

Synthesis and Properties of Triazol-5-one Substituted Phthalocyanines by Microwave Irradiation

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Triazol-5-one substituted phthalocyanines were prepared quickly by the reaction of 4-nitrophthalonitrile with anhydrous metal salts in DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) and DMAE (dimethylaminoethanol) by microwave irradiation. Microwave yields were higher than those of the conventional synthesis methods. All of these complexes are insoluble in polar solvents such as ethanol, ethyl acetate and chloroform. The characterization of the compounds was accomplished by elemental analysis, ¹H NMR (for **I** and **II**), ¹³C NMR (for **I** and **II**), IR and UV-Vis spectral data. In addition, the structure of the starting material (**I**) was determined by single crystal diffraction.

Key Words: Phthalocyanine, microwave synthesis

Introduction

Recently, much attention has been focused on 1,2,4-triazole derivatives for their broad-spectrum fungicidal, insecticidal, herbicidal, anticonvulsant, antitumor and plant growth regulatory activities.¹ Phthalocyanines (Pcs) are very stable dyes with strong absorption coefficients in the visible region (Q band around 700 nm) and are used as dyes and pigments for printing inks, coloring plastics, and in paints and coatings.² In the last 10 years, metal phthalocyanine derivatives have gained popularity as functional materials. For example, phthalocyanines are used in laser-beam printers and photocopiers,³ as liquid crystals,⁴ for photodynamic cancer therapy⁵ and in semiconductors.⁶ Many of these applications depend on the nature of the metal ion incorporated at the center of an 18 π electron phthalocyaninato (-2) macroring as well as on their solubility in a wide range of solvents.⁷ Our primary aim was the synthesis of new phthalocyanines with various functional groups and/or macrocycles. Among these we may cite N-, S and O-, N, S and O- and triazol containing functionalities such as oxathiaethers,⁸ oxadithiadiazas ethers and aza macrocycles.^{9–13}

In recent years, microwave technology has received wide attention in organic chemistry because of its versatility, speed, and cleaner reaction products.¹⁴

In the present paper, we report the preparation and characterization of metal and metal-free phthalocyanines containing substituted triazol-5-one moiety by microwave synthesis.

Results and Discussion

1,2-Dicyano-4-nitrobenzene has been used to prepare monosubstituted phthalonitrile derivatives though base catalyzed aromatic displacement.¹⁵ This is a conventional method for monosubstituted phthalonitrile and phthalocyanines (Pcs). The second method, which is new, is microwave irradiation. Both methods were also applied to prepare starting materials, metal-free and metal Pcs. Starting from **I**, the general route for the synthesis of the new phthalocyanines is shown in the Scheme. The starting material, **I**, was synthesized by the treatment of ethylphenylacetateethoxycarbonylhydrazone with p-fluoroaniline. For **II**, compound **I** and 4-nitrophthalodinitrile were heated in DMF at room temperature for 24 h (for microwave synthesis, 10 min and 350 W in DBU and DMAE). The yields of microwave synthesis were higher than those of conventional methods. The metal-free Pc **1** was synthesized by heating a mixture of the dicyano compound **II** with freshly sublimed hydroquinone in the absence of solvent (for the microwave synthesis, 10 min and 350 W in DBU and DMAE). CuPc (**4**) was synthesized by 2 different methods. For the conventional method, compound **II**, CuCl and urea were heated at 180-190 °C for 32 h under N₂. Microwave synthesis of the metal Pcs (**2-5**) was accomplished in DMAE for 10 min. The yields of microwave syntheses were higher than those of conventional methods. A single crystal of compound **I** was obtained via slow evaporation in ethyl acetate. The new synthesized metal-free and metal Pcs are not soluble in common organic solvents such as ethyl acetate, ethanol and chloroform, but are soluble in hot DMSO and hot DMF.

Elemental analyses, IR, NMR, UV-Vis and X-ray spectra for **I** confirm the proposed structures of the compounds. These products were obtained in sufficient purity after successive washing with different solvents and by column chromatography (silicagel-dmso).

