

Synthesis, spectroscopy, and photophysical properties of newly magnesium (II) phthalocyanine

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ABSTRACT

2(3),9(10),16(17),23(24)-tetrakis-2,6-dimethoxyphenoxy substituted magnesium (II) phthalocyanine, which has very good solubility in polar and non-polar solvents and does not aggregate, was synthesized. Its structure was characterized by spectroscopic methods such as elemental analysis, UV-*vis*, FT-IR, MALDI-TOF mass and ¹H NMR. It has very good solubility in polar aprotic solvents such as dimethyl sulfoxide, *N,N*-Dimethylformamide, tetrahydrofuran, dichloromethane, and non-polar solvents such as toluene, chloroform. Its aggregation properties have been studied both in the solvents mentioned above and in *N,N*-Dimethylformamide at different concentrations. Its photophysical properties were determined in *N,N*-dimethyl formamide. The effects of the nature and presence of 2,6-dimethoxyphenoxy group, which is an antioxidant derivative, on the phthalocyanine skeleton on the spectroscopic and photophysical properties were investigated by comparing it with unsubstituted magnesium (II) phthalocyanine. It can be a good nominee for various technological applications in that it does not aggregate and has good solubility in polar and non-polar solvents, as well as better and favorable fluorescence properties than its analog in the previous study.

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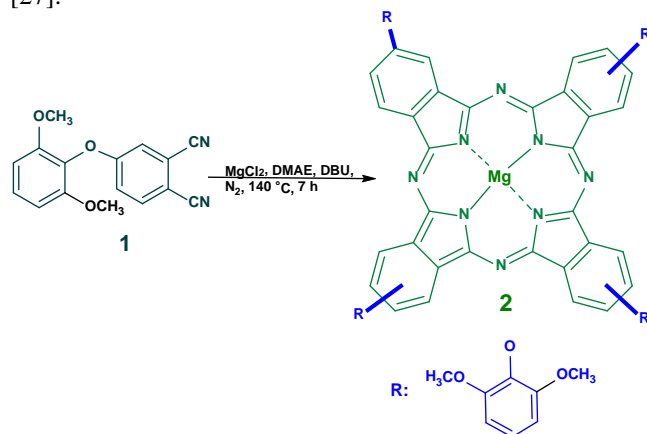
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1. Introduction

Phthalocyanines (Pcs) are synthetic substances related to naturally occurring porphyrins [1]. Pcs have been used in numerous technological applications. Pcs are an interesting class of compounds with increasingly diverse industrial and biomedical applications, photosensitization [1], non-linear optics [2], catalysis [3], photodynamic therapy [4], photocatalysis [5], liquid crystals [6], and gas sensing [7], etc. The wide range of Pc applications are primarily because of their high molar absorption coefficient ($\epsilon > 10^5$) in the far end of the visible spectrum, high triplet state quantum yields, long lifetimes, exceptionally high thermal, chemical and electromagnetic stability [8]. Optical properties of Pcs depend on their solubility and aggregation behavior [9]. Pcs can coordinate with most metals and can be substituted at the periphery with a variety of substituents [10]. In the center of planar π -electron conjugated Pc ring, various metal ions can be coordinated, e.g., Mg²⁺, Zn²⁺, Fe³⁺ [11]. In this way, specific physicochemical and biological properties of Pcs can be modified. [12]. The photophysical properties of Pc are strongly influenced by the presence and nature of the

coordinated central metal ion [12]. Magnesium phthalocyanine (MgPc) and its derivatives, being synthetic analogs of chlorophyll [1]. These are of great interest because of their chemical, catalytic and spectroscopic properties [13, 14], which appear to be significantly different from other divalent metallophthalocyanines [15]. The electrochemical properties of MgPc derivatives make them good candidates for solar energy conversion in laser printers and optical discs [16-18], as well as pigment materials [19-22]. Pcs are mostly hydrophobic compounds and are insoluble in solvent media [22]. To increase the solubility of Pcs, some functional groups such as crown ether, alkyl, alkoxy, alkylthio and donor atoms such as N and O need to be substituted on the peripheral positions of phthalocyanines [23-25]. MgPcs exhibit an intense absorption band in the near-IR spectral region due to the non-planar nature that arises from the magnesium atom being displaced from the Pc plane. This is because the magnesium ion of a molecule interacts with the N-azomethine atom of the neighboring MgPc molecule [26]. This effect will be observed further for MgPcs due to differences in flatness as noted above [26]. The spectra and photophysical behavior

