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Synthesis, characterization and catalytic activity of novel Co(II) and Pd(II)-perfluoroalkylphthalocyanine in fluorous biphasic system; benzyl alcohol oxidation

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Tetrakis[heptadecafluorononyl] substituted phthalocyanine complexes were prepared by template synthesis from 4-(heptadecafluorononyloxy)phthalonitrile with $Co(CH_3COO)_2 4H_2O$ or $PdCl_2$ in 2-*N*, *N*-dimethylaminoethanol. The corresponding phthalonitrile was obtained from heptadecafluorononan-1-ol and 4-nitrophthalonitrile with K_2CO_3 in DMF at 50 °C. The structures of the compounds were characterized by elemental analysis, FTIR, UV–vis and MALDI-TOF MS spectroscopic methods. Metallophthalocyanines are soluble in fluoroalkanes such as perfluoromethylcyclohexane (PFMCH). The complexes were tested as catalysts for benzyl alcohol oxidation with *tert*-butylhydroperoxide (TBHP) in an organic–fluorous biphasic system (*n*-hexane–PFMCH). The oxidation of benzyl alcohol was also tested with different oxidants, such as hydrogen peroxide, *m*-chloroperoxybenzoic acid, molecular oxygen and oxone in *n*-hexane–PFMCH. TBHP was found to be the best oxidant for benzyl alcohol oxidation since higher conversion and selectivity were observed when this oxidant was used. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: biphasic catalysis; oxidation; phthalocyanine

Introduction

The interest of researchers in the phthalocyanine (Pc) has increased due to its useful features.[1–4] The chemical and physical characteristics of these compounds vary with the central metal ion, peripheral substitution and the ligands attached to the central atom. The compounds can be tailored for various applications such as in catalysis,[5] as chemical sensors,[6] and in liquid crystals,[7] photodynamic therapy[8] and electrochromism.[9]

The electrical properties of the phthalocyanine are strongly affected by introducing electron donor and acceptor groups into the Pc ring. In the field of semiconductors, it is known that substitution of the electron donor and acceptor groups leads to the *p*-type and *n*-type characteristics of Pc ring, respectively.[10–13]

Owing to their weak electron-transporting characteristics, fluorinated metallophthalocyanines (MPcs) are currently receiving a great deal of attention. Accordingly a number of researchers have reported on the syntheses and properties of perfluoro-substituted MPcs.[14–19]

The catalytic conversion of alcohols in to their corresponding carbonyl compounds is an important reaction in organic synthesis.[20] Synthetic metalloporphyrins have been investigated extensively as models for the activity of cytochrome P-450.[21,22] However, the main problem with porphyrin is easy decomposition during the catalytic cycle. To overcome this problem, a more stable porphyrin ring through ring substitution using electron withdrawing ligands is required. Metallophthalocyanine complexes have a similar structure to the porphyrin, but the former are more stable. Phthalocyanine complexes of transition metals are also very attractive as potential oxidation catalysts[23,24] because of their availability at low cost, facile preparation on a large scale, and chemical and thermal stability. But the major problem is their extensive insolubility in common organic solvents, which restricts their utility as an oxidation catalyst. This drawback has been partially overcome by immobilization onto inorganic supports, although in this case the activity and the selectivity problems of heterogeneous systems become apparent.[25]

Among the disadvantages associated with the application of homogeneous catalysis for pollution control and the recovery of an expensive catalyst is the problem of separating the catalyst from the reactants and products. One solution is incorporating an organic/aqueous phase or organic/fluorous biphasic system. The use of fluorous biphasic system (FBS) for homogeneous catalytic oxidations is a highly promising area in view of the potential disadvantages of classical homogeneous catalytic systems after the first use of the system reported by Horvath and Rabai in 1994.[26] One of the main advantages of the organic/fluorous phase system with an appropriate choice of organic- and fluorous-phase is that, on warming or under pressure, the two-phase

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organic/fluorous system becomes a single phase. Consequently, catalysis occurs under genuine homogenous conditions, but on cooling/pressure release the two phases are reestablished quickly, allowing facile product/catalyst separation. As a new facile separation and catalyst recovery technique, FBS has been used extensively in organic synthesis.[27,28] The easy separation and recycling of the perfluorinated complexes used in fluorous biphasic catalyst systems is perhaps the most important feature of this technique.

