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# Novel metal-free, metallophthalocyanines and their quaternized derivatives: Synthesis, spectroscopic characterization and catalytic activity of cobalt phthalocyanine in 4-nitrophenol oxidation

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# ABSTRACT

Novel metal-free, Zn and Co phthalocyanines substituted with four 4-[4-((E)-{[4-(dimethylamino) phenyl]imino}methyl)phenoxy] substituents at peripheral positions have been synthesized. Quaternization of the dimethylamino functionality produced quaternized cationic metal-free, Zn and Co phthalocyanines which were soluble in DMF, DMSO and pyridine. The aggregation behavior of these compounds was investigated in different concentrations of chloroform for the metal-free, Zn and Co phthalocyanines, and DMF for the quaternized metal-free, Zn and Co phthalocyanines. The effect of solvents on the absorption spectra was studied in various organic solvents. Cobalt phthalocyanine complex **6** was tested as a catalyst for the oxidation of 4-nitrophenol with different oxidants, such as *tert*-butylhydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), in organic solvent. The novel compounds were characterized using IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV–Vis, MS spectral data and elemental analysis.

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# 1. Introduction

Although more than a century has passed since the discovery of the first phthalocyanine (Pc) compound, they are still very popular for many investigators due to their superlative properties [1,2]. Pcs are highly stable and are capable of including more than 70 metallic and non-metallic ions in the ring cavity, called metallophthalocyanines (MPc). These remarkable macrocyclic compounds possess magnificent physical and chemical properties [3]. Beyond utilization as dyes and pigments, Pcs are used in many fields, such as electrophotography, photovoltaic and solar cells, molecular electronics, Langmuir–Blodgett films, electrochromic display devices, gas sensors, non-linear optics (NLO), optical discs and sensitizers in the photodynamic therapy of cancer (PDT) [4].

A major disadvantage of phthalocyanines, because they are planar macrocyclic systems, is their tendency to aggregate, which results in low solubility, difficulties during purification and characterization. To overcome this complication, several approaches were made; introduction of bulky substituents, charged substituents or monomerizing solvents are widely reported in the literature [5–9]. Because of the insolubility of Pcs in organic and/or inorganic solvents, one of the most important aims of researches on the chemistry of phthalocyanines is to enhance their solubility in various solvents. Whereas peripheral substitution with bulky or long-chain hydrophobic moieties leads to phthalocyanine derivatives soluble in organic solvents, on the contrary, tertiary-amino, sulfo or carboxyl groups result in water-soluble materials [10–13]. Cationic-pc derivatives also present a large and expanding class of compounds which have applications in biology, catalysis and materials [14–17]. Furthermore quaternized amino group containing Pcs are useful in achieving solubility within a wide pH range of aqueous solutions [18–20]. Metallophthalocyanine complexes, especially Co(II) phthalocyanines, are readily available oxidation catalysts and are found to transfer oxygen from various oxygen donors to alkanes, alkenes, phenols and thiols in numerous studies [21,22].

4-Nitrophenol (4-NP) is a toxic and bio-refractory pollutant which can cause considerable damage to the ecosystem and human health. It can damage the central nervous system, liver, kidney and blood of humans and animals. 4-NP and its derivatives are used in the production of pesticides, and as insecticides and herbicides [23]. Nitroaromatics are used in the production of explosives and 4-NP is used in the production of many synthetic dyes [24]. Therefore, 4-NP and its derivatives are common pollutants in many natural waters and in industrial wastewater [25].

Recently, Gül and co-workers have reported phthalocyanines with unsaturated cinnamaldiamine moieties attached to the inner core through phenoxy-bridges and containing Schiff's base groups [26,27]. This paper reports a convenient procedure for the



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synthesis of novel metal-free and metallophthalocyanines and their quaternized derivatives which contain four conjugated Schiff's base groups on peripheral positions in the phthalocyanine framework. Also, the aggregation behavior of the synthesized metal-free, metallophthalocyanines and their quaternized derivatives are investigated in different solvents. In addition, the search for a catalyst that can degrade 4-nitrophenol to products of reduced toxicity led to the use, in this work, of a phthalocyanine complex containing a paramagnetic central metal: CoPc.

# 2. Experimental

### 2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [28].  $4-((E)-\{[4-(Dimethylamino)phenyl]imino\}methyl)phenol$  **1** [29] and 4-nitrophthalonitrile **2** [30] were synthesized and purified according to well known literature procedures.

#### 2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub>. Chemical shifts were reported ( $\delta$ ) relative to Me<sub>4</sub>Si as an internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. GC Agilent Technologies 7820A equipment (30 m × 0.32 mm × 0.50 µm DB Wax capillary column, FID detector) was used for GC measurements. Optical spectra in the UV–Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected.

