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Dyes and Pigments 41 (1999) 101–109

DYES and PIGMENTS

Synthesis and characterization of polyfluoroalkoxysulfonyl phthalonitriles and corresponding zinc and cobalt phthalocyanines

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Received 6 July 1998; accepted 27 July 1998

Abstract

The reaction of 1,2-dicyanobenzene-4-sulfonyl chloride with different polyfluoro alcohols leads to the formation of 1,2-dicyano-4-polyfluoroalkoxysulfonyl benzenes. The tetramerization of such nitriles in the presence of zinc or cobalt salts results in the corresponding phthalocyanines. The influence of solvent and substituents on the aggregation of the phthalocyanine complexes was studied by electronic spectroscopy. The polyfluoroalkoxysulfonyl groups were shown to stabilize both HOMO and LUMO of the complexes in comparison with alkoxy- or polyfluoroalkoxy-substituted analogs. The first oxidation potential for zinc-containing complexes was estimated as 1.47–1.65 V © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorinated phthalonitriles; Substituted phthalocyanine complexes; Aggregation

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1. Introduction

Phthalocyanines are traditionally used as dyes and pigments [1]. Recently their uses have been developed in the context of passive quality switches in lasers, as catalysts, semiconductors and photosensitizers for the photodynamic therapy of cancer [2]. Redox-active d-metal (Mn, Fe, Co) phthalocyanine complexes exhibit very high catalytic activity in the oxidation reactions of thiols, hydrocarbons, hydroquinones, arenes, and amines [3–5]. The oxidation of the phthalocyanine ligand is the main inactivation pathway for such catalysts. Thus, the synthesis of novel phthalocyanine complexes with high oxidation potential of macrocyclic ligands can lead to new highly effective catalytic systems. The most promising way to increase the first oxidation potential of phthalocyanine ligands is the introduction of electron-withdrawing substituents. Recently, high peroxidase and oxygenase activities were observed in transition-metal

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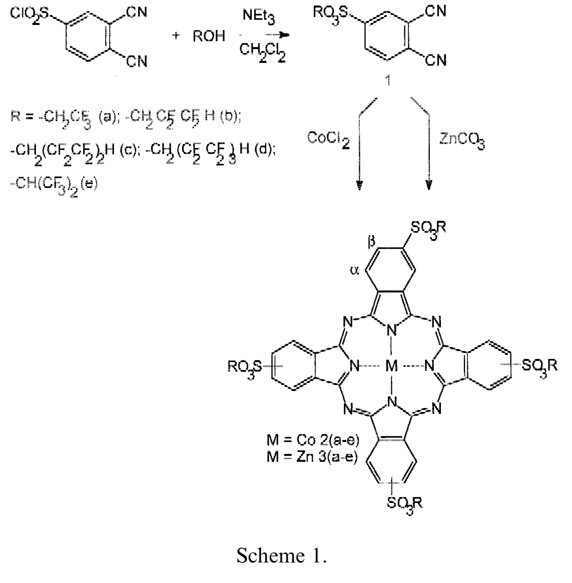
PII: S0143-7208(98)00066-7

phthalocyanine complexes containing four or eight nitro or perfluoroalkyl groups [3–6]. However, all of these complexes, as well as tetra- and octacyano-substituted phthalocyanines [7–9], are poorly soluble in common organic solvents and, therefore, of little use as homogeneous catalysts. The prime objective of the present work is the synthesis and characterization of new readily soluble phthalocyanines with strong electron-withdrawing substituents. Polyfluroalkoxysulfonyl groups are the best candidates for this purpose due to high chemical stability and strong electron-accepting effect of such substituents. By varing the polyfluoroalkyl chain length it is possible to control the lipophylicity and solubility of phthalocyanines containing these substituents. The electronic nature of polyfluroalkoxysulfonyl groups and their effect on properties of dimethylamino azo dyes and luminophors were quantitatively characterized recently by Yagupolskii et al. [10]. The electron-withdrawing effect of polyfluroalkoxysulfonyl groups was shown to be higher than that of the nitro group, slightly smaller than that of the CF_3SO_2 group, and practically the same that of the CHF_2SO_2 group. As would be expected, the change of methyl to the trifluoromethyl group results in an enhancement of the electron-withdrawing ability (σ_p 0.63 and 0.83 respectively). Only minor changes in the electron-withdrawing properties were observed when the polyfluoroalkyl chain length was varied. For example, σ_p constants are 0.83 for the $CF_2CH_2OSO_2-$ and $HCF_2CF_2CH_2OSO_2-$ groups, and 0.84 for the $H(CF_2)_4CH_2OSO_2-$ group, in accord with the decrease in inductive effect with elongation of the chain at the sulfur atom. Polyfluoroalkoxysulfonyl groups exhibit high chemical stability. In contrast to alkoxysulfonyl derivatives, polyfluoroalkoxysulfonyl-substituted compounds are poor alkylating agents. For instance, the alkylation of *N*-methyl- or *N*-ethylanilines with 2,2,3,3-tetrafluoropropyl and 2,2,3,3,4,4,5,5-octafluoropentyl *p*-toluenesulfonate occurs only at 250–280°C, i.e., at temperature 100–150°C higher than for the unfluorinated analogs [11–13]. This observation suggests that polyfluoroalkyl arenesulfonates can be use as starting materials in the synthesis of phthalocyanines.