IR Spectra

Spectral investigations of the synthesized intermediates and the phthalocyanines are in accord with the proposed structures. In this context, comparison of the IR spectral data clearly indicated the formation of compound **I** by the appearance of a new carbonyl (C=O) band for ketone at 1694 cm⁻¹ and by the disappearance of the C-O band at 1205 cm⁻¹ and C=O band (ester carbonyl) at 1740 cm⁻¹. The IR spectrum of compound **II** indicates the presence of the CN band at 2232 cm⁻¹ and the disappearance of the NH band at 3383 cm⁻¹. The IR spectrum of metal-free Pc (**1**) is very similar to that of **II**. A diagnostic feature of the phthalocyanine formation from dicyano derivative **II** is the disappearance of the CN stretching vibration at 2232 cm⁻¹ of the **II**. The IR spectra of the metal phthalocyanines (**2-5**) were very similar to those of the metal-free Pc (**1**). The only difference was the presence of NH vibration assigned to the band at 3428 cm⁻¹ in the free phthalocyanine. This band was absent in the spectra of the metal complexes.

NMR Spectra

In the ¹H NMR spectrum of compound **I** in DMSO-d₆, the aromatic protons appear as a multiplet at 7.29-6.93 ppm, the NH proton as a singlet at 11.80 ppm and the CH₂ protons as a singlet at 3.81 ppm. The ¹³C NMR of compound **I** in DMSO-d₆ gave signals at 163.9 (C=O), 159.0, 154.3, 145.8, 134.8, 129.7, 128.4,

126.5, 116.2, 115.7, and 31.8 (CH₂). In the ¹H NMR spectrum of **II** in DMSO-d₆, aromatic protons appear as a multiplet at 8.90-7.05 ppm and CH₂ protons as a singlet at 3.90 ppm. The ¹H NMR and ¹³C NMR measurements of **II**, and metal-free and metal Pcs were precluded because of their insolubility in common organic solvents such as CDCl₃, DMSO-d₆, C₆D₆ and D₂O.

UV-Vis Spectra

Phthalocyanines **1-5** showed typical electronic spectra with 2 strong absorption regions, one in the UV region at about 340 nm (B band) and the other in the visible region at 702 nm (Q band). These are very similar to those of aza macrocyclic¹⁰⁻¹² substituted phthalocyanines. Although the symmetry of the phthalocyanines is lowered by the heteroatom substituents on each phenyl group, compound **1** still shows Q band absorption of D_{2h} symmetry in organic solvents.⁶ The phthalocyanine complexes showed an intense absorption at 702 nm and a shoulder band of lower intensity at 634 nm.

X-Ray Spectra

The title compound, C₁₅H₁₂FN₃O · H₂O (**I**), contains 2 benzene rings and a triazole ring displays the characteristic features of 1,2,4-triazole derivatives (Figure 1). The asymmetric unit of **I** contains 4 independent molecules. Two of them are H₂O molecules. The O2A and O2B atoms of H₂O molecules display strong hydrogen bonds with N2A and N2B atoms, respectively. These bond lengths can be seen in Table 1. The triazole and 2 benzene rings of the molecule **I** are planar. The maximum deviation from planarity is of the C6A atom of the C1A-C6A ring. The dihedral angles between the 1,2,4-triazole and C1A-C6A and C10A-C15A rings are 86.94(11)° and 89.17(11)°, respectively. In the three-dimensional network, molecule **I** is linked by a weak van der Waals interaction (Figure 2) in addition to intermolecular hydrogen bonds (Table 2). All H atom parameters were freely refined. C-H distances are in the range 0.87(3)-1.11(4) Å, and *U*_{iso} values for H atoms are in the range 0.041 (6)-0.142(15) Å².

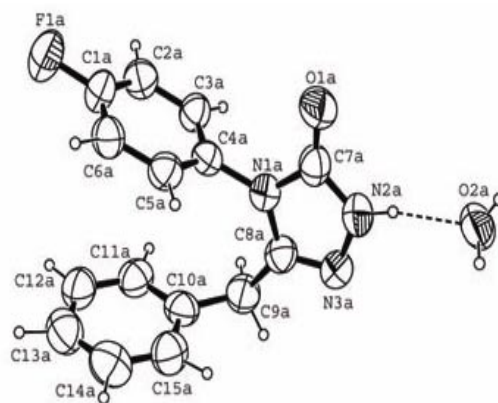


Figure 1. Crystal structure for **I**.