In the literature, three kinds of macrocyclic perfluoroalkyl-derivatized ligands have been used as the catalyst precursor in FBS. The first group is the manganese and cobalt complexes of the tri-substituted triazacyclononane, which show good activity for alkene oxidation with *t*-BuOOH–O_2 in a biphasic system.[29] The second group is the manganese complex of perfluoroalkyl substituted C_2-symmetric salen ligands, which have been evaluated as a chiral catalyst for the aerobic oxidation alkene under FBS-modified Mukaiyama conditions[30] and the oxidation of sulfides with PhIO by fluorous(salen)manganese(III) complexes.[31] The third group is tetra-meso-aryl porphrin with eight C_8F_{17} chains with Co(II) and Mn(II) which are used for epoxidation of alkanes and sulfide oxidation with 2-methylpropanal under aerobic conditions, as described by the Pozzi group.[32,33] The catalytic activity and selectivity of different metallophthaocyanines for alcohol oxidation by different oxidants were investigated with benzyl alcohol as the benchmark compound.[34] Although the catalytic application of metalphthalocyanine complexes has been widely studied for oxidation reactions, the hydrogenation of unsaturated hydrocarbons is reported in only two studies to the best of our knowledge.[35,36]

Herein, we report the synthesis and characterization of some novel heptadecafluorononyl substituted symmetrical Pc derivatives, and the catalytic behavior of these complexes in the oxidation of benzyl alcohol and the first application of **5** complex as a catalyst precursor for the hydrogenation of olefins in organic/fluorous biphasic systems.

Experimental

All chemicals were purchased from Aldrich Chemicals Inc. and used without further purification. 4-nitrophthalonitrile **2** was synthesized by the methods described previously in the literature.[37]