of MgPcs will therefore depend on their flatness. [26]. In this study, combining 2,3-dimethoxyphenoxy group and phthalocyanine, which are bioactive compounds, in one molecule, and in this complex, the non-aggregated and bifunctional new MgPc, which has high solubility in various solvents, was designed, synthesized and its structure was characterized by widely known spectroscopic techniques (Scheme 1). In addition, the photophysical properties of this complex were studied in *N,N*-dimethyl formamide (DMF) and its spectroscopic and photophysical properties were compared with unsubstituted magnesium (II) phthalocyanine [27].



Scheme 1. Synthesis of peripheral-tetrakis-2,6-dimethoxyphenoxy substituted magnesium (II) phthalocyanine 2

2. Experimental section

The used materials, equipment, photophysical formulas and parameters were supplied as supplementary information.

2.1. Synthesis of 2(3),9(10),16(17),23(24)-tetrakis-(2,6-dimethoxyphenoxy) phthalocyaninato magnesium (II) (MgPc) (2)

4-(2,6-dimethoxyphenoxy) phthalonitrile **1** [28] (0.12 g, 0.43 mmol), anhydrous magnesium(II) chloride (0.04 g, 0.43 mmol) and catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1.50 cm³ of 2-Dimethylaminoethanol (DMAE) was heated with stirring at 140 °C in a sealed glass tube for 7 hours under nitrogen atmosphere. The resulting suspensions were cooled to room temperature and then poured into 25 ml of ethanol. The precipitates were filtered off and washed with water, hot ethanol, methanol and acetone. The products were purified using column chromatography on silica gel using dichloromethane (DCM): ethanol (MeOH) (85:15) solvent system as eluent. The phthalocyanine complexes were then dried in vacuo over P₂O₅. The MgPc **2** is soluble in dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), toluene, chloroform (CHCl₃), and dichloromethane (DCM). Mp > 300 °C. Yield: 37.17 mg (28.54%). Calculated for C₆₄H₄₈MgN₈O₁₂

Elemental Analysis: C, 67.11; H, 4.22; N, 9.78; found C, 65.87%; H, 3.79%; N, 9.33%. IR (ATR) $\lambda_{\text{max}}/\text{cm}^{-1}$: 750-1010(C-H str.), 1090-1188(C-N str.), 1230-1330(C-O str.), 1450-1480 (C-H bend.), 1582-1596(C=C str.), 2850-2970 (>CH₂ str.), 3065(=C-H str.). UV-vis (DMF, 1x10⁻⁵ M): $\lambda_{\text{max}}(\text{nm})$, (log ϵ): 362 (4.02), 675 (5.02). MS (MALDI-TOF) m/z: calc.: 1145.42; found: 1146.75 [M+H]⁺. ¹H NMR [500 MHz, CDCl₃, δ (ppm)]: 7.70-7.55(m, Ar-H, 8H), 7.32-7.24(m, Ar-H, 4H), 7.02-6.92(m, Ar-H, 4H), 6.78-6.70(m, Ar-H, 8H), 3.81 (m, O-CH₃, 24H).

3. Results and discussion

3.1. Synthesis and characterization

Precursor molecule **1** for this reaction were synthesized as given in literature [28-32]. The MgPc **2** was synthesized by cyclotetramerization reaction of the 4-(2,6-dimethoxyphenoxy)phthalonitrile **1** presence of DMAE as the solvent, DBU as the catalyzer and anhydrous magnesium(II) chloride under the nitrogen atmosphere (Scheme 1). The MgPc **2** was obtained as bluish green solids, 28.54% in yield. The MgPc **2** was washed several times with hot ethanol, methanol and acetone and then were purified by column chromatography with silica gel using DCM: EtOH (85:15) as an eluent. The MgPc **2** was characterized by FT-IR, ¹H NMR, UV-vis, MALDI-TOF mass spectroscopic techniques, and elemental analysis as well. The analyses are consistent with the predicted structure as shown in the experimental section. Main findings are found suitable for proposed structure of this phthalocyanine. The proposed target structure of the MgPc **2** was affirmed in the FT-IR spectra by the disappearance of the -C≡N vibration at 2231 cm⁻¹ for the phthalonitrile **1** [28-32]. In the FT-IR spectrum of the MgPc **2**, stretching vibrations of aromatic CH groups around 3065 cm⁻¹, aliphatic-CH, CH₂ groups around 2970-2850 cm⁻¹, aromatic -C=C groups around 1596 -1582 cm⁻¹ and -C-H bands around 1480-1450 cm⁻¹ appeared at expected frequencies (Fig.1).