2. Results and discussion

Polyfluoroalkoxysulfonyl groups are readily available by the reaction of sulfonyl chlorides and alcohol-telomeres [10]. Up to now, no phthalonitriles or phthalocyanines with such substituents have been reported. The synthesis of 1,2-dicyano-4-polyfluoroalkoxysulfonyl benzenes is outlined in Scheme 1. 3,4-Dicyanobenzene sulfonyl chloride reacts with corresponding polyfluoro containing alcohols in dichloromethane in the presence of triethylamine. A series of 1,2-dicyano-4-polyfluoroalkoxysulfonyl benzenes were synthesized in high yield by this procedure (Table 1). All the 1,2-dicyano-4-polyfluoroalkoxysulfonyl benzenes prepared were colorless compounds which were highly soluble in common organic solvents. The substituted phthalonitriles were employed to prepare cobalt (II) and zinc phthalocyanine complexes by the reaction with cobalt (II) chloride or zinc carbonate in the presence of ammonium molybdate (see Scheme 1).

The catalytic efficiency of phthalocyanine complexes depends on their aggregation state and the influence of the medium on stabilization of the catalytically active coordination forms [14]. In this connection, the aggregation behavior of the synthesized complexes was studied by electronic



Scheme 1.

Table 1
Yields, melting points, ^{19}F NMR and elemental analyses for compounds **1a–1e**

Compound	R	M.P. (°C)	Yield (%)	^{19}F NMR (acetone-d$_6$) σ (PPM), J_{HF}, Hz	Molecular formula	Elemental analysis (%)		
						C(calc)	H(calc)	N(calc)
1a	-CH_2CF_3	78–79	82	73.57(t, 3F, CF3), J_{HF} 83	$C_{10}HY_3N_2O_3S$	41.58 (41.37)	1.80 (1.72)	9.85 (9.65)
1b	-$CH_2CF_2CF_2H$	101–102.5	95	125.23(m, 2F, CF_2), J_{HF} 139.17; 139.45(dt, 2F, CF_2), J_{HF} 53	$C_{11}H_6F_4N_2O_3S$	41.20 (40.99)	1.88 (1.86)	8.87 (8.69)
1c	-$CH_2(CF_2CF_2)_2H$	107–109	78	119.52 (m, 2F, CF_2); 124.59 (m, 2F, CF_2); 129.80 (m, 2F, CF_2); 139.97, 138.24 (dt, 2F, CF_2); J_{HF} 51	$C_13H_6F_8N_2O_3S$	37.05 (36.96)	1.38 (1.42)	6.80 (6.63)
1d	-$CH_2(CF_2CF_2)3H$	108–110	83	119.16 (m, 2F, CF_2); 121.81 (m, 2F, CF_2); 122.72 (m, 2F, CF_2); 129.15 (m, 2F, CF_2); 137.91 (dt, 2F, CF_2) J_{HF} 51	$C_{15}H_6FI_2N_2O_3S$	34.86 (34.48)	1.20 (1.14)	5.48 (5.36)
1e	-$CH(CF3)_2$	87–89	53	73.14, 73.17 (d, 6F, CF_3); J_{HF} 56.4	$C_{11}H_4F_6N_2O_3S$	37.11 (36.87)	1.13 (1.11)	7.95 (7.82)

