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Synthesis, characterization and catalytic activity of peripherally tetra-substituted Co(II) phthalocyanines for cyclohexene oxidation

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New 3,3-diphenylpropoxyphthalonitrile (5) was obtained from 3,3-diphenylpropanol (3) and 4-nitrophthalonitrile (4) with K_2CO_3 in DMF at 50 °C. The novel cobalt(II) phthalocyanine complexes, tetrakis-[2-(1,4-dioxa-8-azaspiro[4.5]dec-8-yl)ethoxy] phthalocyaninato cobalt(II) (2) and tetrakis-(3,3-diphenylpropoxy)phthalocyaninato cobalt(II) (6) were prepared by the reaction of the phthalonitrile derivatives 1 and 5 with $CoCl_2$ by microwave irradiation in 2-(dimethylamino)ethanol for at 175 °C, 350 W for 7 and 10 min, respectively. These new cobalt(II)phthalocyanine complexes were characterized by spectroscopic methods (IR, UV–visible and mass spectroscopy) as well as elemental analysis. Complexes 2 and 6 are employed as catalyst for the oxidation of cyclohexene using *tert*-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA), aerobic oxygen and hydrogen peroxide (H_2O_2) as oxidant. It is observed that both complexes can selectively oxidize cyclohexene to give 2-cyclohexene-1-ol as major product, and 2-cyclohexen-1-one and cyclohexene oxide as minor products. TBHP was found to be the best oxidant since minimal destruction of the catalyst, higher selectivity and conversion were observed in the products. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: phthalocyanine; cobalt; phthalonitrile; cyclohexene; oxidation; *tert*-butyl hydroperoxide

Introduction

Metalloporphyrin complexes are well known for their ability to actualize a wide range of oxidation reactions in homogeneous systems. These complexes, acting like cytochrome P-450 dependent monooxygenases, catalyze the oxidation of the relatively inert carbon–hydrogen bond under mild conditions.[1–4] Catalytic activities of metallophthalocyanines derived from their structural similarity to metallo-porphyrin complexes have been widely studied because of their rather cheap and facile preparation on a large scale and their chemical and thermal stability. Metallophthalocyanines exhibit a wide range of applications in various areas such as semiconductors, nonlinear optics, electrochromic display devices and liquid crystals.[5]

In particular, cobalt(II) phthalocyanines (CoPc) are habitually utilized in the fields of gas and radiation sensors, optoelectronics, oxidation processes and in medical applications. At the present time, CoPc is regarded as an object for the development of low-dimensional molecular magnets. Molecular magnets are regarded as possible candidates for potential applications in high-density information storage and quantum computers. Such prospective applications give a strong motivation to characterize and study the electronic structure and morphology of cobalt(II) phthalocyanine thin films since these determine the performance of devices. Moreover, the accurate assignment of the valance band and empty-state electronic features is of central importance for the profound understanding of this material and its interfaces with different substances.[6–10]

Transition metal complexes as catalysts for the oxidation of cyclohexene have attracted much attention in recent years, mainly for the oxidation products of cyclohexene, and the derivatives present highly reactive carbonyl groups in cycloaddition reactions.[11] Of the variety of ligands employed so far, noteworthy examples include porphyrin derivatives, macrocyclic compounds, phthalocyanine, and Schiff base.[12–15] Among these substrates, phthalocyanine transition metal complexes are attractive oxidation catalysts and can be prepared simply and cheaply for industrial applications. The catalytic oxidation of cyclohexene is attracting attention because its oxidation products (e.g. 2-cyclohexen-1-one, 2-cyclohexen-1-ol, epoxide) are very useful synthetic intermediates.[16] Synthetic metalloporphyrins, which are used as models of cytochrome P-450, are highly efficient homogeneous and heterogeneous catalysts for cyclohexene oxidation by various oxidants such as iodosylbenzene,[17] hydrogen peroxide and *tert*-butyl hydroperoxide.[18] The aerobic oxidation of olefins catalyzed by metalloporphyrins and metallophthalocyanines is gaining interest from economic and environmental viewpoints.[19] Additionally, cobalt(II) phthalocyanine complexes have been applied as catalysts for selective oxidation of olefins.[20] The oxidation of products such as aldehyde, ketones and alcohols is widely used in chemical industries and in the academic field. The oxidation products of cyclohexene studied in this work are 2-cyclohexen-1-one, 2-cyclohexene-1-ol and cyclohexene oxide. These products are of great importance to industrial processes as well as fine chemical syntheses. Phthalocyanines with different peripheral groups (especially electron-attracting groups such as halogenated, phenyl groups) have been largely studied for their ability in oxidation of cyclohexene.[21]

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Co(II) phthalocyanines are readily available oxidation catalysts and found to transfer oxygen from various oxygen donors to alkanes, alkenes, phenols and thiols in numerous studies.[15,22–33] Herein we report the synthesis and characterization of 4-[2-(1,4-dioxa-8-azaspiro[4.5]dec-8-yl)ethoxy] and 3,3-diphenylpropoxy group-substituted Co(II) phthalocyanines **2** and **6**. We also report on the use of complexes **2** and **6** as catalysts for the oxidation of cyclohexene, with the aim of improving product selectivity and increasing the range of products, and compare their catalytic activity.

Experimental

Materials

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All chemicals, solvents and reagents were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by a reported procedure.[34] 4-Nitrophthalonitrile,[35] 3,3-diphenylpropanol (**3**)[36] and 4-[2-(1,4-dioxa-8-azaspiro[4.5] dec-8-yl)ethoxy]phthalonitrile (**1**)[37] were synthesized according to the literature.

Equipment

FT-IR spectra were obtained on a PerkinElmer 1600 FT-IR spectrophotometer with the samples prepared as KBr pellets. Optical spectra in the UV–visible region were recorded with a PerkinElmer Lambda 25 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were recorded on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analyses were performed on a Costech ECS 4010 instrument. Melting points were measured on an electro thermal apparatus. A domestic microwave oven was used for all syntheses of phthalocyanines. Agilent Technologies 7820A equipment (30 m × 0.32 mm × 0.50 μm DB Wax capillary column, FID detector) was used for gas chromatographic measurements.