# 2.3. Synthesis

# 2.3.1. Synthesis of 4-[4-((E)-{[4-(dimethylamino)phenyl]imino} methyl)phenoxy]phthalonitrile (**3**)

4-((*E*)-{[4-(Dimethylamino)phenyl]imino}methyl)phenol 1 (1.5 g,  $6.25 \times 10^{-3}$  mol) was dissolved in dry dimethyl formamide (DMF) (0.03 L) under a N<sub>2</sub> atmosphere and 4-nitrophthalonitrile **2** (1.1 g,  $6.25 \times 10^{-3}$  mol) was added to the solution. After stirring for 10 min, finely ground anhydrous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (2.6 g,  $18.75 \times 10^{-3}$  mol) was added portionwise over 2 h with efficient stirring. The reaction mixture was stirred under N2 at 50 °C for 3 days. Then the solution was poured into ice-water (100 g). The precipitate that formed was filtered off, washed first with water until the filtrate was neutral and then with diethyl ether and dried in vacuo over phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>). The crude product was crystallized from tetrahydrofuran (THF). Yield: 1.55 g (67%), mp: 184-185 °C. IR (KBr pellet), v<sub>max</sub>/cm<sup>-1</sup>: 3080 (Ar-H), 2925–2896 (Aliph. C-H), 2225 (C°N), 1621 (C=N), 1591, 1561, 1514, 1481, 1359, 1290, 1245, 1206, 1163, 1088, 1062, 1013, 948, 884, 817, 538. <sup>1</sup>H NMR. (DMSO-*d*<sub>6</sub>), (δ, ppm): 8.65 (s, 1H, =C-H), 8.13 (d, 1H, Ar-H), 7.99 (d, 2H, Ar-H), 7.86 (s, 1H, Ar-H), 7.48 (d, 1H, Ar-H), 7.28 (d, 4H, Ar-H), 6.75 (d, 2H, Ar-H), 2.92 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR. (DMSO-*d*<sub>6</sub>), (δ, ppm): 161.14, 156.30, 154.61, 150.11, 140.23, 137.05, 134.85, 130.94, 123.91, 123.31, 123.09, 120.99, 117.47, 116.58, 116.07, 113.25, 109.36, 40.90. MS (ES<sup>+</sup>), (m/z): 367  $[M+H]^+$ . Anal. Calc. for C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O: C, 75.39; H, 4.95; N, 15.29. Found: C, 75.92; H, 5.31; N, 14.88%.

#### 2.3.2. Synthesis of metal-free phthalocyanine (4)

4-[4-((E)-{[4-(Dimethylamino)phenyl]imino}methyl)phenoxy] phthalonitrile **3** (0.3 g,  $0.82 \times 10^{-3}$  mol), 1.8-diazabicyclo[5.4.0] undec-7-ene (DBU) (3 drop) and dry *n*-pentanol (0.003 L) were added to a Schlenk tube and then were heated and stirred at 160 °C for 24 h under N<sub>2</sub>. After cooling to room temperature, the reaction mixture was refluxed with ethanol (0.05 L) to precipitate the product, which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. The obtained green solid product was purified by column chromatography (aluminum oxide) using chloroform:methanol (100:4) as the solvent system. Yield: 0.1 g (33%). IR (KBr pellet),  $v_{max}/cm^{-1}$ : 3289 (N-H), 3078 (Ar-H), 2918-2849 (Aliph. C-H), 1619 (C=N), 1600, 1514, 1469, 1419, 1395, 1344, 1228, 1159, 1090, 1006, 938, 884, 819, 742, 542. <sup>1</sup>H NMR. (CDCl<sub>3</sub>), ( $\delta$ , ppm): 8.40 (m, 4H, =C-H), 7.94 (m, 8H, Ar-H), 7.29-7.03 (m, 28H, Ar-H), 6.70 (m, 8H, Ar-H), 2.98 (s, 24H, CH<sub>3</sub>). UV–Vis (chloroform)  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 702 (4.82), 666 (4.75), 640 (4.36), 607 (4.17), 351 (4.71), 285 (4.66). MS (ES<sup>+</sup>), (*m*/*z*): 1465 [M-2H]<sup>+</sup>. Anal. Calc. for C<sub>92</sub>H<sub>74</sub>N<sub>16</sub>O<sub>4</sub>: C, 75.29; H, 5.08; N, 15.27. Found: C, 75.76; H, 4.76; N, 14.78%.

#### 2.3.3. Synthesis of zinc (II) phthalocyanine (5)

4-[4-((*E*)-{[4-(Dimethylamino)phenyl]imino}methyl)phenoxy] phthalonitrile **3** (0.3 g,  $0.82 \times 10^{-3}$  mol), anhydrous Zn(CH<sub>3</sub> COO)<sub>2</sub> (0.075 g,  $0.41 \times 10^{-3}$  mol) and 0.003 L of *n*-pentanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) under a nitrogen atmosphere and held at reflux temperature for 24 h. After cooling to room temperature, the reaction mixture was refluxed with ethanol (0.05 L) to precipitate the product, which was filtered off. The crude product was collected by filtration and washed with water, ethanol and ether, and then dried. The obtained green solid product was purified by column chromatography (silica gel) with chloroform: methanol (100:5) as the solvent system. Yield: 0.140 g (45%). IR (KBr pellet), v<sub>max</sub>/cm<sup>-1</sup>: 3080 (Ar-H), 2918–2844 (Aliph. C-H), 1617 (C=N), 1600, 1511, 1466, 1393, 1335, 1228, 1157, 1116, 1088, 1043, 944, 886, 817, 746, 540, <sup>1</sup>H NMR, (CDCl<sub>3</sub>), (δ, ppm); 8.51 (m, 4H, =C-H), 7.88 (m, 8H, Ar-H), 7.29-7.05 (m, 28H, Ar-H), 6.71 (m, 8H, Ar–H), 2.94 (s, 24H, CH<sub>3</sub>). UV–Vis (chloroform) λ<sub>max</sub>, nm  $(\log \epsilon)$ : 684 (4.97), 617 (4.29), 360 (4.84), 280 (4.77). MS  $(ES^+)$ , (m/z): 1532  $[M+H]^+$ . Anal. Calc. for C<sub>92</sub> H<sub>72</sub>N<sub>16</sub>O<sub>4</sub>Zn: C, 72.17; H, 4.74; N, 14.64. Found: C, 72.58; H, 5.06; N, 14.24%.