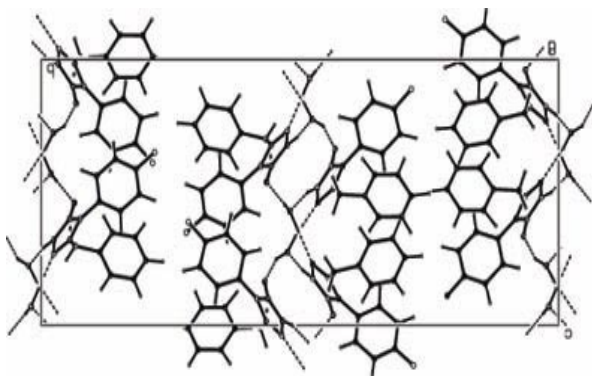


Figure 2. The packing diagram for **I**.

Table 1. Bond distances (Å) for **I**.

F1A -C1A	1.373(4)	C8A-C9A	1.495(5)	F1B-C1B	1.373(4)	C13B-H13B	1.00(4)
C9A-C10A	1.517(5)	O1A-C7A	1.228(4)	C10A-C15A	1.399(5)	C2B-H2B	0.89(3)
O1B-C7B	1.227(5)	C10A-C11A	1.388(5)	O2A-H11	0.71(3)	C12B-H12B	0.92(4)
C11A-C12A	1.377(5)	O2A-H22	0.98(8)	C12A-C13A	1.380(6)	C14B-C15B	1.383(7)
O2B-H44	0.97(7)	C13A-C14A	1.379(6)	O2B-H33	0.88(3)	C11B-H11B	1.02(4)
C14A-C15A	1.375(6)	N1A-C4A	1.443(4)	C2A-H2A	1.03(3)	C13B-C14B	1.353(7)
N1A-C7A	1.383(5)	C3A-H3A	1.01(3)	N1A-C8A	1.380(4)	C9B-H92B	0.86(3)
C5A-H5A	0.88(3)	N2A-C7A	1.340(4)	C6A-H6A	1.01(3)	C12B-C13B	1.388(6)
N2A-N3A	1.397(5)	C9A-H92A	1.02(3)	N3A-C8A	1.298(4)	C9B-H91B	1.02(3)
C9A-H91A	0.93(4)	N2A-H22A	0.80(3)	C11A-H11A	1.11(4)	C11B-C12B	1.373(6)
N1B-C4B	1.445(3)	C12A-H12A	0.97(4)	N1B-C8B	1.376(4)	C6B-H6B	0.99(3)
C13A-H13A	1.07(4)	N1B-C7B	1.393(5)	C14A-H14A	0.99(3)	C10B-C11B	1.397(5)
N2B-N3B	1.396(5)	C15A-H15A	0.98(3)	N2B-C7B	1.349(4)	C10B-C15B	1.370(5)
C1B-C6B	1.364(5)	N3B-C8B	1.303(4)	C1B-C2B	1.360(5)	C5A-C6A	1.389(5)
N2B-H22B	0.97(4)	C2B-C3B	1.383(5)	C1A-C2A	1.349(5)	C9B-C10B	1.505(5)
C3B-C4B	1.370(4)	C1A-C6A	1.361(5)	C4B-C5B	1.377(4)	C4A-C5A	1.370(4)
C2A-C3A	1.386(5)	C5B-C6B	1.377(5)	C3A-C4A	1.378(5)	C8B-C9B	1.488(6)
C3B-H3B	0.94(2)	C14B-H14B	0.98(4)	C5B-H5B	1.05(3)	C15B-H15B	1.01(4)

Table 2. Hydrogen bonds (Å, Deg.) for **I**.