Synthesis

*4-(3,3-Diphenylpropoxy)phthalonitrile (**5**)*

3,3-Diphenylpropanol (**3**) (1 g, 4.71×10^{-3} mol) was dissolved in dry DMF (0.04 L) under N_2 atmosphere and 4-nitrophthalonitrile (**4**) (0.816 g, 4.71×10^{-3} mol) was added to the solution. After stirring for 10 min, finely ground anhydrous K_2CO_3 (1.94 g, 0.12 mol) was added portion-wise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50 °C for 3 days. The solution was then poured into ice-water (0.1 L). The precipitate formed was filtered off, washed first with water until the filtrate was neutral and then with diethyl ether and dried under vacuum over P_2O_5. The crude product was recrystallized from methanol. Yield 1.20 g (75%); m.p. 134–135 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3056 (Ar&bond;H), 2943–2870 (aliph. C&bond;H), 2227 (C&tbond;N), 1598, 1503, 1473, 1453, 1395, 1320, 1256, 1206, 1168, 1088, 1018, 942, 852, 829, 754, 696, 572, 524. ^{1}H NMR ($CDCl_3$), (δ: ppm): 7.70 (d, 1 H, $J = 8.5$ Hz, Ar&bond;H_5), 7.30–7.10 (m, 12 H, Ar&bond;H), 4.23 (t, 1 H, $J = 7.8$ Hz, CH&bond;CH_2), 4.00 (t, 2 H, $J = 6.3$ Hz, CH_2&bond;O), 2.62 (m, 2 H, CH_2&bond;CH_2). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 162.18 (Ar&bond;C_1), 143.77 (Ar&bond;C_{10}), 135.45 (Ar&bond;C_5), 129.01 (Ar&bond;C_{12}), 128.00 (Ar&bond;C_{11}), 126.96 (Ar&bond;C_{13}), 119.78 (Ar&bond;C_6), 119.59 (Ar&bond;C_2), 117.62 (Ar&bond;C_3), 116.01 C_{14}&tbond;N, 115.54 C_{15}&tbond;N, 107.40 (Ar&bond;C_4), 67.52 (C_7), 47.36 (C_9), 34.59 (C_8). MS (ES^+), (*m/z*): 380 $[M + Na + H_2O + H]^+$. $C_{23}H_{18}N_2O$: calcd C 81.63; H 5.36; N 8.28 %; found C 82.01; H 5.61; N 8.91.

*Tetrakis-(3.3-diphenylpropoxy)phthalocyaninato cobalt(II) (**6**)*

4-(3,3-Diphenylpropoxy)phthalonitrile (**5**) (0.3 g, 0.88 mol) and anhydrous $CoCl_2$ (0.057 g, 0.44×10^{-3} mol) were added in 2-(dimethylamino)ethanol (DMAE) (0.003 L). The mixture was then irradiated in a microwave oven at 175 °C, 350 W, for 10 min. After cooling to room temperature the reaction mixture was refluxed with ethanol (0.04 L) to precipitate the product, which was filtered off. The dark-blue solid product was washed with hot ethanol, diethyl ether and dried *in vacuo*. The blue crude product was purified by column chromatography on aluminium oxide using $CHCl_3$:CH_3OH (8:2) as eluent. The obtained solid was dried under vacuum over P_2O_5. Yield 0.160 g (48%); m.p. > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3058 (Ar&bond;H), 2924–2850 (aliph. C&bond;H), 1606, 1523, 1489, 1463, 1410, 1342, 1279, 1229, 1185, 1059, 1020, 958, 844, 821. UV–visible (DMF), λ_{maks} (log ε)nm: 329 (4.99), 607 (4.52), 667 (5.04). MS (ES^+); (*m/z*): 1518 $[M + K + 3Na]^+$. $C_{92}H_{72}N_8O_4Co$: calcd C 78.23; H 5.14; N 7.93 %; found C 77.90; H 5.49; N 8.17.

*Tetrakis-[2-(1,4-dioxa-8-azaspiro[4.5]dec-8-yl)ethoxy]phthalocyaninatocobalt(II) (**2**)*

4-[2-(1,4-Dioxa-8-azaspiro[4.5]dec-8-yl)ethoxy]phthalonitrile (**1**) (0.6 g, 1.91 mol) and anhydrous $CoCl_2$ (0.124 g, 0.95×10^{-3} mol) were added to 2-(dimethylamino)ethanol (DMAE) (0.006 L). The mixture was then irradiated by microwave oven at 175 °C, 350 W, for 7 min. After cooling to room temperature the reaction mixture was refluxed with ethanol (0.04 L) to precipitate the product, which was filtered off. The dark-blue solid product was washed with hot ethanol and diethyl ether and dried *in vacuo*. The blue crude product was purified by column chromatography on aluminium oxide using $CHCl_3$:CH_3OH (9:1) as eluent. The obtained solid was dried under vacuum over P_2O_5. Yield 0.27 g (45%); m.p. > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3044 (Ar&bond;H), 2926–2878 (aliph. C&bond;H), 1607, 1522, 1466, 1408, 1339, 1310, 1281, 1233, 1142, 1125, 1090, 963, 911, 820, 750, 666. UV–visible (DMF), λ_{maks} (log ε) nm: 326 (4.94), 608 (4.54), 664 (5.04). MS (ES^+); (*m/z*): 1312 $[M]^+$. $C_{68}H_{76}N_{12}O_{12}Co$: calcd C 62.24; H 5.84; N 12.81 %; found C 61.77; H 5.39; N 11.83.

General procedure for the oxidation of cyclohexene

Experiments were carried out in a thermostated Schlenk vessel equipped with a condenser and stirrer. The solution of cyclohexene and catalyst in solvent was purified with bubbling nitrogen gas to remove the oxygen. A mixture of cyclohexene (0.76×10^{-3} mol), catalyst (3.81×10^{-6} mol) and solvent (0.01 L) was stirred in a Schlenk vessel for few minutes at room temperature. The oxidant TBHP (1.90×10^{-3} mol) was then added and the reaction mixture was stirred for the desired time. The samples (0.005 L) were taken at certain time intervals. Each sample was injected at least twice in the gas chromatograph, 1 μL each time. Formation of products and consumption of substrates were monitored by gas chromatography (GC).