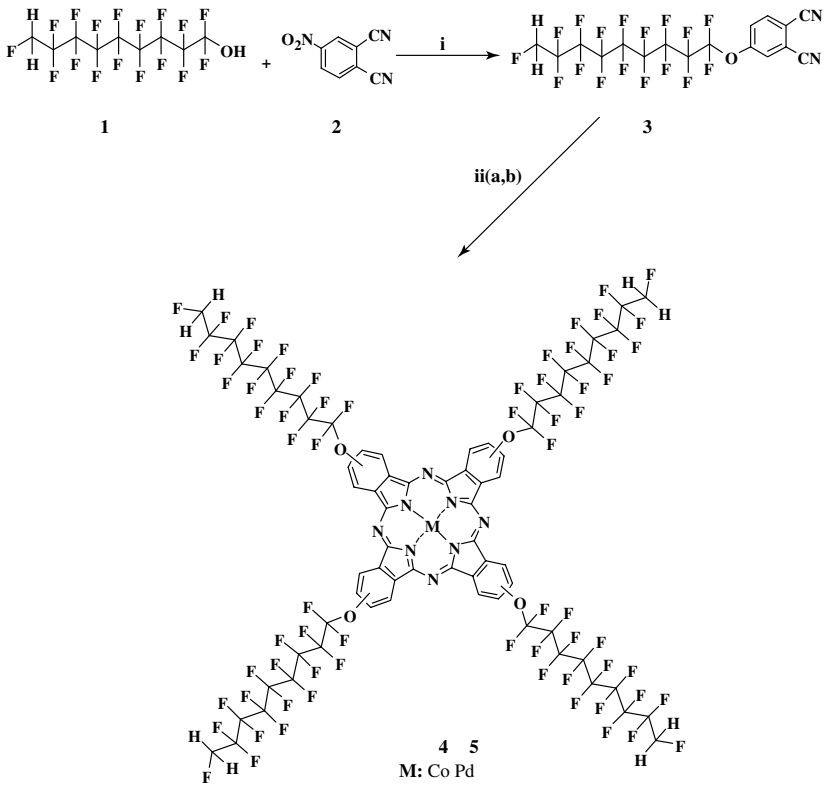
Synthesis

*4-(Heptadecafluorononyloxy)phthalonitrile **(3)***

A mixture of heptadecafluorononan-1-ol **1** (0.90 g, 2.0 mmol), 4-nitrophthalonitrile **2** (0.35 g, 2.0 mmol), and K_2CO_3 (0.83 g, 6.0 mmol) was heated with magnetic stirring in 100 ml of a round-bottomed flask at 50 °C in DMF (30 ml) for 48 h. The cooled reaction mixture was poured into cold water (80 ml) with stirring. The white precipitate was filtered off, washed with water until the filtrate was neutral, and dried in vacuum at 40 °C (Scheme 1). This compound **3** is readily soluble in common organic solvents such as THF, MeOH, EtOH, $CHCl_3$, CH_2Cl_2 and acetone. Yield: 0.84 g (73%), m.p. 112 °C. Anal. calcd for $C_{17}H_5F_{17}N_2O$: C, 35.44; H, 0.87; N, 4.86%; Found: C, 35.27; H, 0.83; N, 4.62%; FT-IR (Table1) and ^{1}H-NMR (Table 2).

*Tetrakis[heptadecafluorononyloxy]-phthalocyaninato cobalt(II) **(4)***

A mixture of compund **3** (0.29 g, 0.50 mmol), $Co(CH_3COO)_2{\cdot}4H_2O$ (0.032 g, 0 .125 mmol) and DMAE (0.2 ml) was heated and stirred



Scheme 1. (i) K_2CO_3, DMF; (ii) a: $Co(CH_3COO)_2{\cdot}4H_2O$, DMAE; b: $PdCl_2$, DMAE.

Table 1. Characteristic IR bands (cm^{-1}) of **3** and its Pc complexes (KBr pellets)

Compounds	Ar–H	-CH_2-	C≡N	C=C	C–O–C	C–F
3	3097–3058	2955–2892	2234	1604–1569	1258	1211–1145
4	3066	2947–2881	–	1612	1234	1203–1142
5	3067	2939–2843	–	1613	1238	1207–1145

Table 2. ^{1}H-NMR chemical shift (δ, *ppm*) and coupling (*J*,Hz) data for **3** in $CDCl_3$

Compounds	Ar–H	-CH_2-
3	7.79 (d, $J = 9$ Hz, 1H) 7.36 (d, $J = 3$ Hz, 1H) 7.27(s and dd, $J = 3$ Hz, 1H)	4.58 (t, $J = 12$ Hz, 2H)

Table 3. MALDI mass (*m/z*) data for Co and Pd–Pc complexes

Compounds	$[M]^+$	$[M + H]^+$	$[M + H + H_2O]^+$
4	2363	2364	2382
5	2410	2411	–

at 170 −180 °C for 6 h in a vacuum sealed, pressure-resistant glass tube of 10 ml (Scheme 1). The cooled reaction mixture was poured into ethanol with stirring and the brownish precipitate was separated by centrifuging. The crude product was washed several times with hot ethanol–THF mixture with stirring until the washing mixture was colorless. The reprecipitated dark blue Pc was dried under vacuum. Compound **4** is soluble in fluoroalkanes and slightly soluble in THF. Yield: 127 mg (43%). Anal. calcd for $C_{68}H_{20}F_{68}N_8O_4Co$: C, 34.55; H, 0.85; N, 4.74%; Found: C, 34.41; H, 0.87; N, 4.81%; MS (MALDI-TOF) (Table 3). FT-IR (Table 1). UV–vis (THF) λ, nm (log ε): 661 (5.02), 602 (4.44), 332 (4.88).

Tetrakis[heptadecafluorononyloxy]-phthalocyaninato palladium(II) ***(5)***

Compound **3** (0.46 g, 0.8 mmol) and $PdCl_2$ (0.035 g, 0.2 mmol) was dissolved in (DMAE) (0.2 ml) in a vacuum sealed glass tube of 10 ml resistant to pressure. After being degassed with vacuum, the mixture was sealed, and heated at 170 −180 °C for 8 h (Scheme 1). The purification of **5** was achieved as described above. Compound **5** is soluble only in fluoroalkanes. Yield: 184 mg (38%). Anal. calcd for $C_{68}H_{20}F_{68}N_8O_4Pd$: C, 33.87; H, 0.84; N, 4.65; Found: C, 33.62; H, 0.89; N, 4.56;%; MS (MALDI-TOF) (Table 3). FT-IR (Table 1). UV–vis (PFCH) λ, nm (log ε): 656 (4.95), 594 (5.26), 332 (5.13).

