)	C(2)–H(2)	0.9300	C(9)–H(9B)	0.9600
C(9)–H(9A)	0.9600	C(9)–H(9C)	0.9600	C(6)–H(6)	0.9300

Table 2
Hydrogen bonds (Å, °) for **I**

N2–H2N···O1	0.86	2.01	2.850(2)	165.1	2_456
C6–H6···O1	0.93	2.57	3.451(3)	157.2	2_557
C9–H9C···F1	0.96	2.33	3.169(3)	145.3	2_667

Table 3
Bond distances (Å) for **II**

C(13)–C(14)	1.3835(17)	C(11)–C(12)	1.3826(15)
C(13)–C(12)	1.4033(16)	C(11)–H(11)	0.9300
C(13)–C(17)	1.4381(16)	C(4)–C(5)	1.3795(18)
C(10)–C(15)	1.3892(16)	C(4)–C(3)	1.3816(17)
C(10)–C(11)	1.3912(16)	C(14)–C(15)	1.3806(16)
C(10)–N(3)	1.4074(14)	C(14)–H(14)	0.9300
N(2)–C(8)	1.2924(15)	C(12)–C(16)	1.4336(16)
N(2)–N(3)	1.3940(13)	C(16)–N(4)	1.1402(16)
C(8)–N(1)	1.3810(15)	C(15)–H(15)	0.9300
C(8)–C(9)	1.4823(17)	C(3)–C(2)	1.3854(19)
O(1)–C(7)	1.2109(14)	C(3)–H(3)	0.9300
N(1)–C(7)	1.3900(15)	C(5)–C(6)	1.3822(17)
N(1)–C(4)	1.4327(14)	C(5)–H(5)	0.9300
N(3)–C(7)	1.3778(14)	F(1)–C(1)	1.3520(14)
C(17)–N(5)	1.1401(17)	C(1)–C(2)	1.363(2)
C(1)–C(6)	1.370(2)	C(2)–H(2)	0.9300
C(9)–H(9B)	0.9600	C(9)–H(9A)	0.9600
C(9)–H(9C)	0.9600	C(6)–H(6)	0.9300

Table 4
Hydrogen bonds (Å, °) for **II**

C(11)–H(11)···O(1)	0.93	2.23	2.8737(15)	126
C(15)–H(15)···N(2)	0.93	2.45	2.7864(17)	101

X-AREA, cell refinement: X-AREA and data reduction: X-RED [19], program used to solve structure: SHELLXS-97 and program used to refine structure: SHELLXL-97 [20], molecular graphics: ORTEP 3 [21] and used to prepare material for publication: WinGX [22] was used.

4.1. 4-(*p*-Fluorophenyl)-3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one (**I**)

A mixture of the corresponding hydrazone (1.74 g, 0.01 mol) and *p*-nitroaniline (1.01 ml, 0.01 mol) was heated to 190 °C for 3 h. The crystal formed on cooling was

recrystallized from water. A single crystal of compound **I** was obtained from ethanol at room temperature *via* slow evaporation. Yield: 0.96 g (50%). This compound was soluble in common organic solvents such as ethyl acetate, dichloromethane, CHCl₃, DMF and DMSO. M.p: 210 °C. IR ($\nu_{\max}/\text{cm}^{-1}$): 3204 (NH), 3067, 2813, 1697 (C=O), 1603, 1589, 1515, 1427, 1384, 1313, 1223, 1061, 848, 800, 603, 518. ¹H NMR (CDCl₃): δ 11.63 (1H, s, NH), 7.52–7.32 (4H, m, Ar), 2.01 (3H, s, CH₃) ppm. ¹³C NMR (CDCl₃): δ 163.89, 159.01, 154.16, 143.72, 129.42, 129.23, 116.34, 115.89 and 12.14 ppm. Crystal data: C₉H₈FN₃O, MW: 193.18 g/mol, triclinic, $a = 6.7625(11)$ Å, $b = 7.1914(12)$ Å, $c = 9.6173(15)$ Å, $V = 446.35(13)$ Å³, $T = 293$ K, space group $P\bar{1}$, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.113$ mm⁻¹, $R_{\text{int}} = 0.0348$. Summary of data containing CCDC 297124 is presented in [23].

