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Ionoelectronics: Cooperative Complexation Properties of a Functionalized Crown Ether Substituted Phthalocyanine

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Phthalocyanine and lutetium bisphthalocyanine derivatives functionalized with crown – ether moieties and a carboxylic ester terminated side chain, are synthesized and characterized. The complexation properties towards potassium ion are studied by UV – visible absorption spectrometry. A procedure is defined to quantitatively determine the positive cooperative effect arising during the complexation processes.

Keywords: Ionoelectronics; Phthalocyanines; Crown Ether

1. INTRODUCTION

Ionoelectronics has been defined as the domain of science whose object is an information processing using ions (especially alkali and alkaline earth cations)[1–3]. Previously, aromatic rigid cores like triphenylene[4] or phthalocyanine[5–7] have been substituted with several crown ether macrocycles making possible a cooperativity between the cation binding sites. A positive cooperative (nonlinear) complexation process has been indeed demonstrated for the formation of potassium ion sandwich complexes with lutetium bisphthalocyanine derivatives substituted with 15-crown-5 ether macrocycles[2,3]. These complexation studies were carried out in solution. In order to obtain a system which can be addressed, the grafting on surfaces is necessary. Following this idea, crown-ether substituted phthalocyanine derivatives possessing a carboxylic acid terminated side chain

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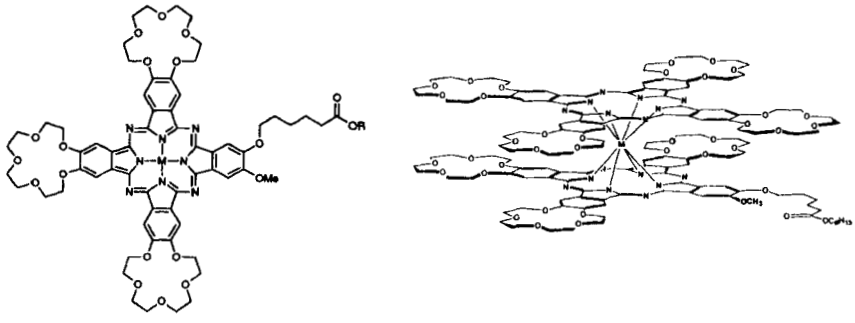
have been synthesized (compounds **1**, **2**) and their complexation properties in solution have been studied.



M = H_2 : **1b**, H_2
= LuOAc : **1b**, $LuOA_C$

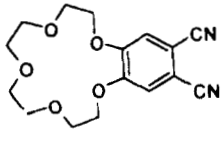
M = Lu : **2**

FIGURE 1 The compounds synthesized and studied in the present publication

The platinum and zinc complexes of **1b** as well as the lutetium and dysprosium derivatives of **2** have been the object of preliminary publications[8,9] concerning their synthesis.

2. SYNTHESIS OF THE COMPOUNDS 1 AND 2

The synthesis of the metal free phthalocyanine derivative has been carried out by reacting three equivalents of the crown ether substituted phtalonitrile **3** and one equivalent of ethyl-hexanoate substituted phthalonitrile **4**.



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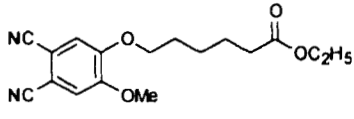

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SCHEME 1

The reaction is carried out as previously described[8,9] in the presence of 1.2 equivalent of $MgCl_2$, 3 equivalents of [1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) in 2.5 ml of n-hexanol *per* mmole of phthalonitriles. This reaction leads to a mixture of magnesium complexes which is directly treated with HCl (1.2 M) in dimethylformamide (DMF) to yield the corresponding metal free derivatives (Fig. 2).