Measurements

FT-IR spectra of all compounds were recorded on a Shimadzu FTIR-8300 spectrophotometer as KBr pellets. UV–vis spectra of **4** and **5** were measured on a Shimadzu UV-1601 UV–vis spectrophotometer. Elemental analyses were performed using the LECO CHNS 932 at The Scientific and Technological Research Council of Turkey (TUBITAK) laboratories in Ankara. ^{1}H NMR spectra of compound **3** were obtained on a Varian Mercury-V·400 MHz spectrophotometer using TMS as internal standard.

MALDI mass measurements were completed at the Hacettepe University in Ankara. Mass spectra were acquired on a Voyager-DE™ PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra were recorded in linear mode and reflectron mode with average of 50 shots.

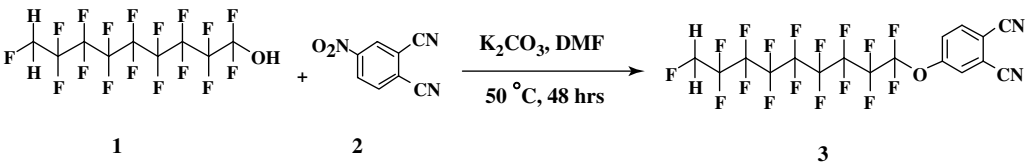
MALDI sample preparation

α-Cyano-4-hydroxycinnamic acid (CHCA) (10 mg/ml in tetrahydrofuran with 0.1% trifluoroaceticacid) was prepared. MALDI samples were prepared by mixing complex (5 mg/ml in tetrahydrofuran) with the matrix solution (1 : 10 v/v) in a 0.5 ml eppendorf® micro tube. Finally 1 µl of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

The homogeneity of the phthalonitrile derivative, **3** was tested in each step by TLC. The products obtained from catalytic reactions were analyzed on a Thermo Finnigan Trace GC using Permabond SE-54-DF-0.25 25 m × 0.32 mm ID coloumn attached to a flame ionization detector and He as carier gas and Thermo Finnigan Trace GC-MS. The metal analyses were conducted on Perkin Elmer Optima 4300 DV ICP-OES and AAS Perkin Elmer Analyst 800. A 50 ml reactor (Parr Inc., 4590 micro Bench Top with 4842 process controller having digital readout for measuring temperature and stirrer speed) and 25 ml visual cell reactor (Tharr Inc. Instrument, USA) were used for catalytic reactions.

General procedure for the oxidation of alcohols under fluorous biphasic conditions

The reactions were carried out in a 25 ml Schlenk vessel which was placed in a thermoregulated bath. The Schlenk vessel was charged with a solution of catalyst in perfluoromethylcyclohexane (PFMCH) (4 ml) and a hexane solution of substrate (4 ml). The oxidant was then added to the mixture. The two-phase mixture



1 2 3

Scheme 2. The synthesis of 4-(heptadecafluorononyloxy)phthalonitrile **3**.

was magnetically stirred at 900 rpm in order to ensure optimum contact between the organic and fluorous phase. After 24 h, the fluorous layer was recovered, washed with acetone (2 × 2 ml) and reused in a further run. Reactions were run at least twice. The oxidation products were identified using standards and by measurements of retention times by gas chromatography. The products were also characterized by GC-MS.

Results and Discussion

Synthesis

The starting molecule **3** for the synthesis of heptadecafluorononyl substituted symmetrical Pcs was obtained by the nitro displacement reaction of heptadecafluorononan-1-ol **1** and 4-nitrophthalonitrile **2**.[13,38]

The perfluroalkyl substituted Pc derivatives were prepared from the phthalonitrile derivative **3** with cobalt(II)acetate [Co $(OAc)_2 \cdot 4H_2O$] and palladium(II)chloride [$PdCl_2$] in DMAE by template reaction.[4,13] MPc complexes **4** and**5** were soluble in fluoroalkanes such as PFMCH and **4** was also soluble in THF.

The IR spectra were obtained from potassium bromide disks. The existence of C≡N groups appeared at 2234 cm^{-1} as a single peak in the spectrum of **3**. The template reaction from the dinitrile derivative was confirmed by the disappearance of C≡N stretching vibration band at 2234 cm^{-1}. The characteristic C–F bands of **3**, **4** and **5** appeared at 1207–1145 cm^{-1} (Table 1).

