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Synthesis and characterization of a new organo-soluble metal-free and metallophthalocyanines bearing flexible moieties

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ABSTRACT

This paper describes a new symmetric metal-free phthalocyanine and its transition metal complexes which were prepared by a condensation of 1,2-dihydroacenaphthylen-1-ol **1** and 4-nitro phthalonitrile **2** with Co(II), Ni(II), Cu(II), and Zn(II) salts in 2-(dimethylamino)ethanol, respectively. The novel phthalocyanines bearing oxygen donor atoms on peripheral position have been characterized by IR, UV–Vis, ^{1}H NMR, ^{13}C NMR, Mass spectra and elemental analysis. The thermal behaviours of **4–8** were investigated by TG/DTA.

1. Introduction

Since their first synthesis early in the last century, phthalocyanines, which are also called as blue-green products, are produced with increasing amount and diversity in many countries per year. The syntheses of metal-free and metallophthalocyanines play an extremely important role not only in the development of chemistry and its related branches but also in the development of current economy.

Phthalocyanines (pcs) and their derivatives have attracted a good deal of interest due to their fascinating features such as high thermal stability [1], semi-conductivity [2], and besides in several application areas such as laser dyes, new red-sensitive photocopying applications [3,4], and optical computer read/write discs. [5]. Pcs are an important industrial commodity which was firstly used in productions of inks, and also colouring for plastics, metal surfaces, dye stuffs for jeans and other clothing [3]. Phthalocyanines' electronic and optical properties for use in many applications, such as chemical sensors [6–9], liquid crystals [10–12], catalysis, considerably depend upon the peripheral and axial substitution patterns [13,14]. Besides, pcs can also be subsequently used in various implementation areas, for instance, production of solar energy conversions [15,16], antimycotic materials [17], corrosion inhibitors [18,19], for the prevention and treatment of infectious diseases [20], eye [21] and neurodegenerative diseases [22]. In the last few years, substituted phthalocyanine derivatives have also been used in photodynamic cancer therapy (PDT) and other processes by visible light [23–27].

Pcs can be obtained by the classical template reactions of phthalonitrile, cyano-benzamide, phthalic acid and phthalamide with metal salts in high-boiling nonaqueous solvents at required temperatures [28,29]. On the other hand, microwave processing techniques have attracted a great deal of potential interest as alternatives to classical thermal processing techniques because of the diverse and convenient advantages of microwave heating, which is selective, direct, rapid, internal, and controllable [30,31]. It is well known that microwave (MW) irradiation can accelerate a great number of chemical processes; in particular, the reaction time and energy input are supposed to be mostly reduced in the chemical processes that are run for a long time at high temperatures under conventional conditions [32].

The present work contains the preparation and the characterization of metal-free (**4**) and metallophthalocyanines (**5–8**) containing 1,2-dihydroacenaphthylen-1-ol moieties by the microwave irradiation. Additionally, we have carried out the thermogravimetric study of tetrasubstituted metal-free phthalocyanine (**4**) and metallophthalocyanines (**5–8**) to compare their thermal stabilities.

2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using Standard Schlenk techniques. All chemicals, solvents, and reagents were of reagent grade quality and were obtained from commercial suppliers. All reagents and solvents were dried and

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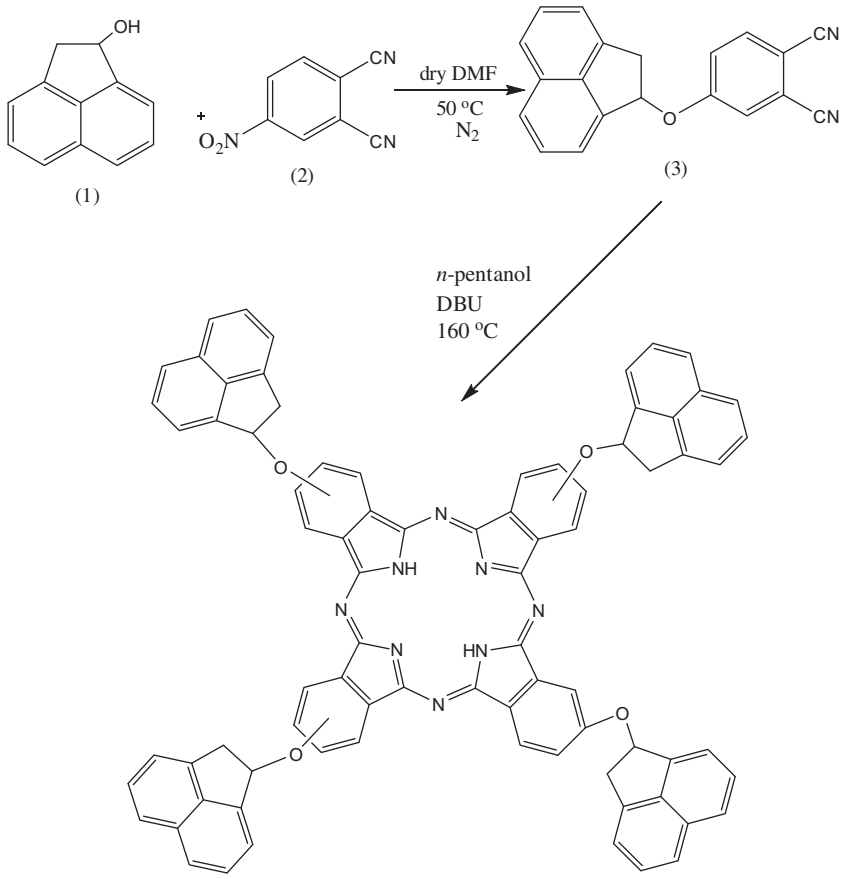