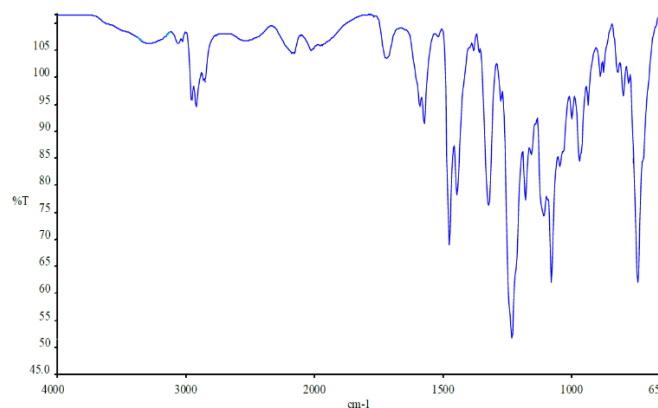


Figure 1. FT-IR spectrum of the MgPc 2.

The ^1H NMR spectrum of the MgPc 2 was recorded in chloroform-d (CDCl_3). ^1H -NMR spectrum of the MgPc 2 showed aromatic protons broad peak at 7.70-6.70 ppm. It is probable that the broadening is due to the chemical exchange caused by aggregation–disaggregation equilibrium [33]. In the ^1H -NMR spectrum of the MgPc 2, the multiple peaks for aromatic protons were observed in the range of 7.70-7.55, 7.32-7.24, 7.03-6.92, and 6.78-6.70 ppm integrating as 8, 4, 4 and 8 protons. The singlet peak for aliphatic protons was observed at 3.91 ppm integrating as 24 protons.

The positive ion MALDI-TOF mass spectrometry is an analysis method used in the characterization of Pcs. In this analysis, mostly the molecule ion type is the porphyrin radical cation (M^+). The MgPc 2 identified easily with 2,5-dihydroxybenzoic acid (DHB) as a MALDI matrix in the reflectron mode using a MALDI-TOF mass spectrometry. The molecular ion peak $[\text{M}+\text{H}]^+$ of the MgPc 2 was observed at m/z : 1146.75 Da (Fig. 2). In addition, elemental analysis result and mass spectrum of the MgPc 2 were good agreement with proposed structure. The elemental compositions (C, H and N) of the MgPc 2 are consistent with the proposed structures.

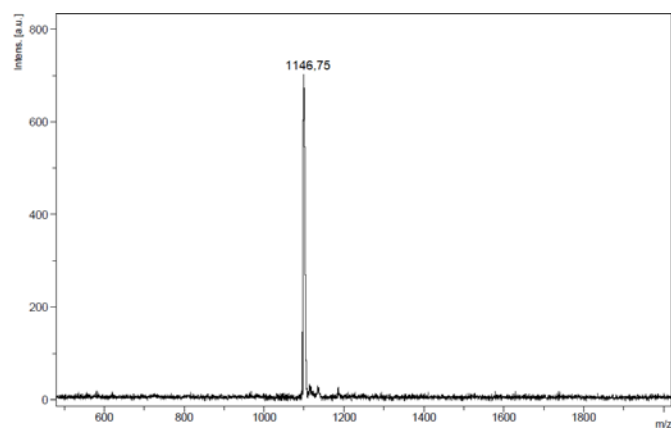


Figure 2. Positive ion MALDI-TOF mass spectrum (reflectron mode) of the MgPc 2, obtained in 2,5-dihydroxybenzoic acid.