The UV–vis spectra of **4** in THF show typical absorption around 660 nm in the Q-band region. As expected, no splitting of the Q-band in the spectra of the **4** was observed. On the other hand, aggregation is usually described as a coplanar association of rings developing from monomer to dimer and higher order complexes. The aggregation degree of Pcs is highly affected by solvation, peripheral substituents, complexed metal ions, concentration and temperature.[39,40] The intense band in the absorption spectra of **5** at around 595 nm is the main band, which is blue shifted and broadened because of PFMCH (solvent effect). This broadening indicates aggregation of the **5**. The Q band observed for all Pc compounds was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands in the UV region at around 332 nm for **4** and **5** were observed due to the transitions from the deeper π levels to LUMO (Fig. 1).

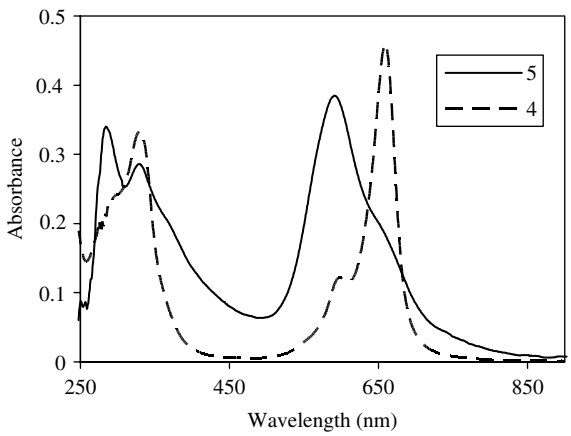


Figure 1. UV–vis spectra of heptadecafluorononyl substituted Pc derivatives **4** in THF and **5** in PFMCH.

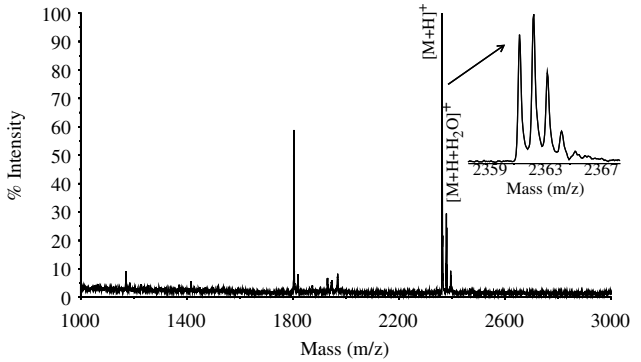


Figure 2. Positive ion and reflectron mode MALDI-MS spectrum of Co complex **4** obtained in α-cyano-4-hydroxycinnamic acid (10 mg/ml in tetrahydrofuran with 0.1% trifluoroaceticacid) MALDI matrix using a nitrogen laser accumulating 50 laser shots. The inset spectrum shows the expanded molecular mass region of the complex.

The ^{1}H-NMR spectra are also in agreement with the proposed structures. The ^{1}H-NMR spectrum of **3** in *d*-*CD*Cl_3 designates the aromatic protons at around 7.26–7.80 ppm as a singlet, a double-doublet and a doublet, and the methylene (-CH_2-) protons of fluoro-substituted aliphatic group between 4.55–4.61 ppm as a triplet (Table 2). Because palladium complex is not soluble in NMR solvents such as $CHCl_3$ and DMSO, the ^{1}H-NMR spectra of compound **5** could not be measured.

MALDI mass spectrum of cobalt complex **4** was obtained using positive ion and reflectron mode in various novel MALDI matrices. However, the suitable MALDI mass spectrum of the complex was obtained in CHCA matrix and is given in Fig. 2. The high-resolution MALDI mass spectrum of the complex was obtained easily using the reflectron mode. The protonated molecular ion peak intensity of the complex was observed at high intensity. This shows that the complex is very stable under laser shot and MALDI-MS conditions. Except for the protonated molecular ion peak, two other peaks following the protonated molecular ion peak were observed but at low intensities. These two peaks characterize the one and two waters adduct to the protonated molecular ion peak. When the high-resolution isotopic mass distribution of molecular ion peak was compared with the theoretical isotopic peak distributions of the synthesized molecule, the isotopic peak distributions were found to be identical. This shows that complex was synthesized correctly. On the MALDI-MS spectrum of the complex, one peak more was observed at reasonably high intensity. This peak characterizes the suitable fragmentation product from the complex, but a reasonable spectrum could not be obtained because of the short life-time of the protonated ion of the complex under MALDI mass spectrometry conditions. As well as the protonated molecular ion peak of the complex, some intense signals representing the fragment ions in the mass range between 600 and 2200 Da were observed. These fragment ions showed that some different site chain fragmentations occurred under the laser shots easily from the complex molecule. All these peaks masses were evaluated and it was found that these ions were due to the fragmentation of the complex.