spectroscopy in different solvents and over a wide concentration range. Complexes **2a–2e** and **3a–3e** show extremely low solubility in aromatic hydrocarbons (benzene, toluene), limited solubility in halogenated aromatics (di- and trichlorobenzene) and high solubility in polar (2-propanol, acetonitrile) or coordinating (pyridine, DMF) organic solvents. Representative electronic spectra of the cobalt (II) and zinc-containing complexes are shown in Fig. 1 and their absorption maxima in Table 2. The cobalt complexes **2a–2e** in coordinating solvents show, in the long-wavelength region, the Q-band at ~670 mn with well-resolved vibronic satellites at ~640 and ~610 nm (Fig. 1a). All the spectra are typical for monomeric phthalocyanine complexes [2]. Lambert-Beer's law which is obeyed for the complexes **2a–2e** over a wide concentration range (10^{-6} – 10^{-4} M), confirm this observation. The electronic spectra of complexes **2a–2e** in polar solvents, for example 2-propanol, exhibit pronounced monomer-aggregate dependence (Fig. 2). At high concentrations (~10^{-4} M), the absorption at ~640 nm, assigned to Q-band of aggregated phthalocyanine complexes [2], is dominant in the spectra of **2a–2e**. On the other hand, at low concentrations (~10^{-6} M), the Q-band of the monomeric phthalocyanine complexes **2a–2e** is the major band in the long-wavelength region (Fig. 2). The effect of the peripheral substituents on the aggregation behavior of the complexes **2a–2e** is most clearly observed in 1,2,4-trichlorobenzene solutions (Fig. 3). Thus, the branching of the polyfluoralkyl chain (complex 2e) leads to stabilization of the monomeric form over a wide concentration range (~10^{-6}–10^{-4} M). A good correlation between aggregation and chain length is observed for complexes 2b–2d with linear polyfluoroalkyl groups (Fig. 3). The longer the polyfluoroalkyl chain, the more intense is the Q-band of aggregates in the electronic spectra. The position of the Q-band for the monomeric complexes **2a–2e** is practically independent of the substituents. Moreover, for phthalocyanine cobalt complexes with four alkoxy, polyfluoroalkoxy, or polyfluoroalkylsulfonyl groups, the Q-band position changes only in a small interval (5–8 nm), in spite of the great difference in the substituent inductive effects. This observation can be qualitatively explained in terms of Gouterman's four-orbital model [15]. Based on semiempirical and ab initio calculations [16–18], the Q-band was assigned to a practically pure transition from HOMO (a_{1u} symmetry) to

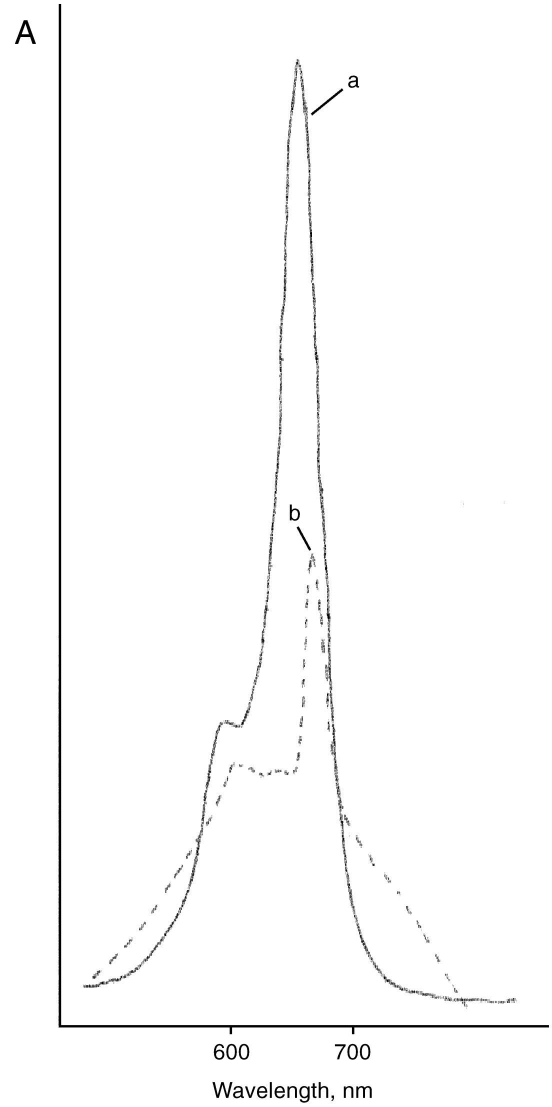


Fig. 1. Electronic spectra of **2a** (a) and **3a** (b) in pyridine.