#### 2.3.4. Synthesis of cobalt (II) phthalocyanine (6)

4-[4-((*E*)-{[4-(Dimethylamino)phenyl]imino}methyl)phenoxy] phthalonitrile **3** (0.25 g,  $0.68 \times 10^{-3}$  mol), anhydrous CoCl<sub>2</sub>  $(0.044 \text{ g}, 0.34 \times 10^{-3} \text{ mol})$  and 0.0025 L of *n*-pentanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) under a nitrogen atmosphere and held at reflux temperature for 24 h. After cooling to room temperature, the reaction mixture was refluxed with ethanol (0.05 L) to precipitate the product, which was filtered off. The crude product was collected by filtration and washed with water, ethanol and ether, and then dried. The obtained green solid product was purified by column chromatography (aluminum oxide) using chloroform:methanol (100:4) as the solvent system. Yield: 0.080 g (31%). IR (KBr pellet), v<sub>max</sub>/cm<sup>-1</sup>: 3076 (Ar-H), 2920-2853 (Aliph. C-H), 1618 (C=N), 1597, 1514, 1469, 1408, 1355, 1232, 1157, 1116, 1094, 1058, 946, 882, 821, 753. UV-Vis (chloroform)  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 673 (4.46), 611 (4.08), 376 (4.70), 282 (4.84). MS (ES<sup>+</sup>), (*m*/*z*): 1524 [M]<sup>+</sup>. Anal. Calc. for C<sub>92</sub>H<sub>72</sub>N<sub>16</sub>O<sub>4</sub>Co: C, 72.48; H, 4.76; N, 14.70. Found: C, 72.80; H, 5.12; N, 14.30%.

# 2.3.5. Synthesis of quaternized metal-free phthalocyanine (4a)

Metal-free phthalocyanine **4** (0.035 g,  $0.024 \times 10^{-3}$  mol) was dissolved in 0.003 L of chloroform and excess methyl iodide

(0.0019 L) was added to this solution. The reaction mixture was stirred at room temperature for 24 h. After cooling to room temperature, the green precipitate that formed was filtered off, washed with chloroform, acetone, diethyl ether and then dried. Yield: 0.035 g (72%). IR (KBr pellet)  $v_{max}/cm^{-1}$ : 3297 (N–H), 3012 (Ar–H), 2928–2856 (Aliph. C–H), 1618, 1593, 1516, 1501, 1471, 1419, 1395, 1309, 1234, 1155, 1112, 1090, 1008, 927, 828, 742. UV–Vis (DMF)  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 697 (4.67), 665 (4.66), 637 (4.33), 609 (4.21), 339 (4.61). MS (ES<sup>+</sup>), (*m*/*z*): 1525 [M–4I–2H]<sup>+</sup>. Anal. Calc. for C<sub>96</sub>H<sub>86</sub>N<sub>16</sub>O<sub>4</sub>I<sub>4</sub>: C, 56.65; H, 4.26; N, 11.01. Found: C, 56.90; H, 4.03; N, 11.32%.

# 2.3.6. Synthesis of quaternized zinc (II) phthalocyanine (5a)

The synthesis and purification was as outlined for **4a**, except zinc phthalocyanine **5** was employed instead of metal-free phthalocyanine **4**. The amounts of reagents employed were: zinc

phthalocyanine **5** (0.05 g,  $0.032 \times 10^{-3}$  mol), excess methyl iodide (0.002 L) in CHCl<sub>3</sub> (0.004 L). Yield: 0.045 g (66%). IR (KBr pellet)  $v_{max}/cm^{-1}$ : 3015 (Ar–H), 2932–2863 (Aliph. C–H), 1619, 1595, 1505, 1488, 1469, 1393, 1333, 1232, 1157, 1116, 1092, 1045, 944, 890, 748. UV–Vis (DMF)  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 677 (5.16), 610 (4.42), 355 (4.83). MS (ES<sup>+</sup>), (*m*/*z*): 1546 [M–4I–3CH<sub>3</sub>]<sup>+</sup>. *Anal.* Calc. for C<sub>96</sub>H<sub>84</sub>N<sub>16</sub>O<sub>4</sub>I<sub>4</sub>Zn: C, 54.94; H, 4.03; N, 10.68. Found: C, 55.21; H, 4.44; N, 10.96%.

# 2.3.7. Synthesis of quaternized cobalt (II) phthalocyanine (6a)

Synthesis and purification was as outlined for **4a** except cobalt phthalocyanine **6** instead of metal-free phthalocyanine **4** was employed. The amounts of reagents employed were: Cobalt phthalocyanine **6** (0.042 g,  $0.027 \times 10^{-3}$  mol), excess methyl iodide (0.0021 L) in CHCl<sub>3</sub> (0.0035 L). Yield: 0.030 g (50%). IR (KBr pellet)  $v_{max}$ /cm<sup>-1</sup>: 3018 (Ar–H), 2931–2865 (Aliph. C–H), 1618, 1594,



Fig. 1. The synthesis of the metal-free and metallophthalocyanines.



