New Soluble Bis (4-fluorophenyl)-methoxy Substituted Phthalocyanines: Synthesis, Characterization, Spectral, Aggregation and Fluorescence Studies

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Abstract: The synthesis, characterization, spectral and fluorescence properties of bis (4-fluorophenyl)-methoxy substituted phthalocyanines were reported for the first time. The new compounds have been characterized by elemental analysis, UV-Vis, FT-IR, \(^1\)H-NMR and mass spectra. All of these new metal free and metallo phthalocyanines exhibited excellent solubility in organic solvents such as chloroform, dichloromethane, THF, DMF and DMSO. The aggregation behaviour of these compounds was investigated in different solvent and concentrations of in CHCl\(_3\). Phthalocyanine complexes did not show any aggregations. General trends are described for fluorescence properties of the compounds, such as CHCl\(_3\) CH\(_2\)Cl\(_2\) THF, DMF, DMSO five different solvent. The effect of the nature of the central metal on the photo physical parameters of the phthalocyanine complexes are also reported in this study.

Key words: Phthalocyanines, spectroscopy, fluorescence, fluorescence quantum yield, aggregation.

1. Introduction

Phthalocyanines the most common and important tetrapyrrrole derivatives have been at the focus of multidisciplinary interests for more than one century [1-6].

Phthalocyanines are macrocyclic compounds containing four N-fused isoindole units that possess interesting physical and chemical properties. Since these compounds have a large \(\pi\)-conjugated system, they absorb strongly in the red visible region, giving a characteristic blue-green color. This property together with their extraordinary stability renders them to be used as industrial pigments for several decades [7]. In addition to this traditional application, these compounds have been extensively studied as advanced materials in various disciplines as a result of their intriguing and tunable characteristics [8, 9]. Some recent focuses have been put on their applications as optical recording materials [10], semiconductors for organic field effect transistors [11-13], nonlinear optics, gas sensors, thermal writing displays, and solar cells [14-16], catalysts for oxidative degradation of pollutants [17, 18], and sensitizers for photovoltaics [19-21] and photodynamic therapy [22, 23]. These macrocyclic compounds are therefore versatile functional dyes receiving much current attention. Specificity in the applications of phthalocyanines can be introduced by modification of the phthalocyanine ring or by changes in the central metal or axial ligands.

A major disadvantage of Pcs is their low solubility in common organic solvents or in water. Their insolubility causes difficulties for many applications rendering the synthesis of soluble derivatives. The solubility of phthalocyanines in apolar solvents can be improved by introducing different kinds of bulky substituents, such as crown ethers, alkyl, alkoxy and alkylthio;
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electron-withdrawing substituents (-F, -Cl, -Br, -NO₂, etc.) and electron donating atoms such as N and O at the periphery of the phthalocyanines [24-28].

Sandwich-type porphyrinato and/or phthalocyanina to complexes, in which two or three tetrapyrrole ligands are held by rare earth, actinide, and early transition metal or main group metals in close proximity, have been intensively studied over several decades in both fundamental academic and applied fields [29]. They are chemically robust and therefore have been used as dyes, pigments, catalysts for the removal of sulfur in oil, and more recently expanding in many fields such as xerography, photovoltaics, electrophotography, thermochromism, optical discs, laser dyes, liquid crystals, molecular metals, electro-catalysis, chemical sensors, magnetic materials, photochemical hole burning, and photodynamic cancer therapy [30]. These diversified possibilities of phthalocyanines generally stem from their large and flat p-conjugation systems of phthalocyanines and the type of central metal.

Aggregation of dye molecules plays an important role in energy and electron transfer, and in light harvesting systems. The propensity of phthalocyanines to form aggregates because of the strong interactions between planar macrocycles in solution is well-known [15].

The substituted metallophthalocyanines could be form two types of aggregations which affect on electronic and optical properties, namely face-to-face H-aggregation and side-to-side J-aggregation [31, 32]. Typically, phthalocyanine aggregation results in a decrease in intensity of the Q band corresponding to the monomeric species, meanwhile a new, broader and blue shifted band is seen to increase in intensity. This shift to lower wavelengths indicates to H-type aggregation among the phthalocyanine molecules. Rare cases red-shifted bands have been observed corresponding to J-type aggregation of the phthalocyanine molecules. Generally, J-aggregates of Pc occurred by utilizing the coordination of the side substituent from one Pc molecule to the central metal ion in a neighbor [33-37]. The substituted zinc Pcs in non-coordinated organic solvents, e.g. chloroform and dichloromethane exhibit J-aggregation [38-40].