The MALDI-MS spectrum of palladium complex **5** of the same ligand was also tested using some different MALDI matrices. The MALDI-MS spectrum of this complex could be obtained only in DHB MALDI matrix and also in linear mode. High-resolution spectra for this complex could not be obtained because of the lower stability of this complex under the MALDI-MS conditions.

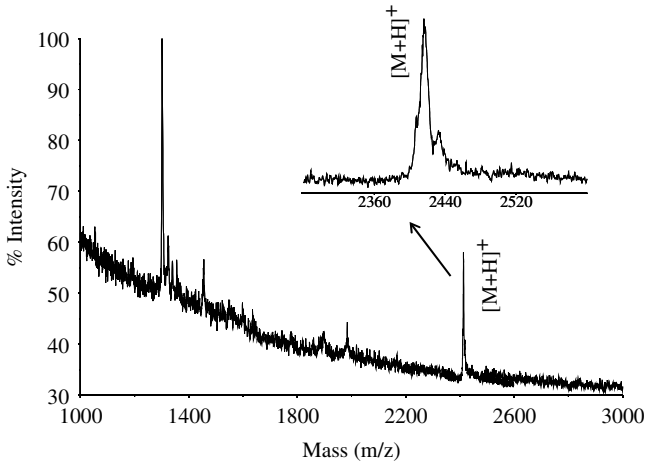


Figure 3. Positive ion and linear mode MALDI-MS spectrum of Pd complex **5** obtained in 2,5-dihydroxybenzoic acid (20 mg/ml in methanol) MALDI matrix using a nitrogen laser accumulating 50 laser shots. The inset spectrum shows the expanded molecular mass region of the complex.

Positive ion and linear mode MALDI-MS spectra of palladium complex were obtained with reasonably high intensity and the MALDI-MS spectrum of the complex is given in Fig. 3. Only one fragment peak was observed and that characterizes the main fragment ion from the synthesized complex.

Catalytic studies

*Oxidation of benzyl alcohol with **4** and **5***

In a typical oxidation reaction, a Schlenk tube was charged with a hexane solution (4 ml) of benzyl alcohol (9.47×10^{-4} mol, 0.1 ml) and a PFMCH solution of complex (1.65×10^{-6} mol in 4 ml). After the addition of desired amount of oxidant, the air inside the Schlenk was evacuated under vacuum and refluxed at different temperatures. Above 20 °C, the deep blue color of homogeneous solution changed to light brown. At the end of the reaction, the oxidation products were readily isolated from the fluorous layer by cooling of the reaction mixture to below 20 °C followed by phase separation of the resulting biphasic system. The catalyst remained in the fluorous phase while the organic substrates and products were in the organic phase. The upper colorless organic phase was removed using a syringe. The fluorous phase was extracted with acetone (2 × 2 ml). This simple workup removes all the reduction products from fluorous phase. The collected acetone and the removed organic phase were combined and analyzed by GC and GC-MS. The absence of both catalysts in the organic phase was checked by UV–vis absorption, because phthalocyanines absorb strongly in UV–vis region, so traces of these compounds could be easily detected in solution.

