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# Synthesis and photophysicochemical properties of novel mononuclear rhodium(III) phthalocyanines

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#### 1. Introduction

Phthalocyanines (Pcs) enjoy widespread use as conventional dyes and pigments, and 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]. Pcs have also found importance in a number of applications as photosensitizers with excellent photosensitizing properties for photodynamic cancer therapy (PDT) [13–16], due to their good singlet oxygen generation ability [17–19], owing to the intense absorption in the red region of visible light [20–22].

In the past few years, a considerable amount of research has been focused on the preparation, chemistry and structure of rhodium phthalocyanine complexes [23]. They have been prepared as Langmuir–Blodgett films [24,25], encapsulated in X and Y type zeolites [26] or bounded to polymer backbones [27]. Therefore, they are of great interest to scientists due to their catalytic [28], electrochemical [29] and photochemical properties [30,31]. A series of pure and axially substituted rhodium(III) phthalocyanine

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#### ABSTRACT

Chloro axially-substituted octa(4-isopropylphenoxy)rhodium(III)phthalocyanine, (*R*)<sub>8</sub>PcRhCl (**3**), was reacted with the nitrogenous bases pyridine (Py) and pyrazine (Pyz) to give the axially-disubstituted octa(4-isopropylphenoxy)rhodium(III)phthalocyanines [(*R*)<sub>8</sub>PcRhCl(L)] (**4**) and (**5**), L = (Py) and (Pyz), respectively. In this study, the fluorescence quantum yield ( $\Phi_{\rm ph}$ ) and the photodegradation quantum yield ( $\Phi_{\rm pd}$ ) values for the newly synthesized rhodium phthalocyanine complexes (RhPcs) **4** and **5** are reported. The complexes have also been fully characterized by elemental analysis, FD mass spectrometry, FT-IR and <sup>1</sup>H NMR spectroscopy.

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complexes of the type PcRh(L)CI, [L = 2-methylpyrazine (mepyz), 4,4'-bipyridine (bpy) or pyridine (py)] have been prepared and studied earlier by Hanack et al. [32], in addition their cyclic voltammetric properties have been investigated, along with those for K[RhPc(CN)] [33]. Another series of axially-substituted (octa*n*-pentylphthalocyaninato)(methyl)rhodium(III) complexes has been synthesized by Chen and Rathke [34]. These complexes are not able to aggregate due to their special structural features [35]. The synthesis of the rhodium phthalocyaninatorhodium(III) salts in inert high boiling solvents or under reduced pressure at *T* < 350 °C have been also reported previously by Homborg et al. [36], Nyokong [37], Chen [38] and Liu [39], in addition to their electrochemical properties.

Regarding our previous studies, the nature of the substituents, such as alkyl, alkoxy chains and bulky groups, either at the peripheral position or on the axial position can strongly influence the essential parameters of a phthalocyanine, such as its solubility, aggregation behavior, electronic absorption and fluorescence spectral properties [40–43].

Therefore, we have described previously the synthesis, photophysical and photochemical properties of indium phthalocyanines incorporating different types of axial and peripheral substituents [44]. To our best knowledge, octa(4-isopropylphenoxy)rhodium(III)phthalocyanines (RhPcs) **3–5** have not been reported before. This is the first report describing their synthesis. The rarity of these phthalocyanines has thus prompted us to study their photochemical and photophysical properties. The new complexes were characterized by UV–Vis, FT-IR and <sup>1</sup>H NMR spectroscopies, FD mass spectra and elemental analysis.



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#### 2. Experimental

#### 2.1. General

All manipulations were performed under nitrogen by using standard Schlenk techniques unless otherwise specified. 4,5-Dichloro-phthalonitrile (1), 4-(*isopropyl*)-phenol and rhodium(III) chloride trihydrate were commercially available (Aldrich) and used as purchased. All other reagents and solvents were reagent grade quality, obtained from commercial suppliers and used as received. Solvents were purified by standard methods and freshly distilled before use.