4.2. 1-(3,4-Dicyanophenyl)-4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1H-1,2,4-triazol-5-one (**II**)

4.2.1. Method A

Compound **I** (0.5 g, 2.50 mmol) was dissolved in dry DMF (100 ml), and 4-nitrophthalonitrile (0.44 g, 2.50 mmol) was added. After stirring for 10 min. at room temperature, finely ground anhydrous K₂CO₃ (excess) was added portion wise in 2 h. With efficient stirring for 24 h at room temperature, the reaction mixture was poured into ice-water (500 g). The crude product was hold for 2 h and filtered off. The mixture was washed with HCl (50 ml, 5%) and then washed with water until the filtrate became neutral, and dried. The product was crystallized from ethanol. A single crystal of compound **II** was obtained from ethanol at room temperature *via* slow evaporation. Yield: 0.5 g (60%). This compound was soluble in hot ethanol, ethyl acetate, chloroform, DMF and DMSO. mp 209 °C. IR ($\nu_{\max}/\text{cm}^{-1}$): 3105, 2928, 2226 (CN), 1722 (C=O), 1593, 1560, 1513, 1493, 1404, 1388, 1371, 1228, 844, 596 and 525. ¹H NMR (CDCl₃): δ 8.50–7.40 (7H, m, Ar), 2.19 (3H, s, CH₃) ppm. ¹³C NMR (CDCl₃): δ 164.52, 159.61, 150.97, 146.87, 140.96, 135.44, 129.94, 129.76, 128.18, 121.06, 120.97, 116.73, 116.27, 115.84, 115.49, 109.46 and 12.15 ppm. Crystal data: C₁₅H₁₀FN₅O, MW:

295.28 g/mol, monoclinic, $a = 12.5350(6)$ Å, $b = 7.9498(5)$ Å, $c = 15.2826(8)$ Å, $V = 1452.52(14)$ Å³, $T = 293$ K, space group $P2_1/c$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.099$ mm⁻¹, $R_{\text{int}} = 0.0302$, summary of data containing CCDC 297125 is presented in [24].

4.2.2. Method B

Compound **I** (0.5 g, 2.50 mmol) and 4-nitrophthalonitrile (0.44 g, 2.50 mmol) were dissolved in DMF (5 ml). K_2CO_3 (excess) were added into this solution in 2 min. with efficient stirring. The mixture was irradiated by microwave at 350 W for 5 min. The above purification methods were also applied to this material.

4.3. Metal-free phthalocyanine (**1**)

4.3.1. Method A

A mixture of compound **II** (0.5 g, 1.56 mmol) and hydroquinone (2 g, excess) was gently heated under N_2 and cooled. The mixture was heated to 200 °C under N_2 and held at this temperature for 2 h. After cooling to room temperature, the reaction mixture was treated with boiling ethanol (50 ml) for 1 h (tree times) and hot water (50 ml) (tree times), dried and purified by column chromatography (silica gel, $\text{CH}_3\text{OH}:\text{CHCl}_3$, 1:80). Yield: 0.2 g (40%). The green product was soluble in chloroform, DMF and DMSO. mp >300 °C. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3429 (NH), 3104, 2925, 2851, 1722 (C=O), 1594, 1556, 1514, 1493, 1404, 1371, 1227, 844, 581 and 525. UV–Vis (λ_{nm}): 267, 673, 706. ¹H NMR (CDCl_3): δ 8.56–7.26 (28H, m, Ar) and 2.25 (12H, s, CH_3). ¹³C NMR (CDCl_3): δ 164.64, 159.81, 151.26, 146.45, 141.04, 135.36, 131.03, 130.51, 129.08, 122.06, 121.22, 117.01 and 29.71 ppm. Anal. Calc. for $\text{C}_{68}\text{H}_{42}\text{N}_{20}\text{O}_4\text{F}_4$ (1279.21 g/mol): C, 63.85; H, 3.31; N, 21.90. Found: C, 65.27; H, 3.45; N, 20.16%.

4.3.2. Method B

Compound **II** (0.5 g, 1.56 mmol) and DBU (1 ml) were added in dimethylaminoethanol (DMAE) (5 ml). The mixture was well stirred, and then irradiated by microwave at 350 W for 8 min. The above purification methods were also applied to this material.