LUMO (e_g symmetry) in the phthalocyanine ligand. Both of these orbitals have non-zero coefficients at the C_β atom, at which position substitution takes place. Thus, the increase in the electron-withdrawing effect of the substituents is expected to stabilize both the HOMO and LUMO orbital, with nearly constant energy gap. The HOMO and LUMO energies can be estimated from electrochemical data. However, such data are not available for the complexes **2a–2e** and **3a–3e**. On the other hand, stabilization of HOMO and LUMO energies going from alkoxy, through polyfluoroalkoxy, to polyfluoroalkyloxysulfonyl complexes can be determined by quantum-chemical calculations. We have carried out such calculations on the semiempirical AM1 [19] and ZINDO/S [20]

Table 2
Electronic spectra of complexes **2a–2e** and **3a–3e**

Complex	Solvent[a]	λ, nm (relative intensity)
2a	TCB	674 (3.14) 640sh 609 (1)
	PY	662 (3.1) 602 (1)
	i-PrOH	652^{b} 626
2a(Co^{III})	i-PrOH/CN^{-}	673 (2.07) 640sh 607 (0.61) 431 (0.41) 319 (1) 280 (1.07)
2b	TCB	674^{b} 640sh 602
	PY	662 (2.9) 602 (1)
	i-PrOH	654^{b} 625
2b(Co^{III})	i-PrOH/CN^{-}	675 (3.72) 640sh 607 (0.72) 429 (0.6) 334 (1) 283 (1.68)
2c	TCB	672^{b}
	PY	662 (2.9) 602 (1)
	i-PrOH	654^{b} 624
2c(Co^{III})	i-PrOH/CN^{-}	673 (2.94) 640sh 607 (0.71) 430 (0.54) 333 (1) 283 (1.2)
2d	TC	672^{b} 623
	PY	68 (3.0) 602 (1)
	i-PrOH	654^{b} 629
2d(Co^{III})	i-PrOH/CN^{-}	674 (3.41) 640sh 607 (0.67) 429 (0.55) 333 (1) 280 (1.78)
2e	TCB	674 (3.70) 640sh 609 (1)
	PY	662 (3.0) 602 (1)
	i-PrOH	656^{b} 625
2e(Co^{III})	i-PrOH/CN^{-}	673 (2.92) 640sh 607 (0.6) 430 (0.52) 333 (1) 282 (1.32)
3a	TCB	683.5^{b} 620 600
	i-PrOH	666^{b} 634 337
	i-PrOH/CN^{-}	690^{b}sh 673 639 610sh 392 329
3b	TCB	680^{b} 630
	i-PrOH	660^{b} 634 337
	i-PrOH/CN^{-}	690^{b}sh 672 640 394 328
3c	TCB	680^{b} 620
	i-PrOH	665^{b} 634 37
	i-PrOH/CN^{-}	690^{b}sh 671 640 610sh 400 328
3d	TCB	685^{b} 640
	i-PrOH	660^{b} 634 336
	i-PrOH/CN^{-}	690^{b}sh 672 640 610sh 400 328
3e	TCB	683^{b} 630
	i-PrOH	666^{b} 634 338
	i-PrOH/CN^{-}	690^{b}sh 672 639 400 328

[a] Abbreviation: TCB-1,2,4-trichlorobenzene; i-PrOH/CN^{-}-isopropyl alcohol-sodium cyanide 100:1.

level for corresponding closed-shell zinc complexes. As can be seen from Table 3, the increase in electron-withdrawing ability leads to stabilization of both HOMO and LUMO. Moreover, the HOMO-LUMO energy gaps are in all cases close to each other, in agreement with the low sensitivity of the *Q*-band position to the substituent at the C_β atoms of the phthalocyanine ligand. The highest stabilization is predicted for polyfluoroalkyloxysulfonyl-substituted complexes (Table 3). Interestingly, the LUMO for all the calculated complexes of symmetry C_{4h} is nearly doubly degenerated. Therefore the effective symmetry of the calculated complexes still is D_{4h}.