The electronic spectrum of the MPcs showed a monomeric behavior evidenced by a single (narrow) Q band for the MgPc 2 up to $\sim 1.00 \times 10^{-5} \text{ mol} \times \text{dm}^{-3}$ in DMF [34]. The electronic absorption spectra of the MgPc 2 showed characteristic a single Q band due to the π - π^* transitions at 682 nm, with shoulders λ_{max} : 634 and 611 nm (Fig. 3). The Soret band (B band) of the MgPc 2 was observed at 362 nm (Fig. 2). In DMF, the substituted MgPc 2 showed 7 nm more red-shifted Q band compared to unsubstituted MgPc [27]. This is due to the presence of 2,6-dimethoxy phenoxy units on the phthalocyanine skeleton.

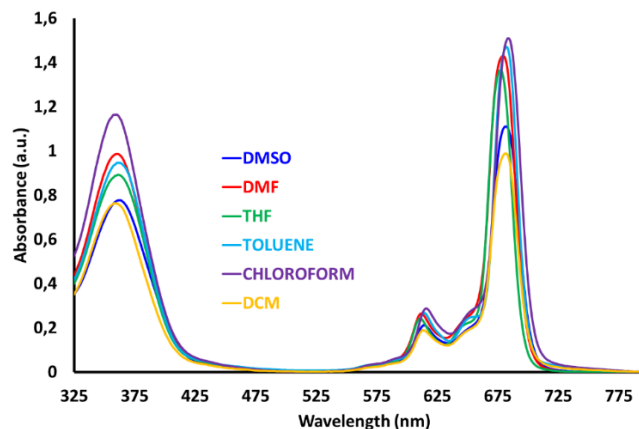


Figure 3. Electronic absorption spectra of the MgPc 2 in different solvents. Concentration = $\sim 1 \times 10^{-5} \text{ mol} \times \text{dm}^{-3}$.

3.2. Aggregation studies

Aggregation can be defined as overlapping of monomers, dimers, and rings in solvent medium [35]. On phthalocyanines aggregation is determined by the concentration of the solution, the nature of the solvent, the temperature, the nature, and position of the substituents on the phthalocyanine skeleton, as well as the metal ion in the phthalocyanine center [35]. In the aggregated state the electronic structure of the complexed phthalocyanine rings is perturbed resulting in alternation of the ground and excited state electronic structures [36]. Dilution studies at different concentrations were researched at ambient temperature in DMF to better determine the aggregation properties of the MgPc 2. To demonstrate compliance with the Lambert-Beer law, a linear regression analysis was performed between the density of the Q-bands and the concentrations of the MgPc 2. The MgPc 2 did not aggregate in DMF at studied concentrations. Increasing the concentration for UV-vis studies of the MgPc 2 with concentrations ranging from 1.20×10^{-5} to $2.00 \times 10^{-6} \text{ M}$ in DMF, did not yield new bands on the higher energy side, which would mean the absence of aggregated species, and the absorption intensity obeys Lambert-Beer's law (Fig. 4).

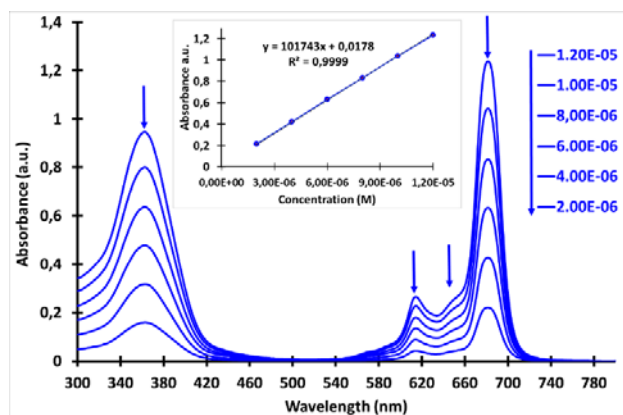


Figure 4. Aggregation behavior of the MgPc 2 in DMF at different concentrations. (Inset: plot of absorbance vs. concentration).