4.4. Nickel (II) phthalocyaninate (**2**)

4.4.1. Method A

A mixture of compound **II** (0.5 g, 1.56 mmol), DBU (1 ml), anhydrous NiCl_2 (0.05 g, 0.39 mmol) and DMAE (10 ml) was heated to 200 °C under N_2 and held at that temperature for 2 h. After cooling to room temperature, the dark green mixture was refluxed with ethanol (50 ml, three times) and ethyl acetate (50 ml, three times). The green product was filtered off, and then washed with boiling water (100 ml), dried and purified by column chromatography (silica gel, $\text{CH}_3\text{OH}:\text{CHCl}_3$, 1:80). Yield: 0.22 g (42%). The green product was soluble in chloroform, DMF and DMSO. mp >300 °C. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3119, 2932, 2841, 1719, 1585, 1559, 1492, 1421, 1363, 1252, 847, 584 and 531. UV–Vis (λ_{nm}): 256, 638 (shoulder), 682. ¹H NMR (CDCl_3): δ 8.50–7.90 (28H, m, Ar) and 2.20 (12H, s, CH_3). ¹³C NMR (CDCl_3): δ 164.21, 161.25, 151.93, 146.88, 142.24, 135.90, 131.36, 131.28, 129.77, 122.67, 121.54, 118.02 and 29.72 ppm. Anal. Calc. for $\text{C}_{68}\text{H}_{40}\text{N}_{20}\text{O}_4\text{F}_4\text{Ni}$ (1335.89 g/mol): C, 61.14; H, 3.02; N, 20.97. Found: C, 62.83; H, 3.17; N, 21.14%.

4.4.2. Method B

Compound **II** (0.5 g, 1.56 mmol) and NiCl_2 (0.05 g, 0.39 mmol) were added in dimethylaminoethanol (DMAE) (5 ml). Then the mixture was irradiated by microwave at 350 W for 8 min. The above purification methods were also applied to this material.

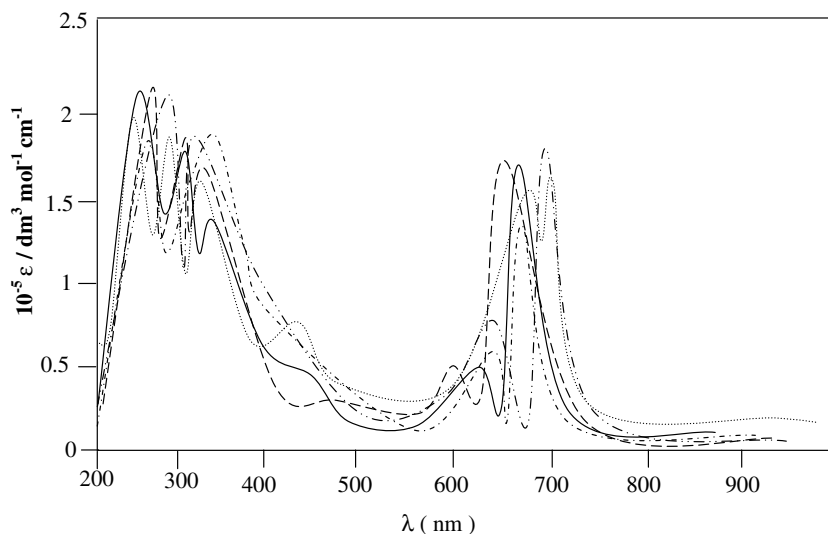


Fig. 5. UV–Vis spectra of compounds **1** (·····), **2** (—), **3** (---), **4** (— · —) and **5** (— · —) in chloroform.

4.5. Zinc (II) phthalocyaninate (3)

4.5.1. Method A

A mixture of compound **II** (0.5 g, 1.56 mmol), DBU (1 ml), anhydrous zinc acetate (0.071 g, 0.39 mmol) and DMAE (10 ml) was heated to 200 °C under N₂ and held at that temperature for 2 h. After cooling to room temperature, the green mixture was refluxed with ethanol (50 ml, three times) and ethyl acetate (50 ml, three times), and filtered off. The product was washed with boiling water (100 ml) and boiling methanol (50 ml). The green product was soluble in chloroform and filtered off, dried and purified by column chromatography (silica gel, CH₃OH:CHCl₃, 1:80). Yield: 0.30 g (57%). The green product was soluble in chloroform, DMF and DMSO. mp >300 °C. IR ($\nu_{\max}/\text{cm}^{-1}$): 3104, 2926, 2854, 1722, 1593, 1561, 1513, 1493, 1371, 1228, 844, 585 and 525. UV–Vis (λ_{nm}): 288, 351, 655 (shoulder), 689. ¹H NMR (CDCl₃): δ 8.50–7.83 (28H, m, Ar) and 2.10 (12H, s, CH₃). ¹³C NMR (CDCl₃): δ 164.76, 160.12, 151.89, 146.78, 141.75, 135.88, 131.25, 131.02, 129.27, 122.21, 121.35, 117.12 and 28.89 ppm. Anal. Calc. for C₆₈H₄₀N₂₀O₄F₄Zn (1342.59 g/mol): C, 60.83; H, 3.00; N, 20.86. Found: C, 61.21; H, 3.19; N, 20.18%.