#### 2.2. Physical and spectroscopic measurements

<sup>1</sup>H NMR spectra were measured on a Bruker ARX 250 (250.133 MHz) NMR spectrometer in DMSO-d<sub>6</sub> as the solvent and TMS as an internal standard; chemical shifts are reported in ppm. FT-IR spectra were recorded on a Bruker IFS 48 spectrometer by preparing pellets with KBr. Melting points were measured on an electrothermal apparatus and were uncorrected. Field desorption (FD) mass spectra measurements were carried out with a Varian MAT 711 A spectrometer and reported as mass/charge (m/z). Elementary analyses were performed on Carlo Erba Elemental Analyzer 1106. Ground state electronic absorption measurements in the UV-Vis region were taken in dimethylsulfoxide (DMSO) using a Perkin-Elmer Lambda 2 spectrophotometer. Fluorescence excitation and emission spectra and the phosphorescence profile were recorded on a Hitachi F-4500 Pc spectrofluorimeter equipped with a photomultiplier tube, using 1 cm path length cuvettes at room temperature. All photo-irradiations were done using a Quartz lamp (300 W). The light source was equipped with a glass cut off filter (Schott) and a water filter, respectively, to filter off ultraviolet and infrared radiations, and cover the red region, 630-750 nm. Light intensity could be modulated by means of a potentiometer.

#### 2.3. Synthesis of RhPcs 3-5

#### 2.3.1. Synthesis of 4,5-bis(4-isopropylphenoxy)phthalonitrile (2)

4,5-Dichloro-phthalonitrile (1) (2.84 g, 14.4 mmol) was dissolved in DMF (50 ml) under nitrogen and 4-(*isopropyl*)-phenol (2.02 g, 14.4 mmol) was added. After stirring for 30 min at room temperature, finely anhydrous potassium carbonate (5 g, 36.24 mmol) was added in portions over 3 h with efficient stirring. The reaction mixture was further stirred at 70 °C for 24 h. Then the mixture was poured into 200 ml ice water, the precipitate that formed was filtered off, washed with water and methanol, and then dried. The crude product was recrystallized from methanol to give **2** as a white crystalline solid (1.90 g, 80.1%). M.p. 172 °C.

IR (KBr)  $v(\text{cm}^{-1})$ : 3080 (w), 3053 (s) (Ar-CH), 2956 (s), 2933 (w), 2855 (m), 2230 (CN), 1599 (CC), 1541 (s), 1469 (s), 1435 (m), 1321 (m), 1210–1235 (C–O–C), 1177 (s), 1133 (s), 1070 (s), 940 (s), 889 (m), 777 (m), 539 (m). <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  (ppm): 1.03–1.30 (m, 12H, 4×CH<sub>3</sub>), 2.3 (hept, 2H, 2×CH-isopropyl), 6.80 (dd, 8H, 8×ArCH-phenoxy), 8.20 (s, 2H, ArCH). MS (EI): m/z (%) 396.49 (90) (M<sup>+</sup>). Anal. Calc. for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.76; H, 6.10; N, 7.07. Found: C, 77.92; H, 6.60; N, 7.19%.

## 2.3.2. Synthesis of 2,3,9,10,16,17,23,24-octa(4-isopropylphenoxy phthalocyaninato)(chloro)rhodium(III), [(R)<sub>8</sub>PcRhCl] (**3**)

A suspension of rhodium(III) chloride trihydrate (0.3 g) in deoxygenated 2-ethoxyethanol (10 ml) was boiled under a stream of dry nitrogen gas until the water was removed, then added to a solution of 4,5-bis(4-isopropylphenoxy)phthalonitrile (**2**) (1.5 g, 4 mmol) and diazabicyclo[5.4.0]undec-7-ene (DBU, 0.45 g, 3 mmol) in deoxygenated 2-ethoxyethanol (10 ml). The mixture was refluxed for 22 h under dry nitrogen. A dark blue solution was formed, cooled to room temperature and then poured into MeOH/H<sub>2</sub>O (3:1). The suspended solution was centrifuged, the precipitated was filtered off, washed with a methanol/water mixture (1/1, v/v) and dried under vacuum. The crude product (1.2 g) was subjected to column chromatography over silica gel using a mixture of *n*-hexane/dichloromethane 5:2 to yield 1.02 g (59%) of complex **3** as a blue violet powder.