Fig. 2. The synthesis of the quaternized metal-free and metallophthalocyanines.

1507, 1489, 1469, 13,383, 1230, 1160, 1113, 1090, 948, 896, 748. UV–Vis (DMF):  $\lambda_{max}$ , nm (log ε): 662 (4.70), 603 (4.23), 335 (4.86). MS (ES<sup>+</sup>), (*m*/*z*): 1584 [M–4I]<sup>+</sup>. *Anal.* Calc. for C<sub>96</sub>H<sub>84</sub>N<sub>16</sub>O<sub>4</sub>I<sub>4</sub>-Co: C, 55.11; H, 4.05; N, 10.71. Found: C, 55.34; H, 3.88; N, 11.05%.

#### 2.3.8. General procedure for the oxidation of 4-nitrophenol

Experiments were carried out in a thermostated Schlenk vessel equipped with a condenser and stirrer. A solution of 4-nitrophenol and catalyst (cobalt complex **6**) in solvent was purified with nitrogen to remove oxygen. A mixture of 4-nitrophenol  $(1.32 \times 10^{-3} - \text{mol})$ , catalyst (cobalt complex **6**)  $(3.28 \times 10^{-6} \text{ mol})$  and DMF as solvent (0.01 L) was stirred in a Schlenk vessel for few minutes at room temperature. The oxidant *tert*-butylhydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) ( $1.64 \times 10^{-3}$  mol) was then added and the reaction mixture was stirred for the desired time. After certain time intervals, samples (0.0005 L) were taken. Each sample was injected in the GC twice, 1 µl each time. Formation of products and consumption of substrates were monitored by gas chromatography.

## 3. Results and discussion

#### 3.1. Syntheses and characterization

Starting from 4-((*E*)-{[4-(dimethylamino)phenyl]imino}methyl) phenol (1) and 4-nitrophthalonitrile (2), a general synthetic route for the synthesis of new phthalocyanines and their quaternized derivatives is given in Figs. 1 and 2. The first step in the synthetic procedure was to obtain  $4-[4-((E)-\{[4-(dimethylamino)phenyl]\}]$ imino}methyl)phenoxy]phthalonitrile. 4-[4-((*E*)-{[4-(Dimethylamino)phenyl]imino}methyl)phenoxy]phthalonitrile was synthesized by heating 4-((*E*)-{[4-(dimethylamino)phenyl]imino} methyl) phenol 1 and 4-nitrophthalonitrile 2 in the presence of K<sub>2</sub>CO<sub>3</sub> as a base in dry DMF at 50  $^\circ C$  for 72 h. The electron-withdrawing capability of dinitrile functionalities makes 4-nitrophthalonitrile susceptible to nucleophilic attack [31-33]. The base catalyzed nucleophilic substitution of the nitro group was performed in dry DMF at 50 °C under an inert nitrogen atmosphere. The self-condensation of the dicyano compound **3** in a high-boiling solvent in the presence of a few drops 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a strong base at reflux temperature under a nitrogen atmosphere afforded the metal-free phthalocyanine **4** as a green solid after purification by column chromatography (aluminum oxide) using CHCl<sub>3</sub>:CH<sub>3</sub>OH (100:4) as the solvent system. Conversion of 3 into the metallophthalocyanine derivatives 5 and 6 was accomplished through the usual cyclotetramerization reactions in the presence of the metal salts  $(Zn(CH_3COO)_2 \text{ and } CoCl_2)$ , with *n*-pentanol as the solvent. Quaternization of the metal-free and metallophthalocyanine complexes was achieved by reaction with excess methyl iodide as a quaternization agent in CHCl<sub>3</sub> at room temperature. The yields of the products were 72% for **4a**, 66% for **5a** and 50% for **6a**. All the phthalocyanines are new compounds. All the new compounds were characterized by means of IR, UV– Vis, MS spectral data and elemental analysis, all of which were compatible with the proposed structures.

In the IR spectrum of compound **3**, stretching vibrations of C°N (2225 cm<sup>-1</sup>) and aliphatic CH (2925–2896 cm<sup>-1</sup>) appeared at the expected frequencies. In the <sup>1</sup>H NMR spectrum of **3**, the OH group of compound **1** disappeared, as expected. In the <sup>13</sup>C NMR spectrum of **3**, the presence of nitrile carbon atoms was indicated, with peaks at  $\delta$  116.07 and 113.25 ppm. In the mass spectrum of compound **3**, the presence of a molecular ion peak at m/z = 367 [M+H]<sup>+</sup> confirmed the proposed structures.