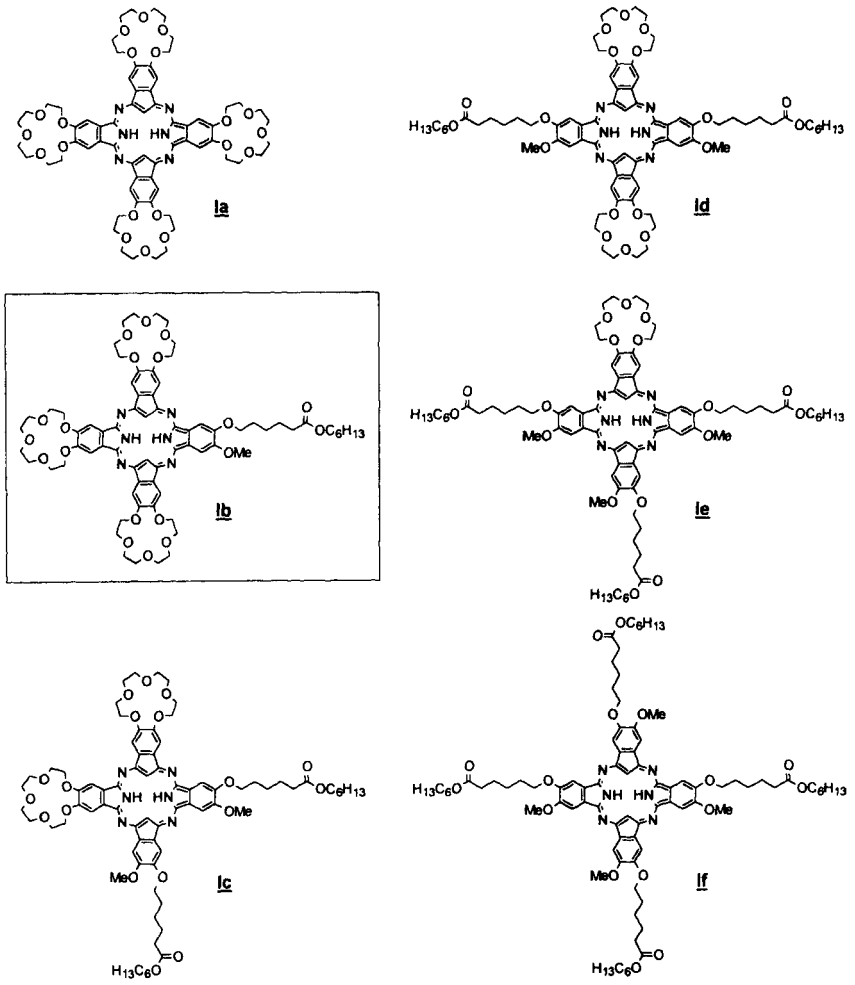
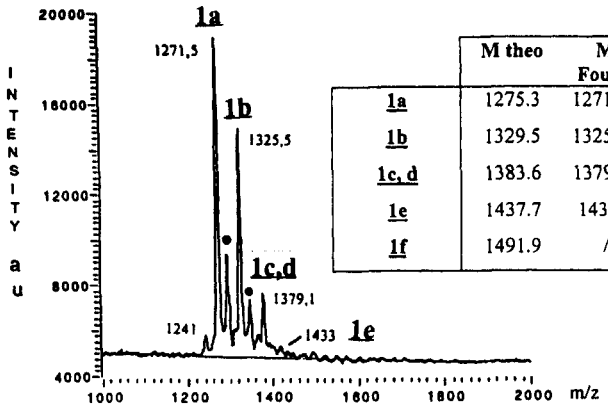


FIGURE 2 The various compounds formed in the reaction of the phthalonitriles **3** and **4**. (only some of the positional isomers are represented)

The following purification procedure has been followed:

- the crude reaction mixture is filtrated over alumina to eliminate polar compounds which are not eluted with the mixture $CHCl_3$/MeOH (95/5). In this way about 70% of the expected amount of product is recovered.
- a preparative thin layer chromatography (TLC) is carried out on alumina (eluent: $CHCl_3$/MeOH: 97/3) and the compound **1b**, $\mathbf{H_2}$ (Rf = 0.45) is further purified by a Soxhlet extraction with AcOMe or acetone which removes some soluble impurities. The green powder obtained is dissolved in CH_2Cl_2 and reprecipitated and washed with AcOMe. The product is dried at 100°C under vacuum (3 torr). Transesterification, to give the hexanoate ester, occurs during the reaction as evidenced by MALDI-TOF mass spectrometry on the crude product partly purified by a soxhlet extraction with heptane (in this solvent all phthalocyanine derivatives are insoluble). The results are shown in Figure 3.



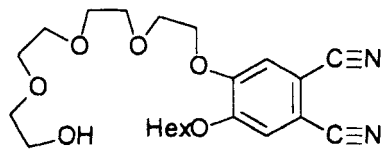
	M theo	M Found	%	% theo [b]
1a	1275.3	1271.5 [c]	53.8 [a]	31.6
1b	1329.5	1325.5 [c]	36.7 [a]	42.2
1c, d	1383.6	1379.1 [c]	9.0 [a]	21.1
1e	1437.7	1433. [c]	0.6	4.7
1f	1491.9	/	/	0.4

FIGURE 3 MALDI-TOF mass spectrum of the crude reaction mixture of the metal free derivatives **1a** – **1f**: Full circles indicate an adduct with Na^+. The table gives the theoretical and experimental relative intensities (%), the expected molar mass (M_{theo}), the one experimentally found (M_{found}) and the corresponding percentage. [a]Average on two spectra [b]Calculated with the hypothesis of a statistical reaction of the two phthalonitrile derivatives **3** and **4**. [c]A systematic shift of 4 units is due to the calibration procedure

Chemical microanalysis of the purified compound **1b**, $\mathbf{H_2}$ also indicates that transesterification occurs. The presence of a water molecule is compatible with the microanalysis results observed.