IR (KBr)  $\nu$ (cm<sup>-1</sup>): 3085 (w), 3050 (s) (Ar-CH), 2950 (s), 2943 (w), 2875 (m), 1602 (CC), 1551 (s), 1460 (s), 1434 (m), 1327 (m), 1215–1240 (C–O–C), 1179 (s), 1143 (s), 1077 (s), 944 (s), 890 (m), 771 (m), 540 (m). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 1.23–1.60 (m, 48H, 16×CH<sub>3</sub>), 2.7 (hept, 8H, 8×CH-isopropyl), 6.70–7.04 (dd, 32H, 32×ArCH-phenoxy), 8.30 (s, 8H, ArCH-Pc). UV–Vis (DMSO),  $\lambda_{max}$  (nm): 648, 629, 584, 345. MS (FD): *m*/*z* (%) 1724.31 (70) (M<sup>+</sup>). *Anal.* Calc. for C<sub>104</sub>H<sub>96</sub>ClN<sub>8</sub>O<sub>8</sub>Rh: C, 72.44; H, 5.61; N, 6.50. Found: C, 71.89; H, 5.99; N, 7.09%.

#### 2.3.3. Synthesis of 2,3,9,10,16,17,23,24-octa(4-

#### isopropylphenoxyphthalocyaninato)(chloro)(pyridine)rhodium(III), [(R)<sub>8</sub>PcRhCl(py)] (4)

Crude octa(4-isopropylphenoxyphthalocyaninato)(chloro)rhodium(III), (**3**) (0.86 g, 0.5 mmol) was stirred in 5 ml of deoxygenated 2-ethoxyethanol with pyridine (0.6 g) and refluxed for 20 h under nitrogen. The reaction mixture was left standing to allow slow cooling and then poured into MeOH/H<sub>2</sub>O (3:1). The mixture was then stirred for 2 h. The mixture was centrifuged. The precipitate was collected, washed with a methanol/water mixture (1/1, v/v) and dried. The crude product was purified by column chromatography (silica gel, CHCl<sub>3</sub>), to remove any excess ligand, and dried (70 °C, 0.01 Torr), to yield 0.59 g (66%) of complex **4** as a blue/purple powder.

IR (KBr)  $\nu$ (cm<sup>-1</sup>): 3086 (w), 3055 (s) (Ar-CH), 2955 (s), 2948 (w), 2879 (m), 1612 (CC), 1558 (s), 1466 (s), 1440 (m), 1331 (m), 1218–1238 (C–O–C), 1176 (s), 1140 (s), 1076 (s), 942 (s), 891 (m), 774 (m), 539 (m). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 1.33–1.68 (m, 48H, 16×CH<sub>3</sub>), 2.5 (hept, 8H, 8×CH-isopropyl), 2.6 (d, 1H, Py-Hc), 5.04 (d, 2H, Py-Hb), 5.17 (d, 2H, Py-Ha), 6.60–7.24 (dd, 32H, 32×ArCH-phenoxy), 8.44 (s, 8H, ArCH-Pc). UV–Vis (DMSO),  $\lambda_{max}$  (nm): 659, 623, 586, 345, 272. MS (FD): *m/z* (%) 1803.41 (77) (M<sup>+</sup>). *Anal.* Calc. for C<sub>109</sub>H<sub>101</sub>ClN<sub>9</sub>O<sub>8</sub>Rh: C, 72.60; H, 5.64; N, 6.99. Found: C, 71.86; H, 6.09; N, 7.19%.

#### 2.3.4. Synthesis of 2,3,9,10,16,17,23,24-octa(4-

isopropylphenoxyphthalocyaninato)(chloro)(pyrazine)rhodium(III), [(R)<sub>8</sub>PcRhCl(pyz)] (5)

Crude octa(4-isopropylphenoxyphthalocyaninato)(chloro)rhodium(III), (**3**) (0.86 g, 0.5 mmol) was stirred in 5 ml of deoxygenated 2-ethoxyethanol with pyrazine (0.9 g) and refluxed for 20 h under nitrogen. The reaction mixture was left standing to allow slow cooling and then poured into MeOH/H<sub>2</sub>O (3:1). The mixture was then stirred for 2 h. The mixture was centrifuged. The precipitate was collected, washed with a methanol/water mixture (1/1, v/ v) and dried. The crude product was purified by column chromatography (silica gel, CHCl<sub>3</sub>), to remove any excess ligand, and dried (70 °C, 0.01 Torr), to yield 0.5 g (61%) of complex **5** as a blue/purple powder.