Scheme 1. The synthesis of the metal-free phthalocyanine (**4**) by using classical method.

purified before use as described by Perrin and Armarego [33]. FT-IR spectra were obtained using a Perkin–Elmer 1600 FTIR spectrophotometer with the samples prepared as KBr pellets. Elemental analyses and metal contents of novel compounds were performed on a Vario MICRO Elemental Analyser at Anadolu University in Turkey. A Seiko II Exstar 6000 thermal analyzer was used to record the DTA curves under a nitrogen atmosphere with a heating rate of 20 °C min^{-1} in the temperature range of 30–900 °C using platinum crucibles. UV–Vis spectra were recorded using a Unicam UV–Vis spectrometer operating in the wavelength range of 200–850 nm with quartz cells. All ^{1}H and ^{13}C NMR spectra were recorded in CDCl3 on a Varian Mercury NMR spectrometer operating at 200 MHz. Chemical shifts are expressed in ppm relative to TMS as an internal standard. Mass spectra were recorded using a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used for carrying out all synthesis of phthalocyanines.

2.1. 4-(1,2-Dihydroacenaphthylen-1-yloxy)phthalonitrile (**3**)

1,2-Dihydroacenaphthylen-1-ol **1** (1 g, 5.88 mmol) was dissolved in anhydrous DMF (8 ml) under a nitrogen atmosphere at 50 °C and 4-nitrophthalonitrile **2** [34] (1.02 g, 5.88 mmol) was added to the solution. After stirring for 15 min, finely ground dry K_2CO_3 (2.84 g, 20.58 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under a nitrogen atmosphere at 50 °C for 3 days. The reaction mixture was monitored by thin layer chromatography (TLC) using chloroform solvent system. At the end of the elapsed period, the obtained mixture was poured into ice (100 g) and it was shown that the light-green product precipitated. This product was filtered off, washed with distilled water and diethylether. Finally, obtained crude product was crystallized from ethanol. Yield: 1.2 g (69%), m.p.: 176–177 °C. *Anal.* Calc. for $C_{20}H_{12}N_2O$: C, 81.07; H, 4.08; N, 9.45. Found: C, 81.03; H, 4.05; N, 9.48%. IR (KBr tablet) ν_{max}/cm^{-1}: 3081 (Ar-H), 2920–2850 (Aliph. C–H), 2227 (C≡N), 1594, 1497, 1325, 1253, 1165, 1019, 838, 780. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.85–7.81 (d, 3H, Ar-H), 7.64 (s, 1H, Ar-H), 7.59–7.56 (t, 2H, Ar-H), 7.43–7.34 (m, 3H, Ar-H), 6.31 (t, 1H, CH), 3.70 (d, 2H, CH_2). ^{13}C NMR ($CDCl_3$) (δ: ppm): 161.32, 140.58, 140.18, 137.90, 135.62, 131.52, 128.73, 128.29, 126.48, 123.59, 121.85, 120.72, 120.55, 120.49, 117.85, 115.90, 115.51, 107.78, 80.41, 38.87. MS (FAB), (*m*/*z*): 296$[M]^+$.

2.2. Metal-free phthalocyanine (**4**)

A standard Schlenk tube was charged with 4-(1,2-dihydroacenaphthylen-1-yloxy)phthalonitrile **3** (0.2 g, 0.675 mmol), 3 ml of anhydrous *n*-pentanol and 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 2 drops) under a nitrogen atmosphere and degassed several times. Then the reaction mixture was stirred at 160 °C for 12 h. After cooling to room temperature, the reaction mixture was stirred with ethanol (30 ml) to precipitate the product. The precipitated dark green product **4** was filtered off, washed with hot ethanol (3 × 50 ml) and dried *in vacuo* over P_2O_5. Finally, it was purified by preparative thin layer chromatography (TLC) using solely chloroform solvent system. This product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO and pyridine. Yield: 40 mg (20%), m.p.: 269–292 °C. *Anal.* Calc. for $C_{80}H_{50}N_8O_4$: C, 80.93; H, 4.24; N, 9.44. Found: C, 80.90; H, 4.26; N, 9.49%. IR (KBr tablet) ν_{max}/cm^{-1}: 3285 (N–H), 3039 (Ar-H), 2916–2847 (Aliph. C–H), 1602, 1520, 1477, 1418, 1344, 1236, 1096, 1015, 936, 776, 746. ^{1}H NMR ($CDCl_3$)