The resistance of a phthalocyanine macrocycle to oxidation depends on its first oxidation potential [2]. In first approximation for closed-shell phthalocyanine complexes, it is proportional to the HOMO energy of the phthalocyanine macrocycle. Usually, it is difficult to measure directly the first oxidation potential for phthalocyanines with electron-withdrawing substituents because of oxidation of solvent [6]. However, the first oxidation potential can be estimated by quantum-chemical calculations. For this purpose, the HOMO energy of some substituted zinc phthalocyanines was compared with the corresponding first oxidation potentials known from CV experiments [21–25]. (Table 3). Only the data for halogenated solvents were used, as in this case the zinc phthalocyanine-complexes are tetracoordinate, while in coordinating solvents they are pentacoordinate with

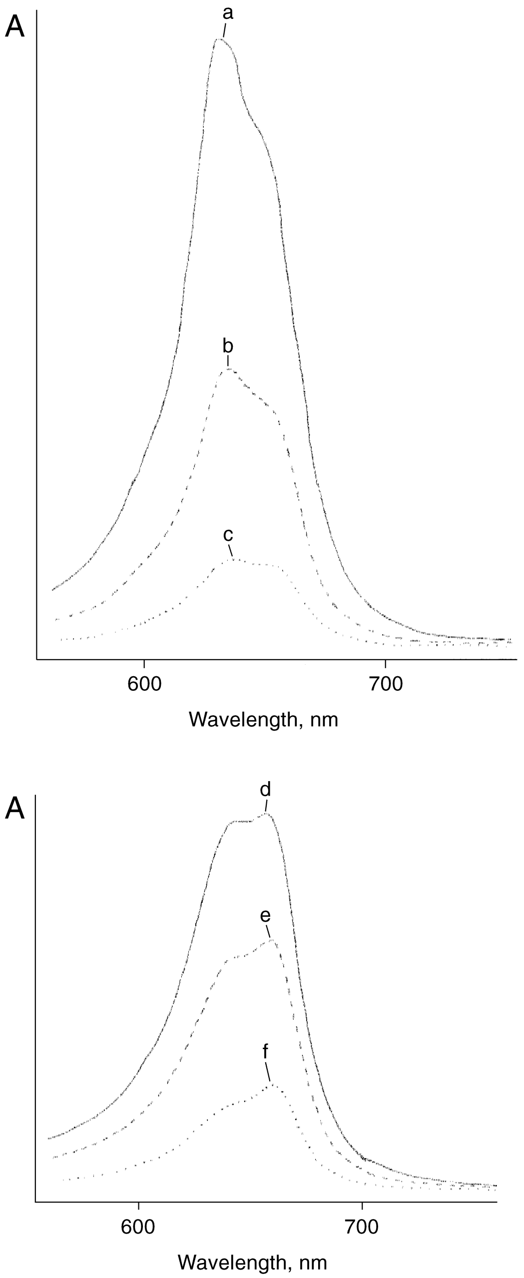


Fig. 2. Electronic spectra of **2b** in 2-propanol: (a) 5×10^{-4} M, (b) 1×10^{-4} M, (C) 5×10^{-5} M, (d) 1×10^{-5} M, (e) 5×10^{-6} M, (f) 1×10^{-6} M.

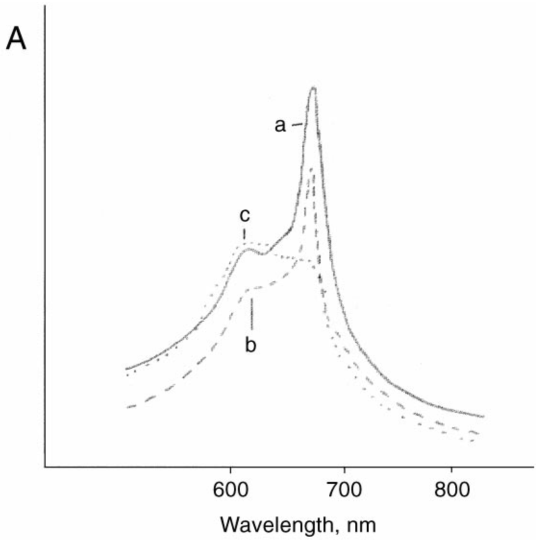


Fig. 3. Electronic spectra of **2b** (a), **2c** (b) and **2d** (c) in 1,2,4-trichlorobenzene (concentration ~8×10^{-5} M).