IR (KBr)  $\nu$ (cm<sup>-1</sup>): 3071 (w), 3049 (s) (Ar-CH), 2965 (s), 2952 (w), 2880 (m), 1610 (CC), 1550 (s), 1463 (s), 1443 (m), 1333 (m), 1220– 1235 (C–O–C), 1173 (s), 1139 (s), 1073 (s), 940 (s), 890 (m), 770 (m), 541 (m). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 1.39–1.70 (m, 48H, 16×CH<sub>3</sub>), 2.6 (hept, 8H, 8×CH-isopropyl), 5.05 (d, 2H, Pyz-Hb), 5.19 (d, 2H, Pyz-Ha), 6.65–7.38 (dd, 32H, 32×ArCH-phenoxy), 8.51 (s, 8H, ArCH-Pc). UV–Vis (DMSO),  $\lambda_{max}$  (nm): 661, 622, 588, 347, 270. MS (FD): *m/z* (%) 1804.40 (72) (M<sup>+</sup>). *Anal.* Calc. for C<sub>108</sub>H<sub>100</sub>ClN<sub>10</sub>O<sub>8</sub>Rh: C, 71.89; H, 5.59; N, 7.76. Found: C, 70.98; H, 6.19; N, 7.99%.

#### 2.4. Photochemical and photophysical parameters

#### 2.4.1. Fluorescence quantum yields

Fluorescence quantum yields were determined by the comparative method, Eq. (1), [45] using ZnPc in DMSO as a standard, where ( $\Phi_F$ ) = 0.20 [46,47].

$$\Phi_{\rm F} = \Phi_{\rm F}({\rm Std}) \frac{F_x \cdot A_{\rm Std} \cdot \eta_x^2}{F_{\rm Std} \cdot A_x \cdot \eta_{\rm Std}^2} \tag{1}$$

where  $F_{(x)}$  and  $F_{(std)}$  are the areas under the emission curves of the sample and standard, respectively.  $A_{(x)}$  and  $A_{(std)}$  are the absorbances of the sample and standard, respectively, and  $\eta_{(x)}$  and  $\eta_{(std)}$  are the refractive indexes of the solvents used for the sample and standard, respectively. The error in the determination of  $\Phi_F$  was 10% (determined from several  $\Phi_F$  values). Both the sample and reference were excited at the same wavelength. At least three independent experiments were performed for the quantum yield determinations.

#### 2.4.2. Phosphorescence quantum yields

Phosphorescence quantum yields were determined by using the optically dilute method, Eq. (2), [48] using a solution of 8-methoxypsoralen as a standard, where ( $\Phi_{phos}$ ) = 0.17 [49].

$$\Phi_{\rm phos} = \Phi_{\rm phos}({\rm Std}) \frac{D_x \cdot A_{\rm Std} \cdot \eta_x^2}{D_{\rm Std} \cdot A_x \cdot \eta_{\rm Std}^2}$$
(2)

where  $\Phi_{\text{phos(std)}}$  is the phosphorescence quantum yield of the standard,  $A_{(x)}$  and  $A_{(\text{std})}$  are the absorbances at the wavelength of the excitation of the sample and standard, respectively,  $\eta_{(x)}$  and  $\eta_{(\text{std})}$ are the refractive indexes of the solvents used for the sample and standard, respectively.  $D_{(x)}$  and  $D_{(\text{std})}$  are the integrated emission intensities of the sample and standard, respectively. Both the sample and reference were excited at the same wavelength. At least three independent experiments were performed for the quantum yield determinations.