Results and Discussion

Synthesis and Characterization

The synthetic routes to novel peripherally tetra-substituted cobalt(II) phthalocyanines **2** and **6** are shown in Figs 1 and 2. The phthalonitrile

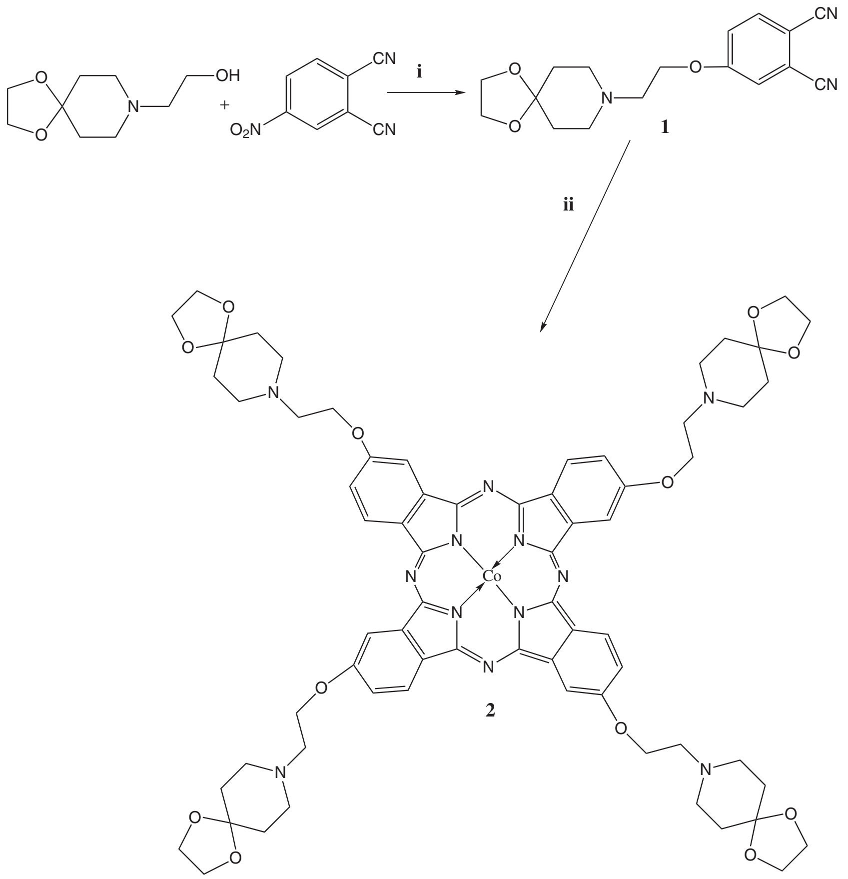

Figure 1. Synthesis of cobalt(II) phthalocyanine **2**. (i) Dry K_2CO_3, dry DMF, 50 °C. (ii) 2-(Dimethylamino)ethanol, microwave oven (MW), 175 °C, 350 W, $CoCl_2$

derivatives **1**[37] and **5** were obtained via a based-catalyzed (K_2CO_3) nucleophilic aromatic substitution reaction. Cyclotetramerization of **1** and **5** occurred in the presence of $CoCl_2$ to form the desired complexes: **2** and **6**, respectively. All of these new cobalt phthalocyanines were purified by column chromatography with aluminum oxide as adsorbent. They were obtained in a yield of 48% for **2** and 45% for **6** and were characterized by spectral data (IR, UV–visible spectroscopy, mass spectral data and elemental analysis). The characterization data of the new compounds are consistent with the assigned formula.

The IR spectra clearly indicate the formation of compound **5** with the appearance of absorption bands at 2227 cm^{-1} (C&tbond;N). In the ^1H NMR spectra of compound **5** aromatic protons appear at 7.70 (d, 1 H, $J = 8.5$ Hz, Ar&bond;H_5), 7.30–7.10 (m, 12 H, Ar&bond;H), and aliphatic protons appear at 4.23 (t, 1 H, $J = 7.8$ Hz, CH&bond;CH_2), 4.00 (t, 2 H, $J = 6.3$ Hz, CH_2&bond;O), 2.62 (m, 2 H, CH_2&bond;CH_2) ppm. The ^{13}C NMR spectra of compound **5** indicated aromatic carbon atoms between 162.18 and 107.40 ppm. Also nitrile carbon atoms for compound **5** were observed (116.01, 115.54 ppm). In the mass spectra of compound **5** the presence of molecular ion peak at $m/z = 380$ $[M + Na + H_2O + H]^+$ confirmed the proposed structures. The results of elemental analysis also confirmed the structure of compound **5**.

After conversion into cobalt phthalocyanine derivatives, the characteristic C&tbond;N stretch at 2231 cm^{-1} for **1** and 2227 cm^{-1} for **5** disappeared in the IR spectra, indicative of metallophthalocyanine formation. The ^1H NMR spectra of cobalt phthalocyanines **2** and **6** could not be taken due to the paramagnetic cobalt(II) centers. In the mass spectrum of cobalt phthalocyanines **2** and **6**, the presence of molecular ion peaks at m/z 1312 $[M]^+$ and 1518 $[M + K + 3Na]^+$, respectively, confirmed the proposed structures. The results of elemental analysis also confirmed the structure of complexes **2** and **6**.

The metallophthalocyanines display typical electronic spectra with two strong absorption regions: one of them in the UV region at about 300–350 nm (B band) and the other in the visible region at 600–700 nm (Q band).[38] The electronic absorption spectra of cobalt phthalocyanines **2** and **6** in DMF at room temperature are shown in Fig. 3. UV–visible spectra of cobalt phthalocyanine **2** (in DMF) split Q bands appeared at 664 and 608 nm, while the split B band remained at 326 nm. UV–visible spectra of cobalt phthalocyanine **6** (in DMF) exhibited an intense single Q band absorption of $\pi \rightarrow \pi^*$ transitions around 667–607 nm and B band in the UV region around 329 nm.[39]

Catalytic Studies

*Oxidation of cyclohexene with **2** and **6***

The catalytic activity and selectivity of **2** and **6** have been studied for the oxidation of cyclohexene with TBHP as the model compound under similar experimental conditions in DMF (Tables 1–4). In a typical catalytic reaction, a Schlenk tube was charged with cyclohexene (0.76×10^{-3} mol), complex **2** (3.81×10^{-6} mol) or complex **6** (3.53×10^{-6} mol) and TBHP (1.90×10^{-3} mol) in DMF (0.01 L) and refluxed at 90 °C with 900 rpm stirring. Control experiments show that cyclohexene oxidation with TBHP, *m*-CPBA and H_2O_2 did not occur in the absence of catalyst under the same reaction conditions, confirming that the catalyst plays a prominent