O2A – H11 .. O1B	0.71(3)	2.07(3)	2.772(4)	168(3)	1.656
O2A – H22 .. N3B	0.98(8)	1.90(8)	2.873(4)	171(10)	2.655
N2A – H22A .. O2A	0.80(3)	1.93(3)	2.713(4)	165(3)	2.554
N2B – H22B .. O2B	0.97(4)	1.75(4)	2.709(4)	171(3)	2.554
O2B – H33 .. N3A	0.88(3)	2.14(3)	2.987(4)	162(3)	2.555
O2B – H44 .. O1A	0.97(7)	1.84(6)	2.763(3)	158(6)	1.655
C2A – H2A .. O1B	1.03(3)	2.58(2)	3.384(4)	134.3(19)	1.556
C6B – H6B .. F1A	0.99(3)	2.55(3)	3.304(4)	133(2)	3.556
C11A – H11A .. O1A	1.11(4)	2.39(4)	3.387(4)	149(3)	1.655
C11B – H11B .. O1B	1.02(4)	2.48(4)	3.384(4)	148(3)	1.655

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 Marmara Research Center. 4-Nitrophthalonitrile was synthesized according to the reported procedure.¹⁶ For the X-ray study, X-ray data collection and cell refinement were achieved with X-Area. The data reduction was performed by X-RED.¹⁷ SHELXS97 was used to solve the structure and SHELXL97¹⁸ was used to refine it. Molecular graphics were prepared using ORTEP III.¹⁹ WinGX²⁰ was used to prepare the material for publication.

Data Acquisition: Cambridge Crystallographic Data Centre deposit@ccdc.cam.ac.uk

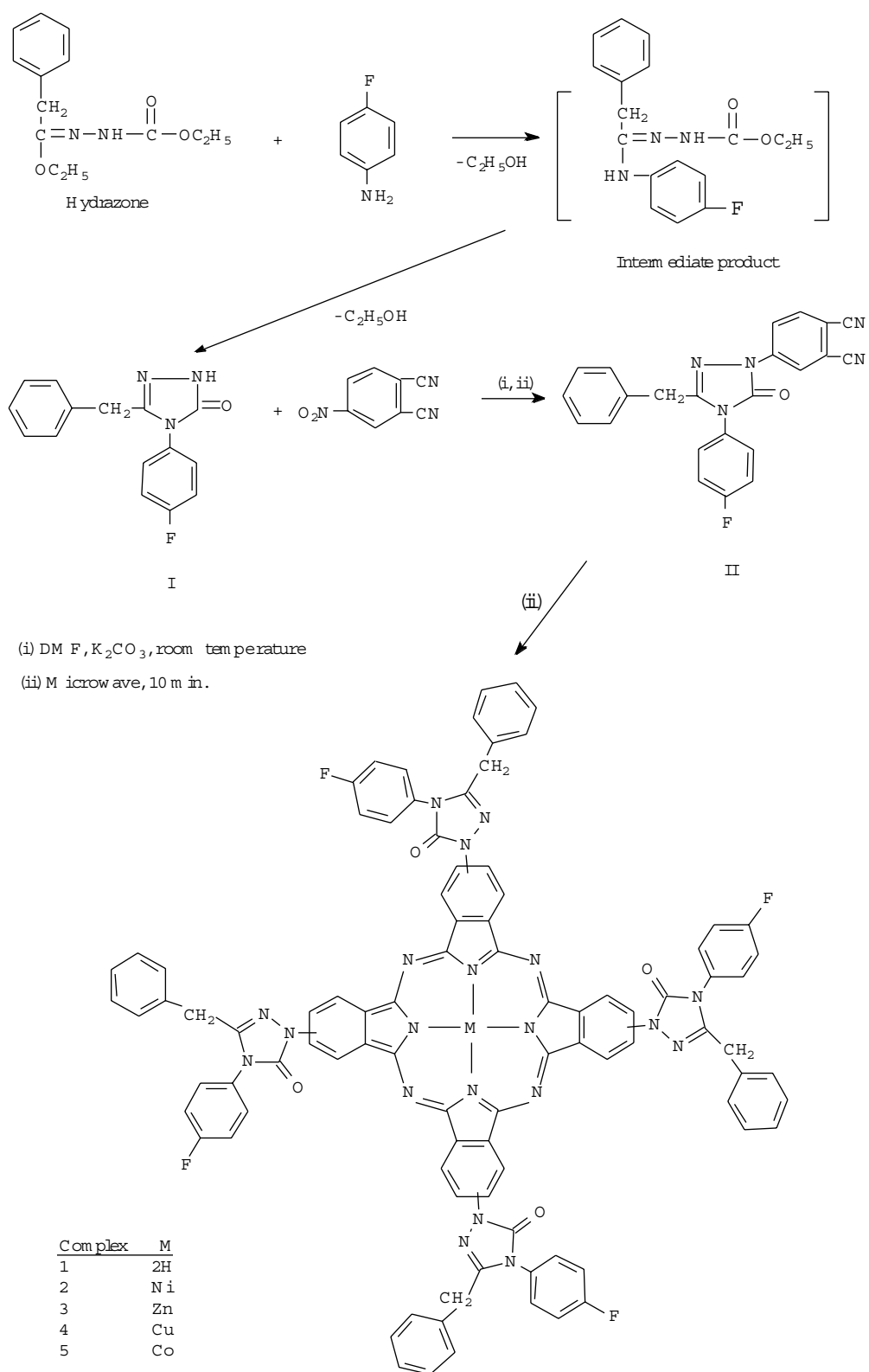
<http://www.ccdc.cam.ac.uk/deposit> Telephone: (44) 01223 762910 Facsimile: (44) 01223 336033. Postal Address: CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK.