The sharp peak in the IR spectrum for the C $\equiv$ N vibration of phthalonitrile **3** at 2225 cm<sup>-1</sup> disappeared after conversion into the metal-free phthalocyanine, indicative of metal-free phthalocyanine formation. The IR band characteristic of the metal-free phthalocyanine ring is an N–H stretching at 3289 cm<sup>-1</sup>. The IR spectra of metal-free **4** and metallophthalocyanines **5** and **6** are very similar, except for the v(NH) vibrations of the inner phthalocyanine core in the metal-free molecule. The NH protons of compound **4** could not be observed owing to the probable strong aggregation of the molecules [34,35]. The <sup>1</sup>H NMR spectrum of **4** indicated characteristic



Fig. 3. UV-Vis spectra of 4, 5 and 6 in CHCl<sub>3</sub>.

Table 1	
UV-Vis spectral data for Pcs <b>4a</b> , <b>5a</b> and <b>6a</b> in various solvents at a concentration of $10 \times 1$	$0^{-6}$ mol dm <sup>-3</sup> .

Solvent	Pcs	Q-Band, $\lambda_{max}$ , (nm)	Log $\varepsilon$	B-Band, $\lambda_{max}$ , (nm)	Log $\varepsilon$
DMF	4a	697, 665, 637, 609	4.67, 4.66, 4.33, 4.21	339	4.61
DMSO	4a	699, 665, 632, 610	4.56, 4.60, 4.49, 4.43	330	4.73
Pyridine	4a	700, 667, 636, 604	4.89, 4.86, 4.43, 4.26	345	4.64
DMF	5a	677, 610	5.16, 4.42	355	4.83
DMSO	5a	678, 609	5.24, 4.50	352	4.92
Pyridine	5a	679, 612	5.20, 4.50	353	4.90
DMF	6a	662, 603	4.70, 4.23	335	4.86
DMSO	6a	658, 599	4.59, 4.11	325	4.77
Pyridine	6a	658, 597	4.57, 4.11	339	4.75

protons at 8.40 (m, 4H, =C-H), 7.94 (m, 8H, Ar-H), 7.29–7.03 (m, 28H, Ar-H), 6.70 (m, 8H, Ar-H) and 2.98 (s, 24H, CH<sub>3</sub>) ppm. In the mass spectrum of compound **4**, the presence of the characteristic molecular ion peak at  $m/z = 1465 \text{ [M-2H]}^+$  confirmed the proposed structure.

The IR spectra of the zinc phthalocyanine **5** and cobalt phthalocyanine **6** clearly indicate the cyclotetramerization of the phthalonitrile derivative **3**, with the disappearance of the C°N peaks at 2225 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectrum of compound **5**, the aromatic protons appeared at 8.51, 7.88, 7.29–7.05 and 6.71 ppm, and the aliphatic CH<sub>3</sub> protons appeared at 2.94 ppm. <sup>1</sup>H NMR measurement of the cobalt phthalocyanine **6** was precluded owing to its paramagnetic nature. The mass spectra of the tetra-substituted phthalocyanines **5** and **6** confirmed the proposed structures, with the molecular ion being easily identified at 1532 [M+H]<sup>+</sup> and 1524 [M]<sup>+</sup>, respectively.

Quaternized tetra-substituted metal-free **4a** and metallophthalocyanines **5a** and **6a** are very soluble in pyridine, DMF and DMSO, as expected. Then tetracationic metal-free and metallophthalocyanines (**4a**, **5a** and **6a**) were obtained from the reaction of the corresponding phthalocyanines (**4**, **5** and **6**) with methyl iodide in chloroform. No major change was found in the IR spectra of **4**, **5** and **6** after quaternization. The MS spectra of compound **4a**, **5a** and **6a**, which show a peak at m/z = 1525 [M-4I-2H]<sup>+</sup>, 1546 [M-4I-3CH<sub>3</sub>]<sup>+</sup> and 1584 [M-4I]<sup>+</sup>, respectively, support the proposed formula for these compounds.

The UV–Vis spectra of the phthalocyanine complexes exhibit characteristic Q and B bands. Two principle  $\Pi \rightarrow \Pi^*$  transitions are seen for phthalocyanines: a Q-band, which is a  $\Pi \rightarrow \Pi^*$  transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the complexes and B bands were observed in the 300–350 nm region [36,37]. The ground state electronic spectra of the compounds showed characteristic absorptions in the Q band region at 702/666 nm for compound **4**, 684 nm for compound **5** and 673 nm for compound **6** in CHCl<sub>3</sub>. B band absorptions of the metal-free and metallophthalocyanines **4–6** were observed at (351, 285), (360, 280) and (376, 282) nm, respectively (Fig. 3).

The ground state electronic spectra of the quaternized tetrasubstituted metal-free **4a** and metallophthalocyanines **5a** and **6a** showed characteristic absorptions in the Q band region at 697/ 665 nm for **4a**, 677 nm for **5a**, 662 nm for **6a** in DMF. The B band region was observed around 335–355 nm in DMF. The shoulder of quaternized metal-free **4a**, zinc(II) **5a** and cobalt(II) **6a** phthalocyanines registered at 637/609, 610 and 603 nm, respectively (Table 1).

#### 3.2. Aggregation studies

Phthalocyanine compounds have a high aggregation tendency due to the interactions between their 18  $\pi$ -electron systems and the aggregation decreases the solubility of these compounds in many solvents. It also seriously affects their spectroscopic, photo-



Fig. 4. UV–Vis spectra of cobalt phthalocyanine 6 in different solvents (Concentration =  $10 \times 10^{-6}$  mol dm<sup>-3</sup>).