In this work, electron-withdrawing (-F), and electron donor atom (O) the synthesis at the periphery of the phthalocyanines and photophysical properties of bis (4-fluorophenyl)-methoxy substituted phthalocyanines are reported for the first time. These complexes show good solubility of phthalocyanines on their photophysical and spectral properties are investigated in CHCl₃, CH₂Cl₂, DMF, THF and DMSO. The effect of metal and solvent on the photophysical and spectral properties of the new complexes were discussed.

2. Experimental

2.1 Materials

All chemicals were reagent grade from Merck and Fluka. Solvents in reactions were distilled from appropriate drying agents prior to use and commercially available reagents were used without further purification unless otherwise stated. Flash column chromatography was carried out using silica gel 60 (0.04-0.063 mm) from Merck.

2.2 Equipment

FT-IR spectra were recorded on a spectrum one Perkin Elmer FT-IR spectrophotometer using ATR. ¹H NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer. Absorption spectra were recorded with an Agilent 8453 UV-visible spectrophotometer. The elemental analyses and Bruker Microflex LT MALDI-TOF mass spectra were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). GC-Mass Spectra were performed on a Agilent 6890N GC-System-5973 IMSD. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectro fluorometer using 1 cm path length cuvettes at room temperature. All chemicals used were of an analytical grade. Solvents were purified with conventional methods.
2.3 Photophysical Parameters

2.3.1 Fluorescence Quantum Yields

Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method using Eq. 1 [41, 42],

$$\Phi_F = \Phi_{F\text{(Std)}} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n^2_{\text{Std}}}$$  

where $F$ and $F_{\text{Std}}$ are the areas under the fluorescence emission curves of the samples (2, 3, 4 and 5) (Table 1) and the standard, respectively. $A$ and $A_{\text{Std}}$ are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. $n^2$ and $n^2_{\text{Std}}$ are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [43, 44] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

2.4 Synthesis

2.4.1 Synthesis of Bis (4-fluorophenyl)-methoxy Phthalonitrile (1)

Mixture of bis (4-fluorophenyl)-methanol (1.00 g, 4.54 mmol) and 4-nitrophthalonitrile (0.79 g, 4.54 mmol) in DMF (25 mL) was stirred under argon atmosphere at room temperature. Anhydrous K$_2$CO$_3$ (1.88 g, 13.60 mmol) was added three equal portions and the reaction mixture was stirred at room temperature for 24 h. Then reaction mixture was dropped into ice, and the precipitate was filtered off, washed with water and methanol and then dried. The crude product was recrystallized from ethanol. Finally the pure product was dried in vacuum. Yield: 1.39 g (88%). FT-IR $\nu_{\max}$/cm$^{-1}$ (KBr pellet): 3078 (Ar-CH), 2230 (C=CH), 1098, 1087 (Ar-F), 1253 (C-O-C-ether); $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 7.60 (d, 1 H, CN-CH), 7.32-7.22 (m, 4 H, Ar-CH), 7.19 (s, 1 H, CN-CH-C), 7.15 (d, 1 H, O-CH-C), 1.14 (s, 2 H, -NH); UV-vis (CHCl$_3$) $\lambda_{\max}$/nm (log $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 341 (4.81), 670 (4.96) and 706 (5.604): MS (MALDI-TOF) m/z: C$_{21}$H$_{12}$F$_2$N$_2$O: C 73.26, H 3.82; N 8.39%.

2.4.2 Synthesis of Metal-free Phthalocyanine (2)

Compound 1 (0.10 g, 0.29 mmol) and 2 mL of dry pentanol were placed in a standard Schlenk tube in the presence of DBU (17 $\mu$L) under an argon atmosphere and this mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into n-hexane. After collecting by filtration, the green product was dissolved in THF and was precipitated by adding it drop-wise into n-hexane. Finally, pure of metallophthalocyanine was chromatographed over a silica gel column using a mixture of CHCl$_3$; n-hexane (50/1 by volume) as eluent.