Syntheses

The synthetic routes for all compounds are outlined in the Scheme and the details are given below.

4-(p-Fluorophenyl)-3-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-one (I): A mixture of the corresponding hydrazone (2.50 g, 0.01 mol) and p-fluoroaniline (1.01 mL, 0.01 mol) was heated to 180 °C over 3 h. The crystals formed on cooling were recrystallized from ethanol. Yield 1.68 g (54%), m.p. 150-151 °C. This compound was soluble in common organic solvents such as ethyl acetate, dichloromethane, CHCl_3 , DMF and DMSO. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3383 (NH), 3060, 2829, 1694 (C=O), 1601, 1573, 1512, 1425, 1315, 1218, 1060, 850, 820, 703, 608, 517. ^1H NMR (CDCl_3 , 200 MHz): δ = 11.80 (1H, s, NH), 7.29-6.93 (9H, m, Ar), 3.81 (2H, s, CH_2) ppm. ^{13}C NMR (CDCl_3 , 200 MHz): δ = 163.9 (C=O), 159.0, 154.3, 145.8, 134.8, 129.7, 128.4, 126.5, 116.2, 115.7, 31.8 (CH_2). **Crystal data:** $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}\cdot\text{H}_2\text{O}$, M = 287.29, orthorhombic, a = 7.5499(4), b = 30.6068(17), c = 12.2274(9) Å, V = 2825.5(3) Å³, T = 293 K, space group $\text{P2}_1\text{2}_1\text{2}_1$ (no. 19), Z = 8, $\mu(\text{Mo-K}\alpha)$ = 0.101 mm^{-1} , 2342 reflections measured and R_{int} = 0.0983. Summary of Data **CCDC** 286838.

1-(3,4-dicyanophenyl)-4-(p-fluorophenyl)-3-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-one (II):
Method A. Compound **I** (0.67 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 K_2CO_3 (excess) was added portionwise over 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 held at 2 h and filtered off. The mixture washed with HCl (50 mL, 5%) and washed with water until the filtrate became neutral, and dried. Yield 0.60 g (65%), m.p. 217 °C (from ethanol). This compound was soluble in DMF and DMSO, IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3083, 2925, 2232 (CN), 1731 (C=O), 1598, 1511, 1496, 1414, 1380, 1237, 1155, 842, 699 and 523. ^1H NMR (CDCl_3 , 200 MHz): δ = 8.90-7.05 (12H, m, Ar), 3.90 (2H, s, CH_2) ppm. ^{13}C NMR (CDCl_3 , 200 MHz): δ = 165.7 (C=O), 159.6, 158.5, 156.6, 155.3, 154.1, 147.6, 145.9, 140.4, 133.9, 130.4, 128.7, 127.4, 126.7, 117.5, 116.6, 115.3 (CN), 114.7 (CN), 32.4 (CH_2). Anal. Calc. For $\text{C}_{23}\text{H}_{14}\text{N}_5\text{O}$ (395.39 g/mol) (%): C, 69.87; H, 3.57; N, 17.71. Found (%): C, 69.94; H, 3.62; N, 17.74. **Method B.** Compound **I** (0.67 g, 2.50 mmol) and 4-nitrophthalonitrile (0.44 g, 2.50 mmol) were dissolved in DBU (5 mL). K_2CO_3 (excess) was