#### 2.4.3. Photodegradation quantum yields

Determination of photodegradation quantum yields ( $\Phi_{pd}$ ) was carried out as previously described in the literature [47,50,51].  $\Phi_{pd}$  was determined using Eq. (3),

$$\Phi_{\rm pd} = \frac{(C_0 - C_{\rm t}) \cdot V \cdot N_{\rm A}}{I_{\rm abs} \cdot S \cdot t} \tag{3}$$

where  $C_0$  and  $C_t$  are the sample (**4** and **5**) concentrations before and after irradiation respectively, *V*, *N*<sub>A</sub>, *S*, *t* and *I*<sub>abs</sub> are the reaction volume, Avogadro's constant, irradiated cell area, irradiation time and the overlap integral of the radiation source light intensity, respectively. A light intensity of  $3.7 \times 10^{16}$  photons s<sup>-1</sup> cm<sup>-2</sup> was employed for the  $\Phi_{pd}$  determinations.

#### 3. Results and discussion

The general synthesis involves firstly, a nucleophilic aromatic substitution reaction between a mixture of the commercially obtained 4,5-dichlorophthalonitrile (**1**) and 4-isopropylphenol at 70 °C in DMF in the presence of  $K_2CO_3$ , to yield the corresponding phthalonitrile, 4,5-bis(4-isopropylphenoxy)phthalonitrile (**2**) in 70–80%.

#### 3.1. Synthesis and characterization

The RhPc complex **3** was synthesized directly by cyclotetramerization of 4,5-bis(4-isopropylphenoxy)phthalonitrile (**2**) in the presence of the metal salt RhCl<sub>3</sub> and diazabicyclo[5.4.0]undec-7ene (DBU) as a catalyst in deoxygenated 2-ethoxyethanol. In this reaction, the long reaction time was necessary for a good yield. Complexes **4** and **5** were prepared by refluxing the parent crude chloro rhodium phthalocyanine [(R)<sub>8</sub>PcRhCl] (**3**) with an excess of the corresponding axial ligand in 2-ethoxyethanol, **4**: L = pyridine (Py) and **5**: L = pyrazine (Pyz), respectively, (see Section 2). The synthetic routes of the axially substituted rhodium phthalocyanines RhPcs **3–5** are shown in Scheme 1.

All of these axially substituted phthalocyanines were purified by column chromatography and obtained in a moderate vield (59% for **3**. 66% for **4** and 61% for **5**). The structures of the newly prepared RhPcs complexes were elucidated using elemental analysis, FT-IR, <sup>1</sup>H NMR, UV-Vis and FD mass spectroscopy. All the analytical and spectral data were consistent with the predicted structures. In the IR spectra, the disappearance of the characteristic nitrile stretch ( $C \equiv N$ ) of the phthalonitrile derivative (2) at around  $2230 \text{ cm}^{-1}$  indicated the formation of the RhPcs complexes **3–5**. The complexes had good solubility and were mainly monomeric in solution (DMSO). Further, they were stable in air as solid materials. The solubility of the mixed axially substituted complexes 4 and 5 were much improved compared to their parent rhodium(III)phthalocyanine  $[(R)_8$ PcRhCl] (**3**) with a chloro ligand, enabling purification by column chromatography and also <sup>1</sup>H NMR measurements in DMSO. These complexes were formed with high purity, also the substituted pyridine and pyrazine axial ligands were chosen because of their stability [52]. A simple <sup>1</sup>H NMR spectrum was obtained for each of the RhPcs complexes 3-5 under ordinary conditions (DMSO and room temperature). They all exhibited well-resolved spectra with sharp peaks in both the aromatic and aliphatic regions implying that any aggregation behavior is totally absent.

The conformation of the phenoxy groups in the RhPcs **3–5** was clarified by the <sup>1</sup>H NMR spectra, which showed one environment for the methyl hydrogens of the iso-propyl groups between 1.23 and 1.70 ppm. The <sup>1</sup>H NMR spectrum of **3** showed a variation of the chemical shifts values to the <sup>1</sup>H NMR spectra of **4** and **5** for the macrocyclic proton resonances due to the presence of the axial pyridine and pyrazine ligands attached to the rhodium metal. The FD mass spectra of **3**, **4** and **5** confirmed the proposed structures and these analyses were consistent with the predicted structures.