Yield: 0.213 g (53%). FT-IR (KBr), $\nu$/cm$^{-1}$: 3280 (NH), 2960, 2894 (C-H), 1603 (C=C), 1506, 1472, 1344, 1220 and 1156 (C-O-C-ether), 1094 (Ar-F); $^1$H NMR(CDC$_3$): $\delta$ (ppm) 7.65-7.25 (m, 12 H, Pc-CH), 7.20-7.10 (m, 32 H, Ar-CH), 6.60 (d, 4 H, O-CH), -1.14 (s, 2 H, -NH); UV-vis (CHCl$_3$) $\lambda_{\max}$/nm (log $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 341 (4.81), 670 (4.96) and 706 (5.604): MS (MALDI-TOF) m/z: C$_{84}$H$_{50}$F$_8$N$_8$O$_4$: C 72.72, H 3.63, N 8.08%; Found: C 72.27, H 3.85, N 7.75; Calc. 1387.33; Found: 1387.41 [M].

2.4.3 General Procedures of Metallophthalocyanine Derivatives (3-4)

A mixture of bis (4-fluorophenyl)-methoxy phthalonitrile 1 (0.10 g, 0.29 mmol), anhydrous metal salts [MgCl$_2$ (0.059 g, 0.29 mmol), ZnCl$_2$ (0.063 g, 0.29 mmol)] and catalytic amount of DBU (17 $\mu$L) in 2.5 mL of dry n-pentanol was heated and stirred at 160 ºC in a standard Schlenk tube for 6 h under N$_2$. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into n-hexane. After collecting by filtration, the green product was dissolved in THF and was precipitated by adding it drop-wise into n-hexane. Finally, pure of metallophthalocyanine was chromatographed over a silica gel column using a mixture of CHCl$_3$; n-hexane (50/1 by volume) as eluent.

2.4.4 Synthesis of Magnesium(II) Phthalocyanine (3)

Yield: 0.184 g (45%). FT-IR (KBr), $\nu$/cm$^{-1}$: 2958, 2892 (C-H), 1606 (C=C), 1505, 1470, 1221 and 1157 (C-O-C-ether), 1096 (Ar-F); $^1$H NMR(CDC$_3$) : $\delta$ (ppm)
7.35-7.25 (t, 12 H, Pc-CH), 7.15-7.05 (m, 32 H, Ar-CH), 6.30 (s, 4 H, O-CH): UV-vis (CHCl₃) λ_max/nm (log ε/dm³mol⁻¹cm⁻¹): 354 (4.73), 686 (5.05): C₈₄H₄₈F₈MgN₈O₄: C 71.57, H 3.43, N 7.95 %; Found: C 72.04, H 3.11, N 7.65: MS (MALDI-TOF) m/z: Calc. 1409.62; Found: 1409.81 [M].

2.4.5 Synthesis of Zinc(II) Phthalocyanine (4)

Yield: 0.243 g (58%), FT-IR (KBr), ν/cm⁻¹: 2961, 2895 (C-H), 1607 (C=C), 1507, 1472, 1224, 1156 (C-O-Ceth), 1097 (Ar-F): ¹H NMR(CDCl₃): δ (ppm) 7.35-7.25 (t, 12 H, Pc-CH), 7.15-7.05 (m, 32 H, Ar-CH), 6.30 (s, 4 H, O-CH): UV-vis (CHCl₃) λ_max/nm (log ε/dm³mol⁻¹cm⁻¹): 351 (4.89), 685 (5.13): C₈₄H₄₈F₈N₈O₄Zn: C 69.54, H 3.33, N 7.72 %; Found: C 69.27, H 3.71, N 7.45: MS (MALDI-TOF) m/z: Calc. 1459.73; Found: 1456.21 [M⁺].

2.4.5 Synthesis of Lutetium (II) Phthalocyanine (5)

A mixture of bis (4-fluorophenyl)-methoxy phthalonitrile 1 (0.10 g, 0.29 mmol), Lu (II) acetate (0.011 g, 0.032 mmol) and catalytic amount of DBU (17 µL) in 2.5 mL of dry n-pentanol was heated and stirred at 180 °C in a standard Schlenk tube for 16 h under N₂. After cooling to room temperature, the reaction mixture was treated with MeOH and the product filtered off and washed with acetone. The crude product was chromatographed over a silica gel column using a mixture of CHCl₃: n-hexane (50/1 by volume) as eluent.