Scheme Syntheses of the ligands and complexes.

added to this solution over 2 min with efficient stirring. The mixture was irradiated by microwave at 350 W for 10 min. The product was purified as described in method A. Yield 0.74 g (80%).

Metal-free phthalocyanine (1): Method A. A mixture of compound **II** (0.62 g, 1.56 mmol) and hydroquinone (2 g, excess) was gently heated under N₂ and cooled. The mixture was heated to 200 °C under N₂ and held at this temperature for 1 h. After cooling to room temperature, the reaction mixture was treated with boiling ethanol (50 mL) for 1 h (3 times) and hot water (50 mL) (3 times), dried and purified by column chromatography (silica gel, DMSO). Yield 0.217 g (35%). The green product was soluble in hot DMF and hot DMSO. IR ν_{max}/cm^{-1} : 3428 (NH), 3109, 2928, 1726 (C=O), 1598, 1561, 1489, 1454, 1407, 1364, 1348, 1259, 823, 704, 608 and 524. UV-Vis $\lambda_{max}(\text{DMSO})/\text{nm}$: 345, 640 (shoulder), 670 and 702. Anal. Calc. For C₉₂H₅₈N₂₀O₄F₄ (1583.60 g/mol) (%): C, 69.78; H, 3.69; N, 17.69. Found (%): C, 69.84; H, 3.65; N, 17.74. **Method B.** Compound **II** (0.62 g, 1.56 mmol) and DBU (1 mL) were added to dimethylaminoethanol (DMAE) (5 mL). The mixture was well stirred, and then irradiated by microwave at 350 W for 10 min. The product was purified as described in method A. Yield 0.40 g (65%).

Nickel(II) phthalocyaninate (2): Method A. A mixture of compound **II** (0.62 g, 1.56 mmol), anhyd. NiCl₂ (0.05 g, 0.39 mmol) and dry quinoline (25 mL) was heated at 180 °C under N₂ and held at that temperature for 24 h. After cooling to room temperature, the dark green mixture was refluxed with ethanol (50 mL, 3 times) and ethyl acetate (50 mL, 3 times). The green product was filtered off, and then washed with boiling water (100 mL), dried and purified by column chromatography (silica gel, DMSO). Yield 0.38 g (60%). The green product was soluble in hot DMF and hot DMSO. IR ν_{max}/cm^{-1} : 3105, 2917, 1721 (C=O), 1596, 1512, 1410, 1270, 1224, 1155, 836, 711 and 518. UV-Vis $\lambda_{max}(\text{DMSO})/\text{nm}$: 340, 470, 634 (shoulder), 683. Anal. Calc. For C₉₂H₅₆N₂₀O₄F₄Ni (1640.27 g/mol) (%): C, 67.37; H, 3.44; N, 17.08. Found (%): C, 67.45; H, 3.47; N, 17.12. **Method B.** Compound **II** (0.62 g, 1.56 mmol) and NiCl₂ (0.05 g, 0.39 mmol) were well stirred in DMAE (5 mL). Then the mixture was irradiated by microwave at 350 W for 10 min. The green product was purified as described in method A. Yield 0.44 g (68%).