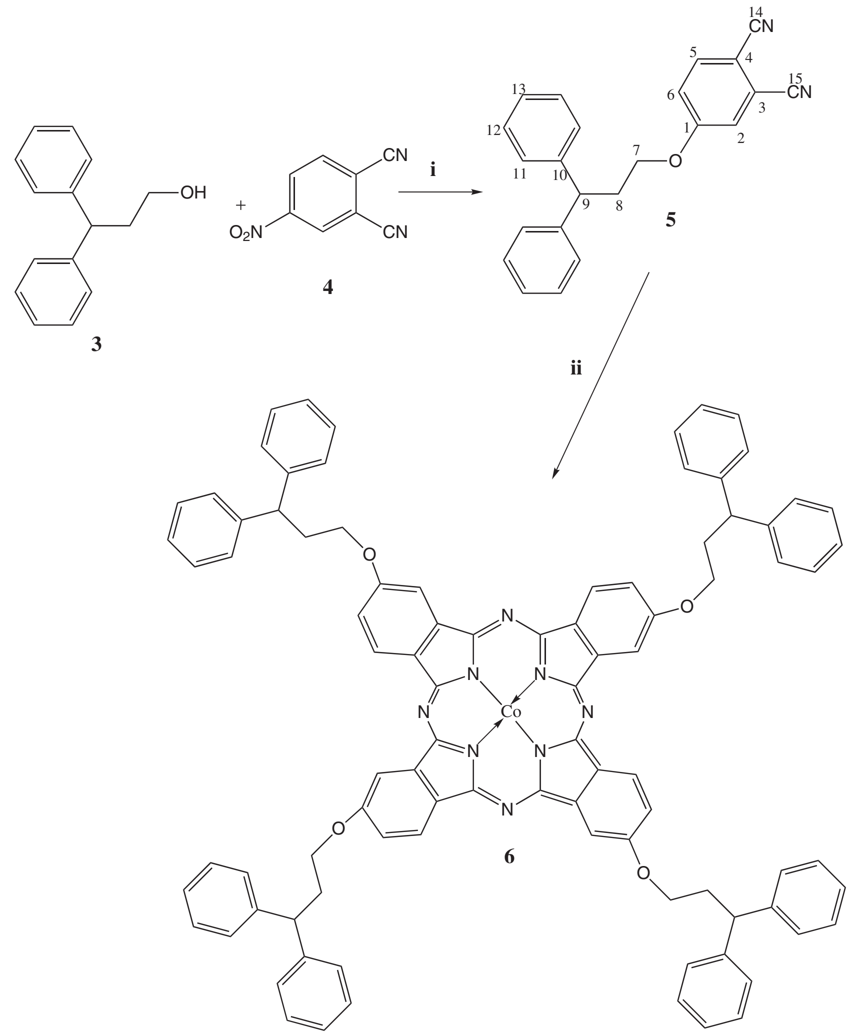

Figure 2. Synthesis of cobalt(II) phthalocyanine **6**. (i) Dry K_2CO_3, dry DMF, 50 °C. (ii) 2-(Dimethylamino)ethanol, MW, 175 °C, 350 W, $CoCl_2$

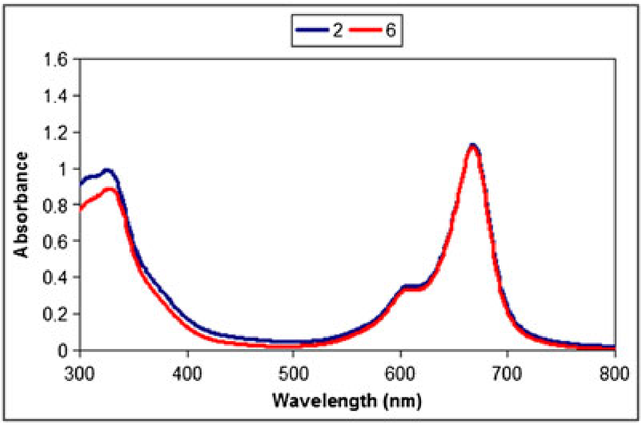

Figure 3. UV–visible spectrum in DMF for complexes **2** and **6**

role in the oxidation process. As shown in Tables 1–4, comparative studies of the catalytic activity of **2** and **6** for oxidation of cyclohexene revealed that both complexes are active catalysts in DMF. The oxidation reactions gave cyclohexenol as the main product and 2-cyclohexen-1-one and cyclohexene epoxide in small yields, which are evidently identified using GC by both spiking and comparison with standards (Fig. 4). In order to obtain maximum conversion of cyclohexene, the catalytic reactions were carried out varying the reaction temperature, time and different oxidants and substrate/catalyst ratio.

The results of the catalytic oxidation of cyclohexene by TBHP in the presence of **2** and **6** are shown in Fig. 5(a) and (b), respectively, which shows the variation of product yield with reaction time. A higher yield was obtained for cyclohexenol than cyclohexenone and cyclohexene epoxide for both catalysts. The yields for cyclohexenone and cyclohexene epoxide were similar for catalysts **2** and **6**. The yield of the three products increased, but leveled off with time. This level-off was most likely due to the degradation of the CoPc catalyst by oxidant with time.

To examine the effect of substrate to cobalt, the molar ratio was carried out in the range of 200–800, while other parameters were kept constant. The experimental conditions were 90 °C, 1.90×10^{-3} mol TBHP and 0.01 L DMF for 3 h. The results are shown in Table 1. As expected, with a decrease of the substrate catalyst molar ratio the reaction rate increased. At each different substrate/catalyst ratio the oxidation of cyclohexene gave the same main product (2-cyclohexene-1-ol) with a selectivity of ~60% and 65% for **2** and **6**, respectively.

Table 1. Effect of amount of substrate on cyclohexene oxidation with complexes **2** and **6**

Catalyst	Subs./cat.	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
2	200/1	55	16	11	92	179	71
6		67	15	15	98	184	73
2	300/1	53	24	11	88	257	102
6		60	15	14	90	255	102
2	400/1	48	22	11	81	315	126
6		56	15	14	85	319	127
2	500/1	46	20	11	77	374	149
6		52	15	14	81	378	151
2	600/1	39	17	9	65	388	129
6		38	12	13	63	376	125
2	800/1	28	12	7	47	375	125
6		24	10	11	45	358	119

[a] 2-Cyclohexen-1-ol.
[b] 2-Cyclohexen-1-one.
[c] Cyclolohexene oxide.
[d] TON, moles of product/moles of catalyst.
[e] TOF, moles of product/moles of catalyst × time.
Conversion was determined by GC.

