



Microwave-assisted synthesis, characterization and spectral properties of non-peripherally tetra-substituted phthalocyanines containing eugenol moieties



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HIGHLIGHTS

- Novel phthalocyanines containing eugenol were synthesized and characterized.
- Electronic absorption spectra of phthalocyanines was reported.
- Spectral properties were compared with previous eugenol substituted phthalocyanines.

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ABSTRACT

The microwave-assisted synthesis and characterization of novel non-peripherally eugenol substituted metallophthalocyanines (M: Co(II), Ni(II), Cu(II), Zn(II)) have been reported for the first time in this study. All the new compounds were characterized by a combination of FT-IR, ¹H NMR, ¹³C NMR, and UV/vis spectroscopy techniques. The crystal structure of compound (**1**) was also determined by the single crystal diffraction technique. Newly synthesized eugenol substituted phthalocyanines have more redshift Q bands (about 17–18 nm) than previously reported eugenol substituted phthalocyanines. Zinc(II)phthalocyanine (**1d**) has an extra absorption band at 746 nm that calling “X band” at UV/vis spectrum.

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Introduction

Phthalocyanines (Pcs) are widely used as conventional dyes and pigments. They have interesting chemical and physical properties [1,2]. The optical and electronic properties of the phthalocyanine (Pc) macrocycle make it suitable for a wide range of technological applications, such as photoconductors in xerographic machines [3], electrochromic displays [4], photovoltaic materials in solar cells [5,6], systems for fabrication of light emitting diodes (LED) [7], optical limiters [8], dyes at recording layers in recordable digital versatile discs (DVDs) [9], liquid crystalline [10], organic conductors [11] and diverse catalytic systems [12].

Phthalocyanines are usually prepared by the high temperature cyclotetramerization processes of either phthalonitrile or phthalic anhydride, in which the template effect afforded by a suitable metal cation is required. The reactions can be carried out in a variety of solvents as well as under solvent-free conditions, but both processes

require temperature ca. 200 °C and long reaction times. The use of microwave energy is one of the most efficient methods for phthalocyanine synthesis. Not only is microwave energy more environmentally friendly, it requires less energy than conventional processes. This method is seen as a selective, direct, rapid, internal and controllable method, leading to shorter reaction durations, higher yields and easier work-up than classical thermal processing. Moreover, by reducing the reaction duration, the formation of side products is avoided and the reproducibility of the reaction is improved [13]. The high-speed synthesis of metal-free phthalocyanine and metallophthalocyanines by using microwave irradiation had been reported previously by Shaabani [14–16], Villemin et al. [17] and Davis et al. [18] by using domestic oven and microwave assisted synthesis. In another study, the synthesis of metal-free and metallophthalocyanines bearing tetraaza macrocyclic moieties under microwave irradiation were investigated [19,20]. Our group previously reported novel phthalocyanines containing diverse substituent synthesized by microwave-assisted synthesis method [21–28].

Eugenol is a phytochemical obtained from *Syzygium aromaticum*, *Ocimum Sanctum*, etc., which finds wide applications of use ranging

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from perfumeries, flavourings, and in medicines [29]. Eugenol affects the peripheral aspects of the cardiovascular system. It shows antidepressant-like activity [30], antibacterial [31,32] and antioxidant activity [33–35]. To date there has been no evidence to demonstrate a significant carcinogenic effect of eugenol in any species at literature [29]. Literature survey shows that phthalocyanines containing eugenol compounds were synthesized and investigated biological properties by our group members [36–39]. These compounds were tetra and octa peripherally eugenol substituted phthalocyanines. Also, single crystals of starting phthalonitrile compounds were published previously [40,41].

It is known that substitution at the non-peripherally (α) positions of phthalocyanines causes red shifting of the Q-band [42,43] and also reduces aggregation tendencies to a greater extent than substitution at the peripherally (β) positions.

The aim of our ongoing research is to synthesize and compare spectroscopic properties of non-peripherally substituted metallophthalocyanines containing eugenol with previously reported phthalocyanines containing eugenol at literature.

Experimental

3-Nitro-1,2-dicyanobenzene was prepared by reported procedures [44]. Eugenol was purchased from Merck Chemical Company. FT-IR spectra were recorded Perkin-Elmer Spectrum 100 Infrared Spectrometer. UV/vis spectra were recorded by Perkin-Elmer UV/vis spectrometer. ^1H NMR and ^{13}C NMR studies were performed by Varian 400 FT-NMR. Elemental analyses were performed by the Instrumental Analyses Laboratory of the TÜBİTAK Gebze Research Center.

3-(2-methoxy 4-allyl-phenoxy)1,2-dicyanobenzene (**1**)