#### 3.2. Ground state electronic absorption spectral studies

The electronic absorption spectra showed monomeric behavior, evidenced by a single (narrow) Q band for complexes **3** and **5**, typical of rhodium phthalocyanine complexes, (Fig. 1) in DMSO, the Q bands for RhPcs **3–5** were observed at  $\lambda_{max} = 648$ , 659, 661 nm, respectively. The Q bands of the mixed axial complexes **4** and **5** were red-shifted by 11–13 nm, when compared to the corresponding chloro-axial RhPc complex **3** in DMSO (Fig. 1 and Table 1). This observed red spectral shift may due to the attached pyridine (py) and pyrazine (pyz) rings to the central rhodium metal. The molar extinction coefficients of the RhPcs **3–5** are listed in Table 1. They remain almost constant, indicating a pure monomeric form [53].

#### 3.3. Interpretation of the photophysical and photochemical data

The photophysical and photochemical parameters of the photosensitising dyes **4** and **5** can be measured in terms of the light harvesting property of the dye, i.e. the molar extinction coefficient ( $\varepsilon$ ), fluorescence quantum yield ( $\Phi_{\rm F}$ ), phosphorescence quantum yield







Fig. 1. UV-Vis spectra of RhPcs 3, 4 and 5 in DMSO.

 $(\varPhi_{\rm phos})$  and photodegradation quantum yield  $(\varPhi_{\rm pd})$ . Both complexes were measured in dimethyl sulfoxide (DMSO) at room temperature and the solutions were further filtered before transferring into a standard spectrophotometer cell.

#### 3.3.1. Fluorescence behavior and quantum yield studies

The excitation wavelengths used for the fluorescence measurements were  $\lambda = 669 \text{ nm}$  for (**4**) and  $\lambda = 667 \text{ nm}$  for (**5**) in DMSO.

Rhodium phthalocyanine derivatives **4** and **5** showed the same fluorescence behavior in the solvent used, and the shape of the excitation spectra were similar to the absorption spectra for both complexes. Fig. 2 shows the fluorescence emission and excitation spectra for complex **4** as an example in DMSO. The fluorescence emission peaks are observed at 662 nm for **4** and 664 nm for **5** in DMSO (Fig. 3).

The Q-bands in the absorption and emission spectra of complexes **4** and **5** differ by 2 nm, indicating that the nuclear configurations in the ground and excited states of these compounds are similar and are not affected by excitation, see Table 1. However in terms of wavelength, the excitation spectra are slightly redshifted when compared to the absorption spectra for both complexes. The fluorescence quantum yields ( $\Phi_F$ ) of the rhodium phthalocyanine complexes **4** and **5** are typical of MPc complexes in DMSO and are reported in Table 1 [54].

The efficiency of the fluorescence process was measured by the quantum yield. This parameter is of major importance from which the whole photophysical behavior can be deduced, and it is commonly given with a 10% error [47].

#### 3.3.2. Phosphorescence behavior and quantum yield studies

As known, rhodium phthalocyanines exhibited both fluorescence and moderately intense phosphorescence spectra in solution at room temperature. The spectra outlined above show that dilute solutions of the rhodium(III) phthalocyanines **4** and **5** in DMSO exhibit both fluorescence and phosphorescence at room temperature. The phosphorescence spectra for complexes **4** and **5** are also

 Table 1

 Spectral, fluorescence, phosphorescence and photodegradation parameters for RhPcs 3-5 in DMSO.

RhPc	$Q_{abs} \lambda_{max} (nm) (Log \varepsilon)$	$Q_{\rm ems} \lambda_{\rm max} ({\rm nm})$	$Q_{\text{Exc}} \lambda_{\text{max}} (nm)$	$Q_{\rm phos} \lambda_{\rm max} ({\rm nm})$	$arPsi_{ m F}$	$arPhi_{ m phos}$	$arPhi_{ m pd}( imes 10^5)$
3	648 (4.17)	698	648	786	0.31	0.51	1.8
4	659 (5.57)	662	669	749	0.33	0.56	1.3
5	661 (5.43)	664	667	747	0.30	0.66	1.7

 $Q_{abs} = Q$  band absorption maximum;  $Q_{ems} = Q$  band emission maximum;  $Q_{phos} = Q$  band phosphorescence maximum;  $Q_{exc} = Q$  band excitation maximum;  $\lambda =$  wavelength;  $\varepsilon =$  molar extinction coefficient;  $\Phi_F =$  fluorescence quantum yield;  $\Phi_{phos} =$  phosphorescence quantum yield;  $\Phi_{pd} =$  photodegradation quantum yield.