Table 2. Effect of different oxidants on cyclohexene oxidation with complex **2**

Catalyst	Oxidant	Alcohol[a]	Ketone[b]	Epoxide[c]	Total conv. (%)	TON[d]	TOF[e] (h^{-1})
2	TBHP	53	24	11	88	263	87
6		67	16	15	90	270	90
2	H_2O_2	46	15	7	68	203	67
6		39	20	14	73	219	73
2	*m*-CPBA	49	19	12	80	239	79
6		18	16	11	45	135	45
2	Free oxidant	—	—	—	—	—	—
6		—	—	—	—	—	—

[a] 2-Cyclohexen-1-ol.
[b] 2-Cyclohexen-1-one.
[c] Cyclolohexene oxide.
[d] TON, moles of product/moles of catalyst.
[e] TOF, moles of product/moles of catalyst × time.
Conversion was determined by GC.

The effect of oxygen source on the reaction rate of cyclohexene oxidation was investigated for TBHP, *m*-CPBA, aerobic oxygen and H_2O_2. With the exception of the oxidant, all experimental conditions were kept constant for the catalytic reactions. The data are given in Table 2 and Fig. 6. There was no conversion for both complexes when the aerobic oxygen was used as oxidant. The results showed that **2** and **6** exhibit significantly higher activity with TBHP than with the other studied oxidants. The control experiment showed that the cyclohexene was not oxidized in the absence of oxidant. We observed that the selectivity of **2**-catalyzed oxidation was not dependent on the nature of the oxidant, but in the case of **6** the selectivity of alcohol decreased while the selectivity of epoxide increased. The substrate-to-oxidant ratio is another important parameter influencing the results of this oxidation reaction. The effect of oxidant/catalyst ratio on the rate of cyclohexene was also studied in the range of 300/1–900/1 (Table 3). The rate of the reaction increased with increasing oxidant/catalyst ratio up to 500/1. Further increase in this ratio led to decreased conversion. It is difficult to explain the oxidant effect at this stage, but it is possible that the coordination around the cobalt ion may change and produce inactive intermediate species.

Investigation into the effect of the reaction temperature on the oxidation of cyclohexene with **2** and **6** showed that as the reaction temperature was raised the catalyst activity increased, but 2-cyclohexen-1-ol selectivity was barely affected. The experiments were conducted in the temperature range 25–90 °C, with oxidant/substrate/catalyst = 500/200/1 and TBHP, in DMF, over 3 h (Table 4). The overall conversion was increased 50% when the temperature was raised from 25 to 90 °C. The highest conversion (92%) was obtained with TOF = 72 for complex **2** and (98%) and with TOF = 64 for complex **6** at 90 °C.

Table 3. Effect of amount of oxidant on cyclohexene oxidation with complexes **2** and **6**

Catalyst	Oxidant/catalyst	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
2	300/1	43	16	8	67	200	66
6		51	15	12	78	231	92
2	400/1	46	18	9	72	215	71
6		53	16	13	82	243	81
2	500/1	53	24	11	88	263	87
6		60	15	14	90	264	88
2	600/1	45	22	12	79	236	78
6		50	20	10	80	234	78
2	900/1	29	19	10	58	173	28
6		39	17	9	65	195	65

[a] 2-Cyclohexen-1-ol.
[b] 2-Cyclohexen-1-one.
[c] Cyclolohexene oxide.
[d] TON, moles of product/moles of catalyst.
[e] TOF, moles of product/moles of catalyst × time.
Conversion was determined by GC.

Table 4. Effect of temperature on cyclohexene oxidation with complexes **2** and **6**

Catalyst	*T* (°C)	Alcohol[a]	Ketone[b]	Epoxide[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
2	25	29	19	3	51	89	35
6		27	13	9	49	97	32
2	50	52	25	9	86	149	59
6		53	13	12	78	154	51
2	70	53	26	11	90	159	63
6		64	16	15	95	188	63
2	90	55	26	11	92	181	72
6		67	16	15	98	194	64

[a] 2-Cyclohexen-1-ol.
[b] 2-Cyclohexen-1- one.
[c] Cyclolohexene oxide.
[d] TON, moles of product/moles of catalyst.
[e] TOF, moles of product/moles of catalyst × time.
Conversion was determined by GC.

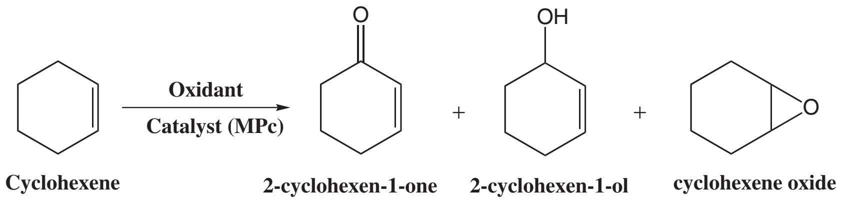

Figure 4. Product formed through oxidation of cyclohexene by TBHP, *m*-CPBA and H_2O_2 in the presence of complexes **2** and **6**

As shown in Table 5, the performance of the Co-Pc catalysts **2** and **6** towards the cyclohexene oxidation was better compared to some other MPc and M-porphyrin catalysts (like Fe, Zn, Cu and Mn). We obtained the best reported results in terms of TOF in the literature for homogeneous oxidation of cyclohexene with TBHP in the presence of Co-Pc.