**Fig. 5.** Absorption spectra of zinc phthalocyanine **5** in chloroform at different concentrations,  $14 \times 10^{-6}$ ,  $12 \times 10^{-6}$ ,  $10 \times 10^{-6}$ ,  $8 \times 10^{-6}$ ,  $6 \times 10^{-6}$  mol dm<sup>-3</sup>.

physical, photochemical and electrochemical properties. Generally, aggregation is highly dependent on concentration, temperature, nature of the substituents, nature of solvents and complexed metal ions [38–42]. Phthalocyanine molecules can form two types of aggregates in solution called H- and J-type [43,44], depending on the nature and position of the substituents. Generally, phthalocyanine molecules form H-type aggregates in solution. J-type aggregation is rarely observed for phthalocyanine molecules. In this study, the aggregation behavior of the metal-free **4** and zinc(II) and cobalt(II) phthalocyanine complexes **5** and **6** was investigated in different solvents (chloroform, dichloromethane, THF, DMF, pyridine and DMSO) (see Fig. 4 for complex **6**). The metal-free phthalocyanine **4** did not show any aggregation in chloroform, dichloromethane, THF or pyridine (Table 2). Also, the zinc(II)

Table 2	
UV-Vis spectral data for Pcs 4, 5 and 6 in vario	us solvents at a concentration of $10 \times 10^{-6}$ mol dm <sup>-3</sup> .

Solvent	Pcs	Q-Band, $\lambda_{max}$ , (nm)	Log $\varepsilon$	B-Band, $\lambda_{max}$ , (nm)	Log $\varepsilon$
CHCl <sub>3</sub>	4	702, 666, 640, 607	4.82, 4.75, 4.36, 4.17	351, 285	4.71, 4.66
$CH_2Cl_2$	4	699, 665, 635, 605	4.72, 4.70, 4.41, 4.24	377	4.75
THF	4	699, 664, 634, 604	4.80, 4.78, 4.45, 4.30	373	4.80
Pyridine	4	702, 669, 638, 608	4.81, 4.78, 4.38, 4.23	378	4.81
CHCl <sub>3</sub>	5	685, 617	4.97, 4.29	360, 280	4.84, 4.77
CH <sub>2</sub> Cl <sub>2</sub>	5	683, 617	4.89, 4.30	356	4.83
THF	5	674, 607	5.17, 4.42	354	4.94
DMF	5	677, 609	5.14, 4.41	359	4.92
DMSO	5	679, 611	5.09, 4.38	360	4.90
CHCl <sub>3</sub>	6	673, 611	4.46, 4.08	376, 282	4.70, 4.84
CH <sub>2</sub> Cl <sub>2</sub>	6	665, 603	4.48, 4.00	323	4.55
THF	6	665, 600	4.58, 3.95	362	4.73
DMF	6	664, 599	4.58, 4.09	372	4.74
Pyridine	6	662, 596	4.58, 4.11	377	4.73



Fig. 6. UV–Vis spectra of quaternized metal-free phthalocyanine 4a in different solvents. (Concentration =  $10 \times 10^{-6}$  mol dm<sup>-3</sup>).



Fig. 7. UV–Vis spectra of quaternized zinc phthalocyanine 5a in different solvents. (Concentration =  $10\times10^{-6}$  mol dm $^{-3}.)$ 

phthalocyanine **5** did not show any aggregation in chloroform, dichloromethane, THF, DMF, DMSO or pyridine. On the other hand, the cobalt(II) phthalocyanine **6** did not show any aggregation in chloroform, dichloromethane or THF but this compound showed a small amount of aggregation in pyridine and DMF.

The aggregation behavior of the metal-free **4** and metallophthalocyanines **5** and **6** was also investigated at different concentrations in chloroform. In chloroform, as the concentration was increased, the intensity of the absorption of the Q band also increased and there were no new bands (normally blue shifted) due to aggregated species for all phthalocyanines (see Fig. 5 for



Fig. 8. UV–Vis spectra of quaternized cobalt phthalocyanine 6a in different solvents. (Concentration =  $10 \times 10^{-6}$  mol dm<sup>-3</sup>).

complex 5). The Beer–Lambert law was obeyed for all of the compounds in concentrations ranging from  $14\times10^{-6}$  to  $6\times10^{-6}\,mol\,dm^{-3}.$ 

Also, the aggregation behavior of the quaternized metal-free **4a** and quaternized zinc(II) and cobalt(II) phthalocyanine complexes **5a** and **6a** was investigated in different solvents (DMF, pyridine and DMSO) (see Fig. 6 for quaternized metal-free Pc, Fig. 7 for complex **5a** and Fig. 8 for complex **6a**). The quaternized metal-free phthalocyanine **4a** did not show any aggregation in DMF or pyridine, but this compound showed aggregation in DMSO due to the coordinating ability of these solvents. On the other hand, quaternized zinc(II) and cobalt(II) phthalocyanine complexes **5a** and **6a** did not show any aggregation in DMSO.

In addition, the aggregation behavior of the quaternized metalfree **4a** and metallophthalocyanines **5a**, **6a** was also investigated at different concentrations in DMF. In DMF, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to aggregated species for all the quaternized phthalocyanines. The Beer– Lambert law was obeyed for all of the compounds in concentrations ranging from  $14 \times 10^{-6}$  to  $6 \times 10^{-6}$  mol dm<sup>-3</sup>.