Eugenol (0.625 g, 3.81 mmol) and 3-nitrophthalonitrile (0.640 g, 3.69 mmol) was dissolved in dry dimethylsulphoxide (3 ml). After stirring for 15 min, newly ground anhydrous K_2CO_3 (0.76 g, 5.50 mmol) was added to this solution. The reaction flask was heated under microwave irradiation at 150 °C for 10 min, with stirring and air-jet cooling. After reaction completed, the mixture was filtered and poured in ice. The formed solid material was filtered off and the crude product was purified by recrystallization from dry ethanol. Yield: 240 mg (85%); m.p. 101 °C. Single crystals were obtained by slow evaporation from ethanol. Yield: 770 mg (% 90); m.p. 89–90 °C. FTIR $_{\text{vmax}}$ /cm $^{-1}$: 3070 (Ar–CH), 2966, 2939, 2917, 2227 (CN), 1636, 1599, 1583, 1570, 1506, 1465, 1417, 1279, 1257, 1155, 1034, 794. ^1H NMR (DMSO- d_6) δ , ppm: 7.746–7.729 (2H, m, ArCH), 7.204–7.184 (1H, d, ArCH), 7.069–7.065 (1H, d, ArCH), 7.069–6.965 (1H, m, ArCH), 6.872–6.847 (1H, d.d, ArCH), 6.026–5.958 (1H, m, =CH), 5.145–5.059 (2H, m, =CH $_2$), 3.71 (3H, s, OCH $_3$), 3.412–3.395 (2H, d, –CH). ^{13}C NMR (DMSO- d_6) δ , ppm: 160.993, 151.105, 140.157, 139.696, 137.684, 136.335, 127.810, 122.656, 121.596, 120.217, 116.682, 116.104, 115.967, 114.255 (CN), 113.843 (CN), 103.452, 56,260 (OCH $_3$), 39.706. Anal. Calcd. For $\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_2$: C, 74.46; H, 4.86; N, 9.64 Found: C, 74.50; H, 4.58; N, 9.50.

Microwave-assisted synthesis of metallophthalocyanines (1a–d)

The general procedure was employed for the synthesis of various metallophthalocyanines (M: Co, Ni, Cu, Zn) were described as follows.

Compound (**1**) (100 mg, 0.344 mmol), metal salt for corresponding metallophthalocyanine (CoCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2$, 0.06 mmol), DMF (3 mL) and 2–3 drops DBU (1,8-diazabicyclo [5.4.0] undec-7-ene) were charged together into a

round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 200 °C for 20 min. After cooling to room temperature, formed solid product was filtered off and washed with ethanol. The obtained green product was purified by column chromatography (silica gel, MeOH– CHCl_3 , 1:10). All synthesized phthalocyanines are soluble in CHCl_3 and DMSO.

Yield, melting point, elemental analysis, FT-IR and UV/vis spectra of the products were as follows.

Cobalt phthalocyanine (**1a**); Yield 80 mg (76%) m.p. >200 °C. FT-IR $_{\text{vmax}}$ /cm $^{-1}$ 2918, 2850, 1636, 1586, 1505, 1463, 1331, 1239, 1119, 745. Anal. Calcd. For $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Co}$: C, 70.87; H, 4.62; N, 9.18. Found: C, 69.95; H, 4.78; N, 9.40. UV/vis (CHCl_3): λ_{max} /nm 264, 301, 623, 691.

Nickel phthalocyanine (**1b**); Yield 82.8 mg (78%) m.p. >200 °C. FT-IR $_{\text{vmax}}$ /cm $^{-1}$ 2920, 2851, 1636, 1586, 1505, 1455, 1333, 1239, 1120, 793. Anal. Calcd. For $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Ni}$: C, 70.88; H, 4.62; N, 9.18. Found: C, 69.90; H, 4.75; N, 9.35. UV/vis (CHCl_3): λ_{max} /nm 257, 298, 624, 693.

Copper phthalocyanine (**1c**); Yield 80 mg (76%) m.p. >200 °C. FT-IR $_{\text{vmax}}$ /cm $^{-1}$ 2918, 2851, 1641, 1585, 1505, 1456, 1335, 1239, 1100, 743. Anal. Calcd. For $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Cu}$: C, 70.60; H, 4.60; N, 9.14. Found: C, 69.92; H, 4.71; N, 9.39. UV/vis (CHCl_3): λ_{max} /nm 262, 307, 630, 701.

Zinc phthalocyanine (**1d**); Yield 85 mg (80%) m.p. >200 °C. FT-IR $_{\text{vmax}}$ /cm $^{-1}$ 2918, 2850, 1643, 1606, 1583, 1505, 1430, 1332, 1234, 1100, 960, 743. Anal. Calcd. For $\text{C}_{72}\text{H}_{56}\text{N}_8\text{O}_8\text{Zn}$: C, 70.49; H, 4.60; N, 9.13. Found: C, 69.92; H, 4.71; N, 9.39. UV/vis (CHCl_3): λ_{max} /nm 261, 312, 644, 702, 746.

X-ray diffraction analysis

Suitable crystal of compound (**1**) was selected for data collection which was performed on a Stoe IPDS diffractometer equipped with a graphite-monochromatic Mo $\text{K}\alpha$ radiation at 296 K. The structure was solved by direct methods using SHELXS-97 [45] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [45] from within the WINGX [46] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.97 Å. Molecular diagrams were created using MERCURY [47]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [48]. Details of data collection and crystal structure determinations are given in Table 1.

Table 1
Crystal data and structure refinement parameters for compound (**1**).

Crystal data	1
Empirical formula	$\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$
Formula weight	290.31
Crystal system	Triclinic
Space group	P–1
a (Å)	8.0984 (12)
b (Å)	8.489 (2)
c (Å)	12.237 (2)
α (°)	73.304 (16)
β (°)	76.311 (13)
γ (°)	73.714 (16)
V (Å 3)	762.2 (2)
Z	2
D_c (g cm $^{-3}$)	1.265
μ (mm $^{-1}$)	0.08
θ range (°)	3.2–26.8
Measured reffs.	6620
Independent reffs.	2934
R_{int}	0.068
S	1.03
$R1/wR2$	0.052/0.129
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (eÅ $^{-3}$)	0.37/–0.25

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