The oxidation system was further examined by UV–visible spectroscopy during the processes in order to investigate the catalytic mechanism for the Co-catalyzed cyclohexene oxidation. The spectra of cobalt(II) phthalocyanines has been the subject of several reports.[15,40–50] The spectrum of metal–phthalocyanine (MPc) complexes is well known and consists of an intense band, called the Q band, in the visible region.[51] The spectrum in Figs 7 and 8 show the typical spectrum of monomeric form of CoPc with a Q band at 664 (for **2**) and 667 nm (for **6**) and also the electronic spectral changes of both catalysts during the course of the catalytic

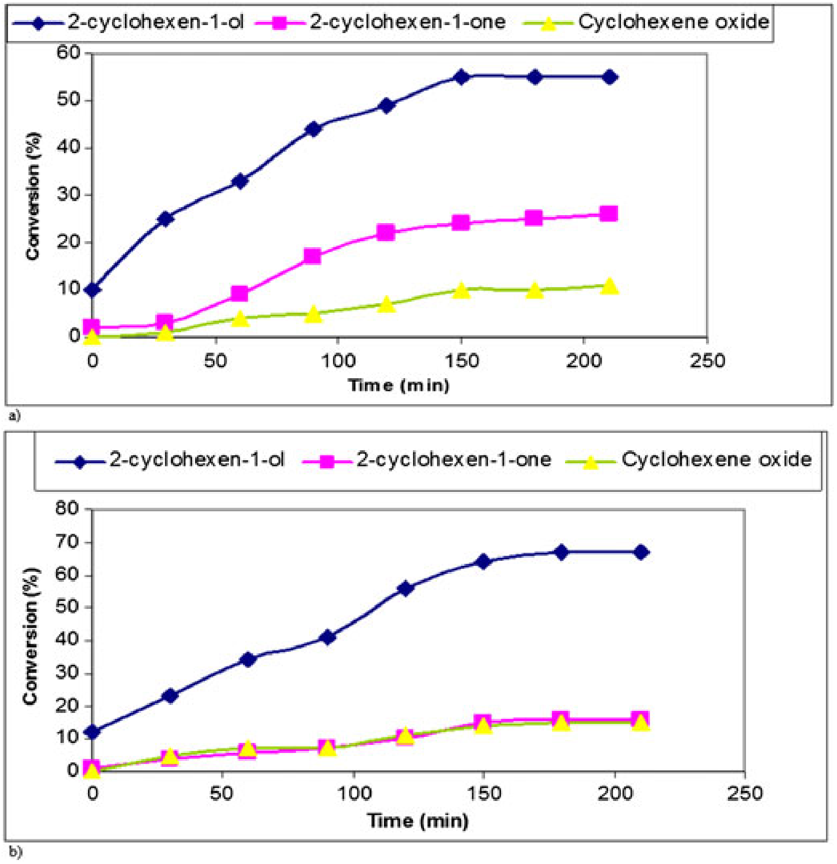

Figure 5. Time-dependent conversion of cyclohexene oxidation with TBHP as an oxidant (a) for catalyst **2** and (b) for catalyst **6**

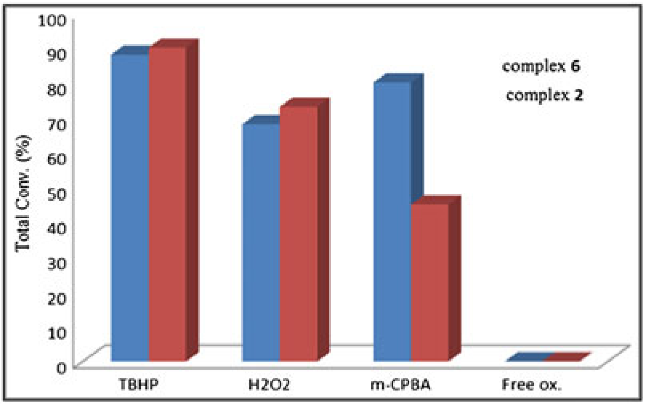

Figure 6. Oxidant effect on cyclohexene oxidation

reaction in the presence of TBHP. The Q band shifted to 672 and 671 nm for complexes **2** and **6**, respectively, with a decrease in intensity of the Q band without any new band being formed. The shift in the Q band is consistent with metal oxidation of Co(II)-Pc to Co(III)-Pc.[30] There is no peak around 480 nm, suggesting ring oxidation. Thus addition of TBHP to solutions of Co-Pc resulted in only metal and not ring oxidation of Co-Pc. As 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 cyclohexene is probably a result of the attack of the phthalocyanine ring by the RO· and ROO· radicals which are produced from TBHP. The color of the solution changed from blue to green as catalysis progressed. However, the reaction products continued to form even after the catalyst had turned yellow, suggesting that once reaction intermediates are formed the reaction can still proceed in the presence or absence of the original form of the catalyst.

Conclusion

We have presented the synthesis and characterization of new peripherally tetra-substituted Co(II) phthalocyanines **2** and **6** using spectroscopic methods. The target symmetrical Co(II) phthalocyanines **2** and **6** were separated by column chromatography and characterized by a combination of UV–visible, IR, ^{1}H NMR, ^{13}C NMR, mass spectroscopic data and elemental analysis. This work has determined catalytic activities of Co(II) phthalocyanines **2** and **6** on cyclohexene oxidation. There are few reports about catalytic studies for Co(II) phthalocyanines. The results show that cyclohexene was converted to 2-cyclohexene-1-ol as a major product, and 2-cyclohexen-1-one and cyclohexene oxide as minor products, with 92% and 98% with **2** and **6** respectively, within 3 h with TBHP in DMF at 90 °C. The most promising observation is that cyclohexenol is found to be the major product in all

Table 5. Catalytic activities towards the homogeneous oxidation of cyclohexene of some previously reported catalysts

Catalyst	Relaxation time (h)	Relaxation temp. (°C)	Oxidant	Conv. (%)	Ref.
Mn(tbpcH$_2$[a])	24	rt[g]	O_2	~45	52
Fe(tbpcH$_2$[a])				~55	
Co(tbpcH$_2$[a])				~30	
Fe(TMP[b])Cl	10 min	25	*m*-CPBA	89	53
Mn(PFTDCPP[c])	3	nr[h]	PhIO	93	54
MnTMpyP	16	rt[g]	PhIO	28	55
FeTMpyP				29	
MoTMpyP				0	
MnTTAPP				39	
Cl$_{16}$FePc[d]	8	nr[h]	TBHP	45.3	22
FePc[d]					
CoPc[d]					
Co[N^O]$_2$ Cu[N^O[e]]$_2$	8	75	H_2O_2	27.6	56
				43.50	
Cu(II)(L-prolinate)$_2$	24	22	O_2	60	57
		40		20	
[Mn(Me$_2$salpnMe$_2$[f])]	8	40	TBHP	50.9	58
[Co(Me$_2$salpnMe$_2$[f])]				42.7	
[Cu(Me$_2$salpnMe$_2$[f])]				36.9	
[Ni(Me$_2$salpnMe$_2$[f])]				23.8	
Co(salen)–POM	6	60	H_2O_2	91	59

[a] tbpcH$_2$, *tetra-tert*-butylphthalocyanine.
[b] TMP, *meso*-tetramesitylporphyrin.
[c] PFTDCPP, 5-(pentaflorophenyl)-10,15-20-tri(2,6-dichlorophenyl)porphyrin.
[d] Pc, phthalocyanine.
[e] N^O, 2-pyrazinecarboxylic acid.
[f] Me$_2$salpnMe$_2$, *N,N*-bis-(α-methylsalicylidene)-2,2-dimethylpropane-1.
[g] rt, room temperature.
[h] nr, not reported.