Fig. 2. Excitation, emission and phosphorescence spectra of RhPc 4 in DMSO.



Fig. 3. Excitation, emission and phosphorescence spectra of RhPc 5 in DMSO.

virtually identical to one another, exhibiting a maximum at 749 and 747 nm, respectively, (Table 1). The phosphorescence quantum yield ( $\Phi_{\text{phos}}$ ) values for **4** and **5** in DMSO are reported in Table 1.

#### 3.3.3. Photodegradation behavior and quantum yields studies

Photodegradation (photobleaching) is a process where phthalocyanines are degraded under light irradiation. It is important for their applications as photocatalysts or as photosensitizers and it can be used to determine the MPc's stability.

The photobleaching stabilities of complexes **4** and **5** were determined in DMSO and in the presence of oxygen because it allows good solubility and deaggregation. In addition, DMSO appears to produce a substantial stabilizing effect upon the phthalocyanine macrocycle [50] and therefore there is good comparability between the different complexes.

Photodegradation for the mixed axially substituted RhPcs complexes **4** and **5** were characterized by the decrease in the intensity of the spectra (both the Q and B bands) without shift in maxima or formation of new bands, when exposed to light and irradiated at constant time intervals over a period of 60 min. The spectral changes observed show the decrease of the absorption spectra without any distortion of the shape, which confirmed that clean photodegradation occurred without any phototransformation, as shown in Figs. 4 and 5.

Photobleaching studies were undertaken in order to determine the effects of different axial ligands on the stability of rhodium



**Fig. 4.** The photodegradation of RhPc **4** in DMSO with after irradiation at constant time intervals over a period of 60 min. (Insert: plot shows the absorbance against time of irradiation).



**Fig. 5.** The photodegradation of RhPc **5** in DMSO with after irradiation at constant time intervals over a period of 50 min. (Insert: plot shows the absorbance against time of irradiation).

phthalocyanines **4** and **5** in the presence of light, as illustrated with the values of the photodegradation quantum yield ( $\Phi_{\rm pd}$ ). The photodegradation quantum yield ( $\Phi_{\rm pd}$ ) values for the complexes are listed in Table 1 and are of the order of  $10^{-5}$ . These values show that the RhPcs 4 and 5 have high stability in DMSO.

#### 3.4. Explanation of the photophysical and photochemical parameters

The excitation spectra of the two complexes **4** and **5** represent mirror images of their emission spectra. Figs. 2 and 3 also show that the complexes absorbing light in the ground state are the same complexes that are being excited. This confirms that the absorbing species are also the fluorescing species. Following the absorption of light at the excitation wavelength of these complexes, electrons are promoted from the ground state to the singlet state by the absorption of a photon. Fluorescence quantum vield values are usually expected to be higher for MPcs with lighter atoms and lower for MPcs with heavier atoms, where intersystem crossing (ISC) of heavier atoms is expected to cause a decrease in fluorescence quantum yield [55].

#### 4. Conclusions

We have successfully synthesized chlororhodium phthalocyanines 3-5 bearing peripheral bulky phenoxy groups decorated with isopropyl groups as substituents at their *p*-position. We show that the RhPc complex **3** is a valuable precursor to prepare the mixed axially substituted RhPcs 4 and 5 in moderate yields. In this study, the spectral and photophysicochemical properties of the soluble peripheral substituted chlororhodium phthalocyanines 4 and **5** were also discussed. Overall, this work shows two key ways in which this class of dves may be employed, namely as photocatalysts due to their low photodegradation yields and as advanced optical chemical sensing materials based on the excellent spectroscopic behaviors of RhPcs in solvents.

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