The catalytic activity and selectivity of **4** and **5** were studied using benzyl alcohol with TBHP as the model compound in PFMCH using different organic/fluorous biphasic systems: acetone–PFMCH, toluene–PFMCH and *n*-hexane–PFMCH. The following reaction conditions were used for all comparison experiments: temperature of 50 °C, 1.82×10^{-6} mol of catalyst (for **4**) and 1.65×10^{-6} mol catalyst (for **5**), substrate/catalyst ratio of 520 (for **4**) and 574 (for **5**), 1.24×10^{-4} mol of TBHP and 24 h reaction at 900 rpm. As shown in Tables 4 and 5, a comparative study of the catalytic activity of **4** and **5** for oxidation of benzyl alcohol under similar conditions revealed that both complexes are very active catalysts in perfluoromethylcyclohexane and show moderate activity under biphasic conditions. Oxidation of benzyl alcohol afforded benzaldehyde, benzoquinone and benzoic acid. In PFMCH, benzyl alcohol converted primarly benzoic acid (60.7%) and benzoquinone (38.5%) by **5** in 24 h reactions. In contrast, the catalytic oxidation of benzyl alcohol in PFMCH by **4** was almost complete to the corresponding acid (93.3%) in a 24 h reaction at 50 °C. Although complex **5** had higher total conversions (99.7%) than **4** (39.4%) in the *n*-hexane–PFMCH system at 50 °C, the aldehyde selectivity of former (4.3%) was poorer (73.7%). The essential role played by the catalyst is evident from the low conversion (5.1%) found in the control experiment carried out in the absence of the catalyst (Table 4).

The effect of oxidants on the oxidation of benzyl alcohol was also investigated. The results are summarized in Table 6 for **4** and in Table 7 for **5**. The results showed that both catalysts exhibit significantly higher activity with TBHP than other studied oxidants: MCPBA, oxone, H_2O_2, O_2 and O_2 + KOH. Aerobic oxidation of benzyl alcohol gave very low conversion with both catalysts.

Table 4. The effect of solvent and temperature on oxidation of benzyl alcohol with TBHP in the presence of **4**

Biphasic system	Temperature (°C)	Reaction time (h)	Total conversion (%)	Aldehyde selectivity (%)	Products (%)			TON
					Aldehyde	Benzoquinone	Benzoic acid	
PFMCH	50	6.0	47.8	71.8	34.3	2.1	11.5	
		24.0	98.7	1.2	1.2	4.2	93.3	552
Toluene–PFMCH	50	2.7	39.6	52.5	21.0	1.0	17.6	222
Acetone–PFMCH	50	4.0	35.8	35.2	12.6	23.2	–	
		24.0	52.5	30.2	16.0	36.5	–	294
n-Hexane–PFMCH	50	2.0	31.8	92.7	29.4	2.4	–	
		24.0	39.4	73.7	28.0	1.4	10.0	220
n-Hexane–PFMCH	30	24.0	39.2	89.3	35.0	4.2	–	219
n-Hexane–PFMCH	70	5.5	26.6	91.4	24.3	2.3	–	
		24.0	36.6	57.5	21.0	15.6	–	205
	90	24.0	22.1	100	21.4	0.7	–	124
n-Hexane–PFMCH[a]	70	24.0	4.1	–	3.6	1.5	–	–

[a] Without catalyst.

Table 5. The effect of solvent and temperature on oxidation of benzyl alcohol by TBHP in the presence of **5**

Biphasic system	Temperature (°C)	Reaction time (h)	Total conversion (%)	Aldehyde selectivity (%)	Products (%)			TON
					Aldehyde	Benzoquinone	Benzoic acid	
PFMCH	50	24.0	99.9	0.7	0.7	38.5	60.7	559
Toluene–PFMCH	50	24.0	66.1	97.0	64.0	2.1	–	379
Acetone–PFMCH	50	24.0	90.4	21.1	19.1	71.3	–	519
n-Hexane–PFMCH	30	24.0	25.3	92.9	23.5	1.8	–	145
n-Hexane–PFMCH	50	24.0	99.7	4.3	4.3	78.8	16.6	572
n-Hexane–PFMCH	70	24.0	37.1	97.3	36.4	0.7	–	213
n-Hexane–PFMCH	90	24.0	11.9	100	11.9	–	–	68

TON = mole of product/mole of catalyst.

Table 6. Oxidant effect on benzyl alcohol oxidation with **4** in *n*-hexane–PFMCH

Oxidant	Reaction time (h)	Total conversion (%)	Aldehyde selectivity (%)	Products (%)		
				Aldehyde	Benzoquinone	Benzoic acid
t-BuOOH	24	39.4	71.1	28.0	1.4	10.0
Oxone	24	4.0	100	4.0	–	–
H_2O_2	24	7.6	100	7.6	–	–
O_2[a]	24	6.5	100	6.5	–	–
O_2 + KOH[b]	24	19.5	100	19.5	–	–
No oxidant	24	Trace	–	–	–	–

[a] 6 bar.
[b] 6 bar + KOH.
Reaction conditions: temperature = 50 °C, catalyst = 1.82×10^{-6} mol, benzyl alcohol = 9.47×10^{-4} mol, oxidant = 1.24×10^{-3} mol.
Oxone = potassium peroxymonosulfate.