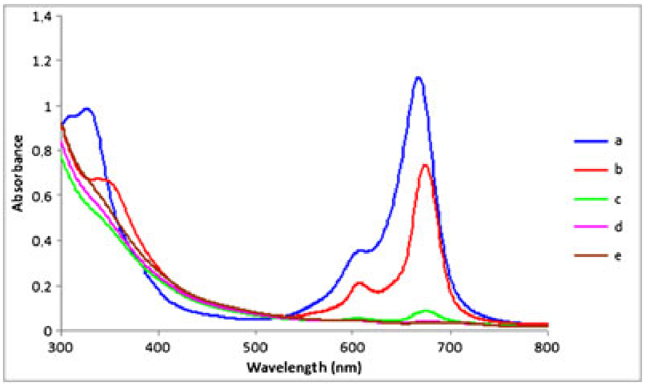

Figure 7. Time-dependent changes in the visible spectrum of the oxidized complex **2** observed on addition of TBHP (1.90×10^{-3} mol) to a reaction mixture containing 0.76×10^{-3} mol cyclohexene and 3.81×10^{-6} mol complex **2** catalyst in 10 ml: (b) 45 min; (c) 90 min; (d) 135 min; (e) 180 min after addition of TBHP. All spectra for the oxidized complex **2** were taken after sixfold dilution with DMF. (a) Visible spectrum of (non-oxidized) complex **2**

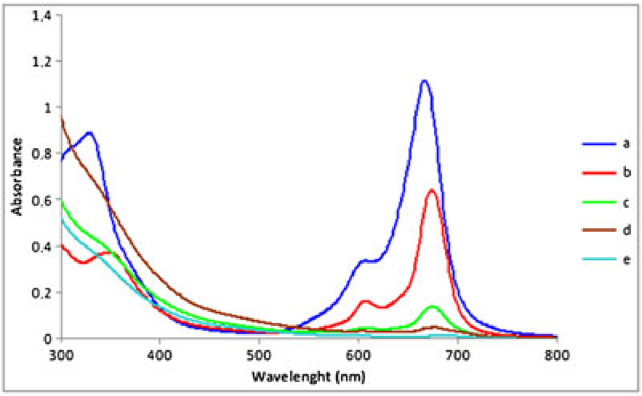

Figure 8. Time-dependent changes in the visible spectrum of the oxidized complex **6** observed on addition of TBHP (1.76×10^{-3} mol) to a reaction mixture containing 0.70×10^{-3} mol cyclohexene and 3.53×10^{-6} mol complex **6** catalyst in 10 ml: (b) 45 min; (c) 90 min; (d) 135 min; (e) 180 min after addition of TBHP. All spectra for the oxidized complex **6** were taken after sixfold dilution with DMF. (a) Visible spectrum of (non-oxidized) complex **6**

of the catalytic tests. Substrate effect, temperature effect and oxidant effect were also discussed in this work. Control experiments performed without catalyst and the corresponding metal salt as catalyst produced no products in the reaction mixture.

Mild reaction conditions, high yields of the products, short reaction time and inexpensive reagents make this catalytic system a useful oxidation method for cyclohexene.