Table 3
Quantum-chemically calculated HOMO and LUMO energies and electrochernical data for some substituted phthalocyanine zinc complexes

Number of substituents	Position[a]	*R*	AM1, (−*n*, eV)		ZINDO/S, (−*n*, eV)		R_{ox}[b]	Ref
			HOMO	LUMO	HOMO	LUMO		
0	-	H	7.11	2.16	5.37	1.27	0.68[c]	21
4	2,9(10),16(17),23(24)	t-Bu	6.98	2.05	5.25	1.16	0.52[d]	22
4	2,9(10),16(17),23(24)	$-OCH_2C(CH_3)_3$	6.96	2.06	5.28	1.19	0.55[c]	23
4	1,8,15,22	$-OCH(CH_2CH_3)_2$	6.86	2.00	5.16	1.12	0.46[d]	24
8	2,3,9,10,16,17,23,24	Cond. t-BuC_4H_3	6.69	2.09	5.02	1.23	0.39[c]	25
4	2,9(10),16(17),23(24)	$-OCH_2CH_3$	6.98	2.07	5.28	1.20	0.54(0.55)[e]	tw
4	2,9(10),16(17),23(24)	$-OCH_2CF_3$	7.48	2.56	5.65	1.57	0.87(0.85)[e]	tw
4	2,9(10),16(17),23(24)	$-SO_3CH_2CF_3$	8.32	3.40	6.62	2.53	1.43(1.63)[e]	tw

[a] For the nomenclature of phthalocyanines see [2].
[b] All data for Pt electrode relatively SCE.
[c] 3DCB.
[d] CH_2Cl_2.
[e] Estimated value from AM1 (ZINDO/S) calculations; tw-this work.

solvent molecule as the axial ligand [2], i.e., the first oxidation potentials of substituted phthalocyanine zinc complexes are dependent on the solvent [2]. Good correlation between the first oxidation potentials and the HOMO energies, as calculated both in the AM1 and ZINDO/S approximations is observed (Fig. 4). From these correlations, the first oxidation potential for complexes **3a–3e** was estimated to be in range of 1.47–1.65 V. Based on these values we may infer that: (i) the cobalt complexes **2a–2e** are potential catalysts for the oxidation process of organic substrates as their involve both the redox-active metal center and are stable to oxidation of the macrocycle; (ii) the oxidative properties of the substituted phthalocyanine complexes can be predicted for new compounds on the basis of quantum-chemical calculations.

The reaction of complexes **2a–2e** with sodium cyanide yields the axially coordinated cobalt (III) complexes of the general formula $Na[Pc^{R4}Co^{III}(CN)_2]$. During the reaction, the initially blue complexes turn green. The axial coordination to two cyanide ions results in appreciable stabilization of the corresponding monomer forms. The electronic spectra of the diamagnetic $Na[Pc^{R4}Co^{III}(CN)_2]$ complexes show a series overlapped bands at ~430 nm, which is characteristic of phthalocyanine

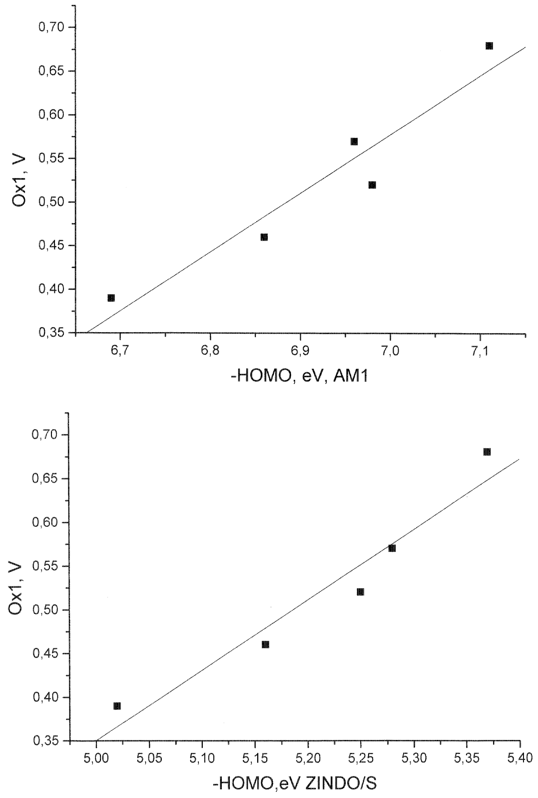


Fig. 4. Correlation between calculated HOMO energies and first oxidation potential for substituted phthalocyanine zinc complexes.