4.5.2. Method B

Compound **II** (0.5 g, 1.56 mmol) and anhydrous Zn(CH₃COO)₂ (0.071 g, 0.39 mmol) were added in dimethylaminoethanol (DMAE) (5 ml). Then the mixture was irradiated by microwave at 350 W for 8 min. The above purification methods were also applied to this material.

4.6. Copper (II) phthalocyaninate (4)

4.6.1. Method A

A mixture of compound **II** (0.5 g, 1.56 mmol), CuCl (0.038 g, 0.39 mmol), urea (1 g, excess) and DMAE (10 ml) was heated at 180–190 °C for 2 h under N₂. After cooling to room temperature, the mixture was diluted with ethanol (50 ml), refluxed and filtered off. The resultant green product was washed with NH₄OH (50 ml, 24%) and then with water until the filtrate was neutral. The product was refluxed with ethanol (50 ml, three times) and ethyl acetate (50 ml, three times), then the liquor filtered, dried and purified by column chromatography (silica gel, CH₃OH:CHCl₃, 1:80). Yield: 0.25 g (48%). The product was soluble in chloroform, DMSO and DMF. mp >300 °C. IR ($\nu_{\max}/\text{cm}^{-1}$): 3103, 2925, 2852, 1721, 1596, 1557, 1515, 1494, 1403, 1372, 1228, 845, 582 and 524. UV–Vis (λ_{nm}): 283, 634 (shoulder), 685. Anal. Calc. for C₆₈H₄₀N₂₀O₄F₄Cu (1340.74 g/mol): C, 60.92; H, 3.01; N, 20.89. Found: C, 62.54; H, 3.19; N, 22.14%.

4.6.2. Method B

Compound **II** (0.5 g, 1.56 mmol) and CuCl (0.038 g, 0.39 mmol) were well stirred in DMAE (5 ml). Then the mixture was irradiated by microwave at 350 W for 8 min.

The above purification methods were also applied to this material.

4.7. Cobalt (II) phthalocyaninate (5)

4.7.1. Method A

A mixture of compound **II** (0.5 g, 1.56 mmol), DBU (1 ml), anhydrous CoCl₂ (0.05 g, 0.39 mmol), ammonium molybdate (excess) and DMAE (10 ml) was heated to 200 °C under N₂ and held at that temperature for 2 h. After cooling to room temperature, the green mixture was refluxed with ethanol (50 ml, three times) and ethyl acetate (50 ml, three times), and filtered off, dried and purified by column chromatography (silica gel, CH₃OH:CHCl₃, 1:80). The green product was soluble in chloroform and filtered off, and dried. Yield: 0.20 g (38%). The green product was soluble in chloroform, DMF and DMSO. mp >300 °C. IR ($\nu_{\max}/\text{cm}^{-1}$): 3105, 2927, 2854, 1723, 1594, 1560, 1513, 1490, 1373, 1227, 845, 586 and 525. UV–Vis (λ_{nm}): 257, 648 (shoulder), 682. Anal. Calc. for C₆₈H₄₀N₂₀O₄F₄Co (1336.13 g/mol): C, 61.13; H, 3.02; N, 20.97. Found: C, 63.17; H, 3.19; N, 22.53%.

4.7.2. Method B

Compound **II** (0.5 g, 1.56 mmol) and CoCl₂ (0.05 g, 0.39 mmol) were well stirred in DMAE (5 ml). Then the mixture was irradiated by microwave at 350 W for 8 min. The above purification methods were also applied to this material.

5. Supplementary material

CCDC 297124 and 297125 contain the supplementary crystallographic data for 4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one and 1-(3,4-dicyanophenyl)-4-(*p*-fluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- [24] CCDC number 297125 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.