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References

[1] M. J. Napa, C. A. Tolman, *Inorg. Chem.* **1985**, *24*, 4711.
[2] W. Nam, Y. M. Goh, Y. J. Lee, M. H. Lim, C. Kim, *Inorg. Chem.* **1999**, *38*, 3238.
[3] X. B. Zhang, C. C. Guo, J. B. Xu, R. Q. Yu, *J. Mol. Cat. A: Chem.* **2000**, *154*, 31.
[4] K. T. Moore, I. T. Horvath, M. J. Therien, *Inorg. Chem.* **2000**, *39*, 3125.
[5] J. Simon, T. Toupance, in *Comprehensive Supramolecular Chemistry*, Vol. *10* (Ed.: D. N. Reinhoudt), Pergamon Press, Exeter, **1996**, 637.
[6] G. Das, B. Sain, S. Kumar, M. O. Garg, D. G. Murali, *Catal. Today* **2009**, *141*, 152.
[7] J. Yang, D. Mu, Y. Gao, J. Tan, A. Lu, D. Ma, *J. Natur. Gas. Chem.* **2012**, *21*, 265.
[8] Y. Y. Yao, F. X. Sheng, X. P. Wu, W. Y. Lv, W. X. Zhu *J. Funct. Mater.* **2011**, *42*, 2171.
[9] G. Lu, Y. Zhou, Y. Xiang, D. Xia, *J. Porphyr. Phthalocyan.* **2010**, *14*, 904.
[10] J. K. Joseph, S. L. Jain, B. Sain, *Ind. Eng. Chem. Res.* **2010**, *49*, 6674.
[11] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, *J. Catal.* **2001**, *202*, 245.
[12] A. Sakthivel, S. E. Dapurkar, P. Selvam, *Appl. Catal. A: Gen.* **2003**, *246*, 283.
[13] H. Kameyama, F. Narumi, T. Hattor, H. Kameyama, *J. Mol. Catal. A: Chem.* **2006**, *258*, 172.
[14] J. P. M. Niederer, W. F. Holderich, *Appl. Catal. A: Gen.* **2002**, *229*, 51.
[15] N. Sehlotho, T. Nyokong, *J. Mol. Catal. A: Chem.* **2004**, *209*, 51.
[16] Z. Bohstrom, I. Rico-Lattes, K. Holmberg, *Green Chem.* **2010**, *12*, 1861.
[17] W. Adam, C. Mock-Knoblauch, C. R. Saha-Moller, M. Herderich, *J. Am. Chem. Soc.* **2000**, *122*, 9685.
[18] N. A. Stephenson, A. T. Bell, *J. Mol. Catal. A: Chem.* **2007**, *275*, 54.
[19] O. Vakuliuk, F. G. Mutti, M. Lara, D. T. Gryko, W. Kroutil, *Tetrahedron Lett.* **2011**, *52*, 3555.
[20] E. M. Gaigneaux, R. Maggi, P. Ruiz, B. Delmon, *J. Mol. Catal. A: Chem.* **1996**, *109*, 67.
[21] N. Grootboom, T. Nyokong, *J. Mol. Catal. A: Chem.* **2002**, *179*, 113.
[22] N. Sehlotho, T. Nyokong, *J. Mol. Catal. A: Chem.* **2004**, *219*, 201.
[23] B. Basu, S. Satapathy, A. K. Bhatnagar, *Catal. Rev. Sci. Eng.* **1993**, *35*, 571.
[24] M. Chibwe, L. Ukrainczyk, S. A. Boyd, T. J. Pinnavaia, *J. Mol. Catal. A: Chem.* **1996**, *113*, 249.
[25] S. M. S. Chauhan, B. Kalra, P. P. Mohapatra, *J. Mol. Catal. A: Chem.* **1999**, *137*, 85.
[26] V. M. Kothari, J. J. Tazuma, *J. Catal.* **1976**, *41*, 180.
[27] T. Ichinohe, H. Miyasaka, A. Isoda, M. Kimura, K. Hanabusa, H. Shirai, *Funct. Poly.* **2000**, *43*, 63.
[28] T. V. Rao, K. N. Rao, S. L. Jain, B. Sain, *Synth. Commun.* **2002**, *32*, 1151.
[29] M. Ozer, F. Yılmaz, H. Erer, I. Kani, Ö. Bekaroglu, *App. Organomet. Chem.* **2009**, *23*, 55.
[30] F. Zhao, J. Zhang, T. Abe, D. Wöhrle, M. Kaneko, *J. Mol. Catal. A: Chem.* **1999**, *145*, 245.
[31] H. Turk, Y. Cimen, *J. Mol. Catal. A: Chem.* **2005**, *234*, 19.
[32] Y. Cimen, H. Türk, *Appl. Catal. A* **2008**, *340*, 52.
[33] F. Yılmaz, M. Özer, I. Kani, O. Bekaroglu, *Catal. Lett.* **2009**, *130*, 642.
[34] D. D. Perin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2nd edn, Pegamon Press, Oxford, **1989**.
[35] J. G. Young, W. J. Onyebuagu, *J. Org. Chem.* **1990**, *55*, 2155.
[36] A. G. Pinna, G. Cignarella, G. Loriga, G. Murineddu, J. M. Mussinu, S. Ruiu, P. Faddad, W. Frattad, *Bioorg. Med. Chem.* **2002**, *10*, 1929.
[37] E. T. Saka, C. Göl, M. Durmuş, H. Kantekin, Z. Bıyıklıoğlu, *J. Photochem. Photobiol. A: Chem.* **2012**, *241*, 67.
[38] M. K. Sener, A. Koca, A. Gül, M. B. Koçak, *Polyhedron* **2007**, *26*, 1070.
[39] I. Gürol, V. Ahsen, O. Bekaroğlu, *J. Chem. Soc. Dalton Trans.* **1994**, *4*, 497.
[40] Z. Bıyıklıoğlu, H. Kantekin, I. Acar, *Inorg. Chem. Commun.* **2008**, *11*, 1448.
[41] B. Agboola, K. I. Ozoemena, T. Nyokong, *Electrochim. Acta* **2006**, *51*, 4379.
[42] M. Gulppi, S. Griveau, F. Bediuoi, J. H. Zagal, *Electrochim. Acta* **2001**, *46*, 3397.
[43] Z. Bıyıklıoğlu, H. Kantekin, *Dyes Pigments* **2009**, *80*, 17.
[44] G. Gümüş, A. Gül, V. Ahsen, *New J. Chem.* **1997**, *21*, 589.
[45] J. Haber, M. Kłosowski, J. Połtowicz, *J. Mol. Catal. A: Chem.* **2003**, *201*, 167.
[46] A. U. Ugur, A. Erdogmus, A. Koca, U. Avcıata, *Polyhedron* **2010**, *29*, 3310.
[47] I. A. Akinbulu, T. Nyokong, *Polyhedron* **2010**, *29*, 1257.
[48] A. Alemdar, A. R. Ozkaya, M. Bulut, *Polyhedron* **2009**, *28*, 3788.
[49] J. Obirai, T. Nyokong, *Electrochim. Acta* **2005**, *50*, 5427.
[50] V. B. Sharma, S. L. Jain, B. Sain, *Tetrahedron Lett.* **2003**, *44*, 383.
[51] M. J. Stillman, T. Nyokong, in *Phthalocyanines: Properties and Applications*, Vol. *1* (Eds: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1989**, 244.
[52] K. Kasuga, T. Tsuboi, M. Handa, T. Sugimori, K. Sagobe, *Inorg. Chem. Commun.* **1999**, *2*, 507.
[53] M. H. Lim, S. W. Jin, Y. J. Lee, G. J. Jhon, W. Nam, C. Kim, *Bull. Korean Chem. Soc.* **2001**, *22*, 93.
[54] G. D. Fabio, R. John, S. Lindsay, G. F. Antonio, D. Marilda, *J. Mol. Catal. A: Chem.* **2000**, *164*, 97.
[55] E. M. Serwickaa, J. Połtowicza, K. Bahranowskib, Z. Olejniczakc, W. Jones, *Appl. Catal. A: Gen.* **2004**, *275*, 9.
[56] C. Pratap, K. Shigeru, K. Toshinori, S. Shigeo, *Polyhedron* **2009**, *28*, 370.
[57] S. Goberna-Ferrón, V. Lillo, J. R. Galán-Mascarós, *Catal. Commun.* **2012**, *23*, 30.
[58] M. Salavati-Niasari, P. Salemi, F. Davar, *J. Mol. Catal. A: Chem.* **2005**, *238*, 215.
[59] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, N. Rasouli, *Catal. Commun.* **2008**, *9*, 219.