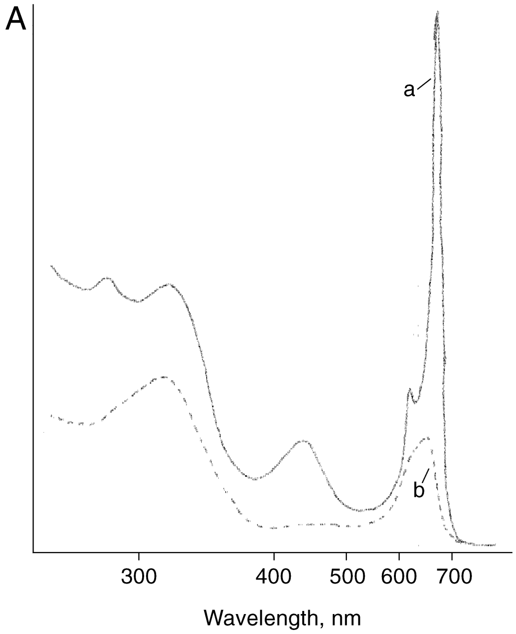


Fig. 5. Electronic spectra of **2e** in 2-propanol before (a) and after (b) addition of sodium cyanide.

cobalt (III) complexes [2,26,27] (Fig. 5). Interestingly, the band at ~330 nm in complexes **2a–2e** does not shift on oxidation of the central ion, while in unsubstituted [2] or tetra(perfluoroalkoxy)-substituted [26] phthalocyanines under the same conditions, this band splits into two components located at ~300 and ~360 nm. This observation might reflect the influence of the electron-withdrawing peripheral substituents, but we cannot accept this hypothesis for lack of unequivocal assignment of the band at ~360 nm in the phthalocyanine cobalt (III) complexes.

The electronic spectra of the zinc complexes **3a–3e** in various solvents are close to those the of cobalt complexes **2a–2e**, the main difference being that the former are more aggregated compared to the latter. All attempts at preparing monomeric zinc complexes in coordinating solvents or chlorinated aromatic hydrocarbons were unsuccessful. Sodium cyanide additives only partially decompose the aggregates (Fig. 6) and this can be accounted for by the difference in the coordination chemistry of the zinc and cobalt phthalocyanine complexes [2]. Thus, for cobalt phthalocyanine complexes with axial ligands, the penta- and hexacoordinate forms are usually in equilibrium: $Pc^{Rn}Co + nL = Pc^{Rn}CoL \leftrightarrow Pc^{Rn}CoL_2$ [2,26–28].

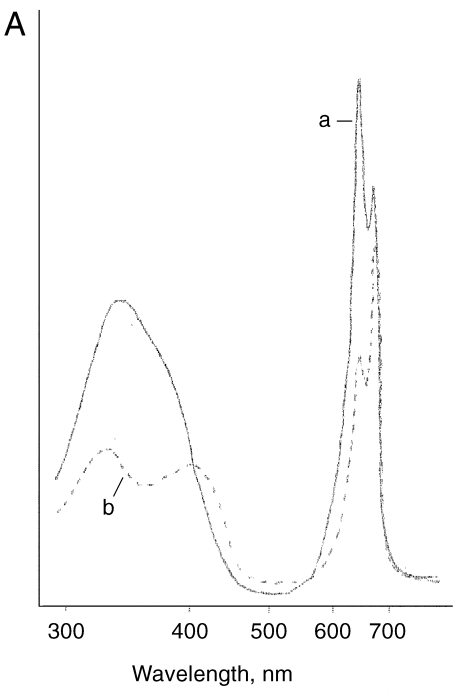


Fig. 6. Electronic spectra of **3e** in 2-propanol before (a) and after (b) addition of sodium cyanide.

The hexacoordinate form $Pc^{Rn}CoL_2$ is totally monomeric while the pentacoordinate entity exists as a monomer or dimer: $Pc^{Rn}CoL \leftrightarrow LCoPc^{Rn}$—$Pc^{Rn}CoL$.

On the other hand, only the pentacoordinate form ($Pc^{Rn}ZnL$) and, therefore, the presence of dimeric, non-covalent aggregates is expected [2,21–25] for the corresponding zinc complexes.

3. Conclusion

The main objective of the present work was to synthesise new highly soluble phthalocyanine redox-active and redox-inactive 3d-metal complexes with strong electronwithdrawing substituents on the periphery of the macrocyclic ligand. The aggregation state of all the cobalt and zinc complexes was found to depend on the solvent and on the structure of the polyfluorinated chain. Judging from the first oxidation potential estimated by quantum-chemical calculations, the cobalt complexes **2a–2e** may be promising catalysts for the oxidation of organic substrates.