4. Photophysical properties

4.1. Fluorescence spectra

Fig. 5 shows fluorescence emission, absorption and excitation spectra of the MgPc 2 in DMF. Fluorescence spectra of the MgPc 2 were observed at 690 nm for emission and at 674 nm for excitation in DMF. The Stokes shift value of the MgPc 2 was found as 16 nm. The observed Stokes shift of the substituted MgPc 2 was higher than unsubstituted magnesium phthalocyanine in DMF [27]. The MgPc 2 showed similar fluorescence behavior in DMF (Fig. 5). The proximity of the wavelength of the MgPc 2 of the Q-band absorption to the Q band maxima of the excitation spectrum for the MgPc 2 suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation [34, 37].

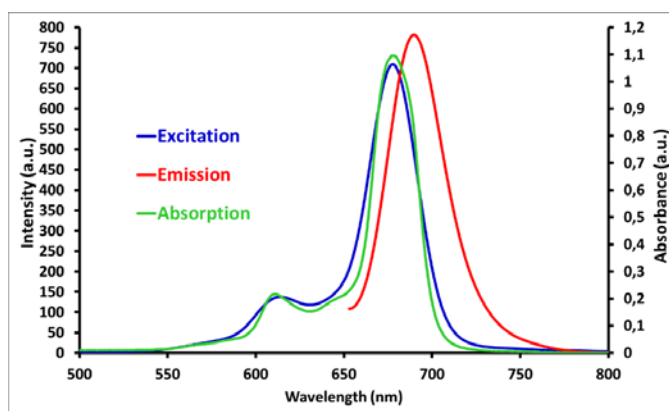


Figure 5. Absorption, excitation, and emission spectra of the MgPc 2 in DMF. Excitation wavelength= 640 nm

4.2. Fluorescence quantum yield and lifetime

The fluorescence quantum yield (Φ_F) is the ratio of the number of molecules that luminesce to the total number of the excited molecule. The Φ_F value of the MgPc 2 in DMF was found to be 0.27. The Φ_F value of the MgPc 2 was lower than unsubstituted magnesium (II) phthalocyanine in DMF [27], which implies that the presence of the 2,6-dimethoxyphenoxy units reduced the fluorescence quenching of the Pc molecule. The Φ_F value of the MgPc 2 is similar and typical of the other studied magnesium (II) Pc in DMF [37-47]. Fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before fluorescing, and its value is directly related to that of Φ_F , i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Any factor that shortens the fluorescence lifetime of a fluorophore indirectly reduces the value of Φ_F . Such factors include internal conversion and intersystem crossing. As a result, the nature and the environment of a fluorophore determine its fluorescence lifetime. τ_F value of the MgPc 2 was calculated using the Strickler-Berg equation. In DMF, the τ_F value of the substituted MgPc 2 is 4.65 ns and longer compared to

unsubstituted magnesium (II) phthalocyanine [27], suggesting less quenching by substitution. The τ_F value of the MgPc 2 is typical for the metallo-phthalocyanines [37-47]. The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) value of the MgPc 2 are $5.81 \times 10^{-7} \text{ s}^{-1}$ and 17.22 ns, respectively. The k_F value of the MgPc 2 is higher than unsubstituted magnesium (II) phthalocyanine in DMF [27]. The τ_0 of substituted the MgPc 2 is shorter when compared to magnesium (II) phthalocyanine in DMF [27]. It was determined to have richer fluorescent properties than its counterpart in the previous studies [27-30].

5. Conclusions

The synthesis and characterization of peripheral-tetrakis-2,6-dimethoxyphenoxy substituted magnesium (II) phthalocyanine 2 were presented in this study. The elemental analyses, FT-IR, ^1H NMR, UV-vis, fluorescence spectroscopy and MALDI-TOF-MS spectra confirmed the proposed structures of this phthalocyanine. It showed good solubility and non-aggregated species in dimethylsulfoxide, *N,N*-dimethylformamide, tetrahydrofuran, toluene, chloroform, and dichloromethane, which make it a candidate to use for many applications in different fields of science and technology. It is reported to have predominantly monomeric species in the solvents studied and show similar fluorescent behavior. It was reported that the presence of magnesium (II) metal ion as an alkaline earth metal in the phthalocyanine cavity, as well as enhancing its photophysical properties by substituting 2,6-dimethoxyphenoxy groups from peripheral positions to the phthalocyanine ring. It can also be a promising candidate for various technological applications, as it has rich photophysical properties.

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