Yield: 0.292 g (34%), FT-IR (KBr), ν/cm⁻¹: 2960, 2894 (C-H), 1604 (C=C), 1507, 1472, 1224 and 1157 (C-O-Ceth), 1094 (Ar-F): ¹H NMR(CDCl₃): δ (ppm) 7.66-7.20 (m, 24 H, Pc-CH), 7.06-6.90 (m, 64 H, Ar-CH), 6.24 (s, 8 H, O-CH): UV-vis (CHCl₃) λ_max/nm (log ε/dm³mol⁻¹cm⁻¹): 349 (4.69), 685 (4.86): C₁₆₈H₉₆F₁₆LuN₁₆O₈: C 68.50, H 3.28, N 7.61%; Found: C 68.27, H 3.62, N 7.95.

3. Results and Discussion

3.1 Synthesis and Characterization

Scheme 1 gives the synthetic route to novel phthalocyanines 2-5 discussed in this work. Peripherally tetra-substituted metal free 2, magnesium 3, zinc 4, and lutetium 5 phthalocyanines are prepared by template cyclotetramerization of newly synthesized bis (4-fluorophenyl)-methoxy phthalonitrile1. The syntheses of complexes 2-5 were achieved by treatment of phthalonitrile 1 with anhydrous metal salts in dry 1-pentanol at reflux under argon atmosphere in the presence of 1,8-diazabicyclo (5.4.0) undec-7-ene (DBU) as a strong base (Scheme 1).

All of these new metal free and metallo phthalocyanines were purified by column chromatography. They were obtained in a moderate yield (53% for 2, 45% for 3, 58% for 4 and 34% for 5) and were characterized by elemental analysis together with the spectral data (¹H NMR, FTIR, Mass and UV-Visible spectroscopies). The characterization data of the new compounds are consistent with the assigned formula as shown in the experimental section.

Phthalocyanines generally have poor solubility in most organic solvents; nevertheless introduction of fluoro phenoxy substituents on the ring increase the solubility.

All studied phthalocyanine complexes 2-5 exhibited excellent solubility in organic solvents such as chloroform, dichloromethane, THF, DMF and DMSO. The characteristic vibrations corresponding to C≡N were observed at 2230 cm⁻¹ for 1. Aromatic C-H and aliphatic C-H peaks occurred at 3078 cm⁻¹ and 2,961-2,834 cm⁻¹ for the phthalonitrile (1). After conversion into metal free and metallophthalocyanines 2, 3, 4 and 5 the characteristic sharp C≡N stretch at 2230 cm⁻¹ for phthalonitrile 1 disappeared. The IR spectra of metal-free 2 and metallophthalocyanines 3, 4 and 5 are very similar. The significant difference is the presence of N-H vibrations of the inner phthalocyanine core which are assigned to a weak vibration at 3280 cm⁻¹ in the metal-free compound. The synthesized phthalocyanine complexes 2-5 showed characteristic vibrations belong to ether groups (C-O-C) at ca. -1250 cm⁻¹, aromatic CH stretching at ca. 3070 cm⁻¹ and aliphatic CH stretching
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![Scheme 1 Synthetic route of tetra ((4-fluorophenyl)-methoxy) substituted metal free, magnesium, zinc, and lutetium phthalocyanine derivatives (i) (for 2) DBU, 1-pentanol, 12 h, argon atm, (ii) MgCl₂ (for 3), ZnCl₂ (for 4), (iii) Lu (II) acetate (for 5), DBU, 1-pentanol, 16 h, argon atm.]