Zinc(II) phthalocyaninate (3): Method A. A mixture of compound **II** (0.62 g, 1.56 mmol), anhyd. zinc acetate (0.071 g, 0.39 mmol) and dry quinoline (25 mL) was heated at 180 °C under N₂ and held at that temperature for 24 h. After cooling to room temperature, the green mixture was refluxed with ethanol (50 mL, 3 times) and ethyl acetate (50 mL, 3 times), and filtered off. The product was washed with boiling water (100 mL), dried and purified by column chromatography (silica gel, DMSO). Yield 0.48 g (75%). The green product was soluble in hot DMF and hot DMSO. IR ν_{max}/cm^{-1} : 3100, 2922, 2840, 1708 (C=O), 1605, 1488, 1399, 1319, 1218, 1152, 825, 772, 696 and 507. UV-Vis $\lambda_{max}(\text{DMSO})/\text{nm}$: 340, 472, 635 (shoulder), 691. Anal. Calc. For C₉₂H₅₆N₂₀O₄F₄Zn (1646.97 g/mol) (%): C, 67.09; H, 3.43; N, 17.01. Found (%): C, 67.18; H, 3.45; N, 17.08. **Method B.** Compound **II** (0.62 g, 1.56 mmol) and Zn(CH₃COO)₂ (0.071 g, 0.39 mmol) were well stirred in DMAE (5 mL). Then the mixture was irradiated by microwave at 350 W for 10 min. The green product was purified as described in method A. Yield 0.53 g (81%).

Copper(II) phthalocyaninate (4): Method A. A mixture of compound **II** (0.62 g, 1.56 mmol), CuCl (0.038 g, 0.39 mmol) and urea (1 g, excess) was heated at 180-190 °C for 32 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, 3 times) and ethyl acetate (50 mL, 3 times); then the crude

product was filtered, dried and purified by column chromatography (silica gel, DMSO). The product was soluble in hot DMSO and hot DMF. Yield 0.19 g (30%). The green product was soluble in hot DMF and hot DMSO. IR ν_{max}/cm^{-1} : 3049, 2924, 2846, 1714 (C=O), 1599, 1510, 1404, 1222, 1152, 833, 772, 702 and 518. UV-Vis $\lambda_{max}(\text{DMSO})/\text{nm}$: 340, 472, 634 (shoulder), 695. Anal. Calc. For $\text{C}_{92}\text{H}_{56}\text{N}_{20}\text{O}_4\text{F}_4\text{Cu}$ (1645.13 g/mol) (%): C, 67.17; H, 3.43; N, 17.03. Found (%): C, 67.26; H, 3.48; N, 17.10. **Method B.** Compound **II** (0.62 g, 1.56 mmol), CuCl (0.038 g, 0.39 mmol) and urea (1 g, excess) were well stirred in DMAE (5 mL). Then the mixture was irradiated by microwave at 350 W for 10 min. The green product was purified as described in method A. Yield 0.35 g (55%).

Cobalt(II) phthalocyaninate (5): Method A. A mixture of compound **II** (0.62 g, 1.56 mmol), anhyd. CoCl_2 (0.05 g, 0.39 mmol, excess), ammonium molybdate (0.05 g) and ethyleneglycol (25 mL) was heated at 180 °C under N_2 and held at that temperature for 24 h. After cooling to room temperature, the green mixture was refluxed with ethanol (50 mL, 3 times) and ethyl acetate (50 mL, 3 times), and filtered off, dried and purified by column chromatography (silica gel, DMSO). The green product was soluble in hot DMF and hot DMSO. Yield 0.38 g (60%). IR ν_{max}/cm^{-1} : 3065, 2923, 2851, 1720 (C=O), 1598, 1511, 1407, 1228, 1155, 838, 751, 707 and 515. UV-Vis $\lambda_{max}(\text{DMSO})/\text{nm}$: 340, 468, 637 (shoulder), 673. Anal. Calc. For $\text{C}_{92}\text{H}_{56}\text{N}_{20}\text{O}_4\text{F}_4\text{Co}$ (1640.51 g/mol) (%): C, 67.36; H, 3.44; N, 17.08. Found (%): C, 67.44; H, 3.46; N, 17.13. **Method B.** Compound **II** (0.62 g, 1.56 mmol) and CoCl_2 (0.05 g, 0.39 mmol, excess) were well stirred in DMAE (5 mL). Then the mixture was irradiated by microwave at 350 W for 10 min. The green product was purified as described in method A. Yield 0.48 g (75%).

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