#### 3.3. Catalytic studies

#### 3.3.1. Oxidation of 4-nitrophenol with complex 6

Complex **6** has been used as a catalyst for the oxidation of 4-nitrophenol in DMF (90 °C, oxidant/substrate/cat = 500/200/1). In a typical catalytic reaction, The Schlenk tube was charged with 4-nitrophenol ( $0.65 \times 10^{-3}$  mol), cobalt complex **6** ( $3.28 \times 10^{-6}$ )

Table 3

Table /

The experimental results of 4-nitrophenol oxidation with cobalt complex 6.

Substrate (substrate/cat)	Oxidant	T (°C)	<i>t</i> (h)	Total conv. (%)	TON	$TOF(h^{-1})$	Hydroquinone selectivity (%)	Products <sup>a</sup> (%)
4-Nitrophenol (200/1)	TBHP	90	3	96	190	63	92	88.4 (hydroquinone)
4-Nitrophenol (400/1)	TBHP	90	3	80	317	105	91	7.6 (benzoquinone) 73.1 (hydroquinone)
4-Nitrophenol (600/1)	TBHP	90	3	68	404	134	88	6.9 (benzoquinone) 60 (hydroquinone)
4-Nitrophenol (800/1)	TBHP	90	3	61	483	161	88	8 (benzoquinone) 54 (hydroguinone)
4 Nitrophonol (1000/1)	TRUD	00	2	20	276	125	74	7 (benzoquinone)
4-1411000101 (1000/1)	TDHP	50	ر	00	370	123	/4	9.6 (benzoquinone)

Reaction conditions:  $1.64\times10^{-3}$  mol TBHP,  $3.28\times10^{-6}$  mol cobalt complex  $\boldsymbol{6}$  in 0.01 L DMF.

<sup>a</sup> Conversion was determined by GC.

Tuble 1				
The experimental results	of 4-nitrophenol	oxidation with	cobalt comp	lex

Entry	Substrate (substrate/cat)	Oxidant	T (°C)	<i>t</i> (h)	Total conv. (%)	TON	Hydroquinone selectivity (%)	Products <sup>a</sup> (%)
1	4-nitrophenol (200/1)	TBHP	90	3	96	190	92	88.4 (hydroquinone)
								7.6 (benzoquinone)
2	4-nitrophenol (200/1)	TBHP	70	3	87	172	91	79.7 (hydroquinone)
								7.3 (benzoquinone)
3	4-nitrophenol (200/1)	TBHP	50	3	65	128	87	57 (hydroquinone)
								8 (benzoquinone)
4	4-nitrophenol (200/1)	TBHP	25	3	57	112	85	49 (hydroquinone)
								8 (benzoquinone)
5	4-nitrophenol (200/1)	$H_2O_2$	90	3	67	132	94	63 (hydroquinone)
								4 (benzoquinone)
6	4-nitrophenol (200/1)	m-CPBA	90	3	37	73	78	29 (hydroquinone)
								8 (benzoquinone)

6.

*Reaction conditions:*  $0.65 \times 10^{-3}$  mol 4-nitrophenol,  $1.64 \times 10^{-3}$  mol TBHP,  $3.28 \times 10^{-6}$  mol cobalt complex **6** in 0.01 L DMF.

<sup>a</sup> Conversion was determined by GC.



**Fig. 9.** Time-dependent conversion of 4-nitrophenol oxidation. *Reaction conditions:*  $1.32 \times 10^{-3}$  mol 4-nitrophenol,  $1.64 \times 10^{-3}$  mol TBHP,  $3.28 \times 10^{-6}$  mol cobalt complex **6** in 10 ml DMF.

mol) and TBHP ( $1.64 \times 10^{-3}$  mol) in DMF (0.01 L) and refluxed at 90 °C with 900 rpm stirring. Control experiments showed that 4-nitrophenol oxidation with *tert*-butylhydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) did not occur in the absence of the catalyst under the same reaction conditions, confirming that the catalyst plays a prominent role in the oxidation process.

To examine the effect of the substrate to cobalt, the molar ratio was varied over the range 200–1000, while other parameters were kept constant. The experimental conditions were 90 °C,  $1.64 \times 10^{-3}$  mol TBHP, 0.01 L DMF for 3 h. The results are expected, as the substrate catalyst molar ratio decreases, the reaction rate

increases. 4-Nitrophenol was converted to hydroquinone (88.4%) and benzoquinone (7.6%) [45,46] with a TON of 190 by catalyst **6** in DMF after 3 h at 90  $^{\circ}$ C (Table 3).

To compare the oxidant effect, experiments were carried out using TBHP, *m*-CPBA and H<sub>2</sub>O<sub>2</sub> separately under similar reaction conditions for cobalt complex 6. The results presented here show that of the three oxidants, TBHP is the most efficient oxygen source for the catalyst, in terms of giving higher yields of the products (Table 4, entry 1). When *m*-CPBA was employed as an oxidant, total destruction of the phthalocyanine ring was observed without formation of the intermediate Co(III) phthalocyanine species. Thus, the lowest activity was observed for the oxidation of 4-nitrophenol, which proceeded with 37% yield over 3 h with a TON of 73 when using *m*-CPBA in DMF for the catalyst (cobalt complex 6) (Table 4, entry 6). Table 4 (entry 5) also shows that even though the product yields using H<sub>2</sub>O<sub>2</sub> as the oxidant were lower than those for TBHP, a higher selectivity for one of the products (hydroquinone) was obtained with H<sub>2</sub>O<sub>2</sub> as the oxidant compared to TBHP in DMF.