at ca. -2960-2895 cm⁻¹. The aromatic fluorur (Ar-F) peaks for all compounds were observed at -1,095 cm⁻¹. The IR spectra of the neutral double-decker phthalocyanine 5 displayed an intense band at 1,330 cm⁻¹ for the Pc⁻ π-radical anion [45]. The ¹H NMR spectra of tetra-substituted phthalocyanine complexes 2-5 showed broad absorptions when compared with that of corresponding phthalonitrile derivative 1. It is likely that broadness is due to both chemical exchange caused by aggregation-disaggregation equilibrium in CDCl₃ and the fact that the product obtained in this reaction is a mixture of four positional isomers which are expected to show chemical shifts which slightly differ from each other for tetra substituted complexes 2-5. The bis (4-fluorophenyl)-methoxy substituted phthalocyanines were found to be pure by ¹H NMR with all the substituents and ring protons observed in their respective regions. The tetra substituted phthalocyanines 2 to 5 showed the phthalocyanine ring protons as unresolved multiplets (most likely due to the presence of isomers). The phthalocyanine ring protons for peripherally tetra substituted complexes were observed in the range 7.65 to 7.25 ppm for 2 integrating for 12 protons, 7.35 to 7.25 for 3 integrating for 12 protons, 7.35 to 7.24 for 4 integrating for 12 protons and 7.66 to 7.20 ppm for 5 integrating for 24 protons as expected. The aromatic protons for complexes (2-5) were observed at 7.20 to 7.10 for 2, 7.15 to 7.05 ppm for 3, 7.15 to 7.05 ppm for 4 integrating totally for 32 protons and 7.06 to 6.90 ppm for 5 integrating totally for 64 protons as expected. The O-CH protons for complexes 2-5 were observed at 6.60 ppm for 2, 6.30
ppm for 3, 6.30 ppm for 4 integrating totally for 4 protons and 6.24 ppm for 5 integrating totally for 8 protons for all studied phthalocyanine complexes, as expected. Although the presence of isomers as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals, the observed spectra of all studied complexes were relatively well-resolved. Metal-free derivative 2, of protons in the inner core of phthalocyanine are screened by aromatic $\pi$ electrons of the macrocycle, so they appeared at -1.10 ppm in the $^1$H NMR. In addition to these verifying results for the structures, the mass spectra of compounds 3-4 gave the characteristic molecular ion peaks at m/z: 1387.41 [M], 1409.81 [M], 1456.21 [M$^3$], respectively, confirming the proposed structures (Fig.1, using complex 2 as example).

3.2 Ground State Electronic Absorption

The ground state electronic spectra are especially useful to identify the structure of the phthalocyanines. Generally, UV-Vis spectra of phthalocyanines show typical electronic spectra with two strong absorption bands known as Q and B bands. The Q-band in the visible region at ca. 600-750 nm is attributed to the $\pi-\pi^*$ transition from HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc (-2) ring and the B band in the UV region at ca. 300-400 nm arises from the deeper $\pi-\pi^*$ transitions [46], but contains a small contribution from n-$\pi^*$ transition.

The ground state electronic absorption spectra of the peripherally tetra-substituted phthalocyanine complexes 2 to 5 showed monomeric behavior evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes in CHCl$_3$, CH$_2$Cl$_2$ THF, DMF, DMSO. In the UV-Vis spectrum of metal-free phthalocyanine 2, the characteristic split Q band was observed at 670 and 706 nm in chloroform which can be attributed a$_{1u}$ $\to$ eg transition [47]. A typical spectrum of the metal-free phthalocyanine 2 showed B band at 341 in chloroform (Fig. 2). The UV-Vis absorption spectra of metallophthalocyanines 3, 4 and 5 in chloroform were observed the intense Q absorption at 686, 685 and 686 nm. In addition, the intense B band absorptions were observed at 354 nm for 3, 351 nm for 4 and 348 nm for 5 in CHCl$_3$, respectively (Figs. 3-5).

Fig. 1  MALDI-TOF mass spectra of 2.
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Fig. 2 Absorption spectral changes of 2 in CHCl₃ at different concentrations: $4 \times 10^{-6}$ (A), $6 \times 10^{-6}$ (B), $8 \times 10^{-6}$ (C), $10 \times 10^{-6}$ (D), $12 \times 10^{-6}$ (E), $14 \times 10^{-6}$ (F) mol/L.

Fig. 3 Absorption spectral changes of 3 in CHCl₃ at different concentrations: $2 \times 10^{-6}$ (A), $4 \times 10^{-6}$ (B), $6 \times 10^{-6}$ (C), $8 \times 10^{-6}$ (D), $10 \times 10^{-6}$ (E), $12 \times 10^{-6}$ (F) mol/L.
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Fig. 4  Absorption spectral changes of 4 in CHCl₃ at different concentrations: 2 × 10⁻⁶ (A), 4 × 10⁻⁶ (B), 6 × 10⁻⁶ (C), 8 × 10⁻⁶ (D), 10 × 10⁻⁶ (E), 12 × 10⁻⁶ (F) mol/L.