Although the oxidant O_2 with KOH by **5** did not increase the conversion, the catalytic activity of **4** increased (6.5—19.5%) under the same conditions. Similar behavior has been reported for the aerobic oxidation of secondary alcohols with **4**.[41] The control experiment showed that the benzyl alcohol was not oxidized in the absence of oxidant (Tables 6 and 7).

The effect of reaction temperature was tested for both catalyst precursors, using 1.24×10^{-2} mol TBHP, substrate/catalyst ratio of 520 for **4** and 547 for **5**, and 24 h reaction time in an *n*-hexane–PFMCH system (Tables 4 and 5). The results obtained are presented in Fig. 4. For complex **4**, the activity remains almost constant around 39% (average TON = 215) between 30 to 70 °C and slightly decrease to 22.1% (TON = 124) at 90 °C with 100% selectivity of benzaldehyde, where the results indicate that presumably the same active species acts in that temperature range. We observed that the benzoic acid formed only at 50 °C. The maximum conversion was obtained (99.7%, TON = 572) with the product distribution of 4.3% aldehyde, 78.8% benzoquinone

Table 7. Oxidant effect on benzyl alcohol oxidation with **5** in *n*-hexane–PFMCM

Oxidant	Reaction time (h)	Total Conversion (%)	Aldehyde selectivity (%)	Products (%)		
				Aldehyde	Benzoquinone	Benzoic acid
t-BuOOH	24	99.8	4.3	4.3	78.8	16.6
MCPBA	24	31.3	100	31.3	–	–
Oxone	24	5.4	100	5.4	–	–
H_2O_2	24	2.4	100	2.4	–	–
O_2[a]	24	1.8	100	1.8	–	–
O_2+ KOH[b]	24	NR	–	–	–	–
No oxidant	24	Trace	–	–	–	–

[a] 6 bar.
[b] 6 bar + KOH.
Reaction conditions: temperature = 50 °C, catalyst = 1.82×10^{-6} mol, benzyl alcohol = 9.47×10^{-4} mol, oxidant = 1.24×10^{-3} mol.
MCPBA = *m*-chloroperoxybenzoic acid; oxone = potassium peroxymonosulfate.

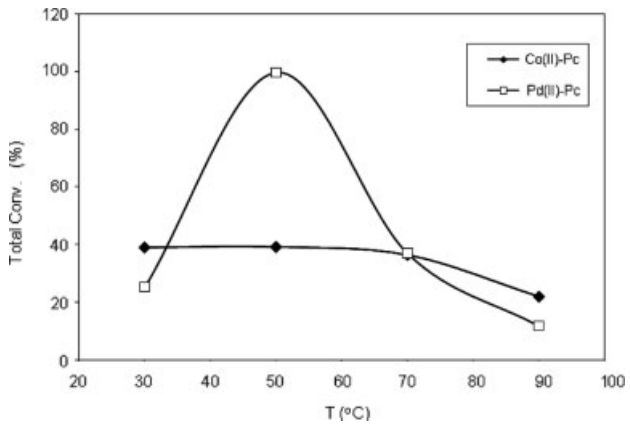


Figure 4. Temperature effect of benzyl alcohol oxidation in *n*-hexane–PFMCH.

and 16.6% benzoic acid at 50 °C for **5**. Figure 4 shows the activity of **5** complex increased almost four times, from 25.3 to 99.7% of conversion, when the temperature was raised from 30 to 50 °C. However, at relatively high temperature, the activity decreased dramatically by about eight times (11.9%, TON = 68) at 90 °C.

Conclusion

In conclusion, the novel cobalt (II) and palladium (II) complexes of heptadecafluorononyl-substituted symmetrical Pc derivatives were synthesized from 4-(heptadecafluorononyloxy)phthalonitrile, and characterized using spectroscopic methods. We have demonstrated that the new perfluoroalkylated **4** and **5** complexes are effective catalysts for the benzyl alcohol oxidation with TBHP in a fluorous biphasic system.

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