4. Experimental

Electronic spectra were recorded on a Specord M-40 spectrophotometer and ^{1}H-NMR spectra a Gemeni-200 spectrometer. Quantum-chemical calculations were performed with the HyperChem 5.02 program (HyperCube Inc.). The starting geometry was calculated by the Molecular Mechanics method (MM+ force field) using the Polack-Ribiere gradient optimization algorithm. All the calculations were carried out for the $C4_h$ randomers. The same results were obtained for other randomers of D_{2h}, C_2, and Cs symmetry.

The yields and analytical data for all the starting compounds and phthalocyanine complexes are presented in Tables 1, 4 and 5.

*4.1. Polyfluoroalkyl 3,4-dicyano-4-benzenesulfonates **1a–1g** (typical procedure)*

To a solution of the appropriate alcohol (5 mmol) and triethylarnine (5 mmol) in anhydrous dichloromethane (20 ml) was added at 0–5°C, a solution of 3,4-dicyano-benzenesulfonyl chloride [29] in the same solvent (10 ml). The mixture was stirred at room temperature for 24 h and poured into water (75 ml). The organic layer was separated and the aqueous phase was extracted with dichloromethane (3×10 ml). The combined organic phases were dried ($MgSO_4$), filtered, and evaporated in vacuum. The residue was crystalized from benzenehexane.

*4.2. Polyfluroalkoxysulfonyl-substituted cobalt (**2a–2g**) and zinc (**3a–3g**) phthalocyanine complexes (typical procedure)*

Mixture of a 4-substituted phthalonitrile **1a–1g** (1 mmol), anhydrous cobalt(II) chloride or zinc carbonate (1 mmol) and a catalytic amount of ammonium molybdate was heated for 1.5 h at 190–200°C. The resulting product was washed with 5% aq HCl (3×10 ml), water (5×10 ml) and dried. All the complexes were purified by column chromatography on alumina with ethyl acetate (complexes **2a–2g**) or dichloromethane-acetone (2:1) (complexes **3a–3g**) as eluents.

Table 4
Yields and elemental analyses for compounds **2a–2e**

Compond	*R*	Yield (%)	Molecular formula	Elemental analysis (%)		
				C(calc)	H(calc)	N(calc)
2a	$-CH_2CF_3$	45	$C_{40}H_{20}F_{12}N_8O_{12}S_4CO$	36.62 (37.20)	1.35 (1.64)	8.78 (9.18)
2b	$-CH_2CF_2CF_2H$	50	$C_{44}H_{24}F_{16}N_8O_{12}S_4CO$	39.22 (39.19)	2.08 (1.78)	8.32 (8.31)
2c	$-CH_2(CF_2CF_2)_2H$	52	$C_{52}H_{24}F_{32}N_8O_{12}S_4CO$	35.80 (35.71)	1.51 (1.37)	6.21 (6.41)
2d	$-CH_2(CF_2CF_2)_3H$	55	$C_{60}H_{24}F_{48}N_8O_{12}S_4CO$	33.72(33.53)	1.11 (1.16)	5.27 (5.21)
2e	$-CH(CF_3)_2$	37	$C_{44}H_{16}F_{24}N_8O_{12}S_4CO$	35.20 (35.41)	1.04 (1.07)	7.40 (7.51)

Table 5
Yields and elemental analyses for compounds **3a–3e**

Compound	R	Yield (%)	Molecular formula	Elemental analysis (%)		
				C(calc)	H(calc)	N(calc)
3a	$-CH_2CF_3$	42	$C_{40}H_{20}F_{12}N_8O_{12}S_4Zn$	39.40 (39.18)	1.70 (1.63)	8.97 (9.14)
3b	$-CH_2CF_2CF_2H$	51	$C_{44}H_{24}F_{16}N_8O_{12}S_4Zn$	38.85 (39.02)	1.65 (1.77)	8.12 (8.27)
3c	$-CH_{12}(CF_2CF_2)_2H$	54	$C_{52}H_{24}F_{32}N_8O_{12}S_4Zn$	35.34 (35.71)	1.36 (1.33)	6.13 (6.38)
3d	$-CH_2(CF_2CF_2)_3H$	55	$C_{60}H_{24}F_{48}N_8O_{12}S_4Zn$	33.27 (33.44)	1.12 (1.15)	5.05 (5.20)
3e	$-CH(CF_3)_2$	38	$C_{44}H_{16}F_{24}N_8O_{12}S_4Zn$	35.11 (35.27)	1.11 (1.06)	7.38 (7.78)

Acknowledgements

One of the authors (V.N.N.) is thankful to HyperCube Inc. for a two week license under the HyperChem 5.02 program.

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