Fig. 5  Absorption spectral changes of 4 in CHCl₃ at different concentrations: 4 × 10⁻⁶ (A), 6 × 10⁻⁶ (B), 8 × 10⁻⁶ (C), 10 × 10⁻⁶ (D), 12 × 10⁻⁶ (E), 14 × 10⁻⁶ (F) mol/L.
3.3 Aggregation Studies

Aggregation is mostly described as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexes metal ions and temperature. High aggregation tendency of phthalocyanine and porphyrazine compounds due to the interactions between their 18 π-electron systems often cause weak solubility or insolubility in many solvents. The spectroscopic, photophysical, photochemical and electrochemical properties of the phthalocyanines and porphyrazines were seriously affected by the aggregation [48-54].

In this study, the aggregation behavior of all phthalocyanines compounds was investigated in different solvents such as CHCl₃, CH₂Cl₂, DMF, THF and DMSO. All the synthesized metallo phthalocyanines 2-5 did not any aggregation in CHCl₃, CH₂Cl₂, DMF, THF and DMSO. The aggregation behavior of all phthalocyanines 2-5 (in CHCl₃) (Figs. 2-5) were also studied at different concentrations for determination of the aggregation depends on concentration. This paper studied phthalocyanines did not show any aggregation concentration ranges between 2 × 10⁻⁶ M and 14 × 10⁻⁶ M. For complexes, as the concentration was increased, the intensity of absorption of the Q band also increased in parallel and there were no new bands (normally blue shifted), which might be attributed to aggregated species, were observed.

3.4 Fluorescence Spectra

The fluorescence behavior of the metal free 2, magnesium 3, zinc 4 and lutetium5 phthalocyanine complexes were studies in CHCl₃, CH₂Cl₂ THF, DMF, DMSO. The complexes and the standart were excited at the same appropriate wavelength. All spectral and fluorescence data are given in Table 1.

Table 1 UV-Vis spectral and photophysical parameters for all compounds.

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<th>λₐ(Ems)/nm</th>
<th>λₐ(Exc)/nm</th>
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<td>15</td>
<td>0.0035</td>
</tr>
</tbody>
</table>
The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for 2, 3, 4 and 5. For complex 3 the emission spectrum shows little less broadening when compared to excitation spectra. Fig. 6 shows the absorption, fluorescence excitation and emission spectra for complex 3 as an example in CHCl₃.

Complex 2 and 3 showed similar emission spectra in all solvents. Complex 4 also showed a similar emission spectra in all solvents but is slightly lower emissions in the DMF solution. Complex 5 also showed slightly lower emissions in the CH₂Cl₂ solution. Fig. 7 shows the absorption, fluorescence excitation and emission spectra for complex 5 as an example in DMF.

The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for both complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation [55]. The Stokes’ shifts range from 9 to 18 nm, which is usual for ZnPc derivatives [56]. The small stokes shifts suggest that the structural change between the ground and excited states are small. The Q bands of all the excitation spectra suggests that following excitation, there were some changes in the molecule, presumably due to loss of symmetry. This loss of symmetry may be the cause of the slight broadening of the fluorescence spectra stated above [57].

Fluorescence quantum yield (ΦF) values can be affected by a number of factors that include temperature, molecular structure and solvent parameters, such as polarity, viscosity, refractive index, and the presence of heavy atoms in the solvent molecule [58].

Table 1 shows ΦF values of Pc derivatives studied in this work. Complex 4 showed similar ΦF values in all solvents. DMF, yielded the highest ΦF values of 0.2202 for complex 3 and CH₂Cl₂, yielded the lowest ΦF values of 0.0022 for complex 5. ΦF values in the five solvents demonstrate that fluorescence is influenced by the environment of the fluorescing molecule, e.g., solvent parameters.

4. Conclusion

This work has described the synthesis, spectral, aggregation and fluorescence properties of bis (4-fluorophenyl)-methoxy substituted phthalocyanines. The purpose of this study, electron-withdrawing (-F), and electron donor atom (O) the synthesis at the periphery of the phthalocyanines. The synthesis of the novel compounds were confirmed by FT-IR, UV-Vis, mass and NMR spectroscopies, as well as elemental analysis. All studied phthalocyanine compounds 2, 3, 4 and 5 have good solubility in common organic solvents such as such as CHCl₃, CH₂Cl₂, THF, DMF, DMSO without aggregation. The photophysical properties of the phthalocyanines 2, 3, 4 and 5 were investigated in
CHCl₃, CH₂Cl₂, THF, DMF, DMSO. The effect of the nature of the central metal on the photophysical parameters of the phthalocyanine complexes 2, 3, 4 and 5 are also reported in this study.

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References


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