The time dependence of the catalytic oxidation of 4-nitrophenol for the catalyst (cobalt complex **6**) was studied with TBHP at 90 °C with a relative ratio of oxidant/substrate/cat of 500/400/1. The result is presented in Fig 9. An initiation period was not observed for catalyst, the 4-nitrophenol conversion increased as the reaction time was prolonged. Selectivity of the products was not significantly changed on increasing the reaction time. The presence of electron withdrawing ring substituent groups on the phthalocyanine complexes did not affect the rate of formation of active intermediates with the Co–Pc complex, and the rates of oxidation, in terms of conversion, are very close to each other.

The oxidation system was further examined by UV–Vis spectroscopy during the reaction in order to investigate the catalytic



**Fig. 10.** Time-dependent changes in the visible spectra of the oxidized cobalt complex **6** observed on addition of TBHP  $(1.64 \times 10^{-3} \text{ mol})$  to a reaction mixture containing  $1.32 \times 10^{-3}$  mol 4-nitrophenol and  $3.28 \times 10^{-6}$  mol cobalt complex **6** catalyst in 10 ml DMF: (b) 60 mir; (c) 120 mir; (d) 180 mir; min after addition of TBHP. All spectra for the oxidized cobalt complex **6** were taken after sixfold dilution with DMF. (a) The visible spectrum of the non-oxidized cobalt complex **6**.

mechanism for the Co-catalyzed 4-nitrophenol oxidation. The spectrum of cobalt(II) phthalocyanine **6** has been a subject several reports [47,48]. The spectra of MPc complexes are well known and consist of an intense band called the Q band in the visible region [49]. The spectrum (a) in Fig. 10 is typical spectrum for a monomeric form of cobalt complex **6**, with a Q band at 661 nm. Fig. 10 shows the spectral changes observed for the Co-Pc complex by addition of TBHP to the solution during the catalytic process. For cobalt complex 6, there was a shift in the Q band from 661 to 667 nm, and a decrease in the intensity of the Q band without any new bands being formed. The shift in the Q band is consistent with metal oxidation of CoII–Pc to CoIII–Pc [50]. There was no peak around 596 nm, which suggests ring oxidation. Thus addition of TBHP to solutions of Co-Pc resulted in only metal and not ring oxidation of the Co-Pc. As the catalysis progressed, there was a gradual decrease in the intensity of the Q band of the Co-Pc catalyst, suggesting catalyst degradation, as is typical [22] of MPc catalysts in homogeneous catalysis. The decomposition of the phthalocyanine complex during the oxidation of 4-nitrophenol is probably the result of the attack of the phthalocyanine ring by RO<sup>•</sup> and ROO<sup>•</sup> radicals. The color of the solution changed from green to light yellow as the catalysis progressed. However, the reaction products continued to form even after the catalyst had turned colorless, suggesting that once reaction intermediates are formed, the reaction can still proceed in the presence or absence of the original form of the catalyst.

# 4. Conclusion

In conclusion, this work has described the synthesis, characterization and aggregation behavior of new peripherally tetra-4-[4-((*E*)-{[4-(dimethylamino)phenyl]imino}methyl)phenoxy] substituted metal-free and metallophthalocyanines and their quaternized derivatives. The target symmetrical metal-free and metallophthalocyanines were separated by column chromatography and characterized by a combination of UV–Vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS spectroscopic data and elemental analysis. The solvent effect (chloroform, dichloromethane, DMF, DMSO, THF and pyridine) on the aggregation of these tetra-substituted phthalocyanines was found to be monomeric in chloroform, dichloromethane, THF and pyridine, and zinc(II) phthalocyanine **5** in chloroform,

dichloromethane, THF, pyridine, DMF and DMSO. On the other hand, cobalt(II) phthalocyanine 6 was found to be monomeric in chloroform, dichloromethane and THF, but this compound showed a little aggregation in DMF and pyridine. Quaternized metal-free phthalocyanine 4a did not show any aggregation in DMF or pyridine, but this compound showed aggregation in DMSO. In contrast, the quaternized zinc(II) and cobalt(II) phthalocyanine complexes 5a and 6a did not show any aggregation in DMF, pyridine or DMSO. Also, we have studied the aggregation behavior of these new metal-free, metallophthalocyanines **4-6** and their quaternized derivatives 4a-6a in different concentrations in chloroform and DMF, respectively. No aggregation was demonstrated in chloroform or DMF for concentration between  $14\times 10^{-6}$  and  $6\times 10^{-6}\,mol\,dm^{-3}.$  The results show that 4-nitrophenol was converted to products (hydroquinone and benzoquinone) in 96% conversion with cobalt complex **6**, within 3 h with TBHP in DMF at 90 °C. Control experiments performed without catalyst and using the corresponding metal salt as a catalyst produced no product. Mild reaction conditions, high yields of the products, short reaction time and inexpensive reagents make this catalytic system a useful oxidation method for 4-nitrophenol.

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