Side reactions have been shown to occur when the phthalocyanine derivatives are formed in addition to the previously mentioned transesterification. In particular the cleavage of the crown ether macrocyle has been detected when incom-

pletely pure **1b**, H_2 was reacted to synthesize the lutetium bisphthalocyanine complex (see further section). MALDI-TOF spectra indicate a parent ion (M + 102) which corresponds to the reaction of the hexanol anion derived from on the crown ether substituted phthalonitrile:



SCHEME 2

The cleavage is facilitated by Mg^{2+} and more significantly by Ca^{2+} when these ions are added in the reaction mixture. In these cases, the cleavage of the crown-ether macrocyles is predominant.

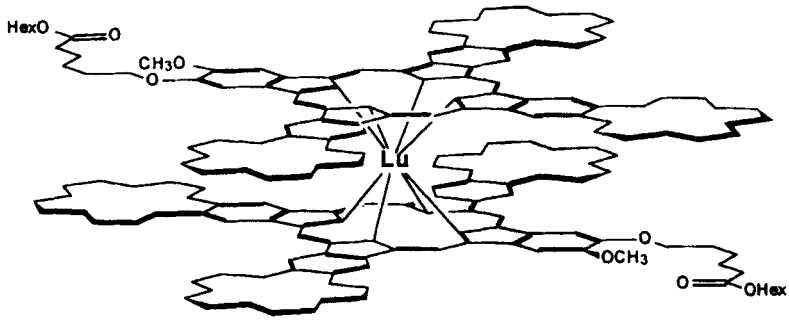
The transformation of the unsubstituted phthalocyanine PcH_2 into the corresponding lutetium complex PcLuX (X = AcO^-) has been described[10]. The metal free derivative is first transformed into the corresponding dianion by using n-BuLi in DMSO which is in turn transformed into PcLnOAc by adding $Ln(OAc)_3$ (Ln = Pr, Nd, Eu, Dy, Ho, Er, Yb, Lu)[10]. This method affords very satisfactory yields (90–93%). Another procedure[11,12] uses the β – dicetonate lanthanide derivative instead of $Ln(OAc)_3$. The first method has been used for treating **1b**, H_2 (leq.) with n-BuLi (2.4 eq.) and $Lu(OAc)_3(H_2O)_x$ (3 eq.) in DMSO. $Lu(OAc)_3$ has been previously dried at 160°C under vacuum. The formation of s-PcLuOAc (s : substituted) is followed by thin layer chromatography (final product Rf=0, starting material Rf=0.45; eluent: $CHCl_3$/MeOH: 97/3) and UV – visible absorption spectra. A quantitative conversion is observed in DMSO under reflux after approximately 30min. A partial purification is carried out by reprecipitation of the product in a mixture Et_2O/EtOAc (90/10) with a yield of 96%. The product has not been further purified.

The compound **2** has been synthesized by reacting the previous derivative **1b**, **Lu OAc** (1 eq.) with 8 eq. of the phthalonitrile **3** in the presence of DBU (6 eq.) in hexanol. The desired product is isolated with the following procedure:

- precipitation of a mixture of compounds from the reaction medium with hexane
- filtration over Celite®: the impurities are eluted with solvent mixtures from hexane to pentane / $CHCl_3$ (80/20), the desired fraction is obtained with the eluent $CHCl_3$/MeOH (95/5).

- Preparative thin film chromatography on alumina (eluent: $CHCl_3$/MeOH: 97.5/2.5%) yielding Rf = 0.45 for **2** and Rf = 0.65 for the difunctionalized derivative represented below, (derivative 8).
- filtration over Bio-Beads® SX3 (eluent: $CHCl_3$).
- reprecipitation from $CHCl_3$ with diethyl-ether.

During the reaction the following compound (derivative **8**):



8

SCHEME 3

has been isolated and characterized by MALDI-TOF mass spectrometry.

3. COMPLEXATION PROPERTIES OF 1b, H_2

It has been previously demonstrated[2,13,14] that the ion induced formation of sandwich complexes with crown ether substituted phthalocyanine derivatives yields important and characteristic changes in their UV-visible absorption spectra in solution. However, depending on the anion used, cations which can enter the macrocyclic cavity may also lead to aggregation[14]. The aggregation may also be obtained by using high polarity solvents even in the absence of salt[14]. The structure of the aggregates in these latter cases is not known with certainty. The same type of behavior has been observed for **1b, H_2**. (Fig. 4).

Solutions of salts in $CHCl_3$ / MeOH (90/10) are added to **1b, H_2**. In this way, the overall percentage of MeOH at the end of the titration is relatively small (< 0.4 %). Na SCN and NaOAc, whose cation can both enter the macrocyclic cavity lead to very different results: AcO^- does not indicate any aggregation

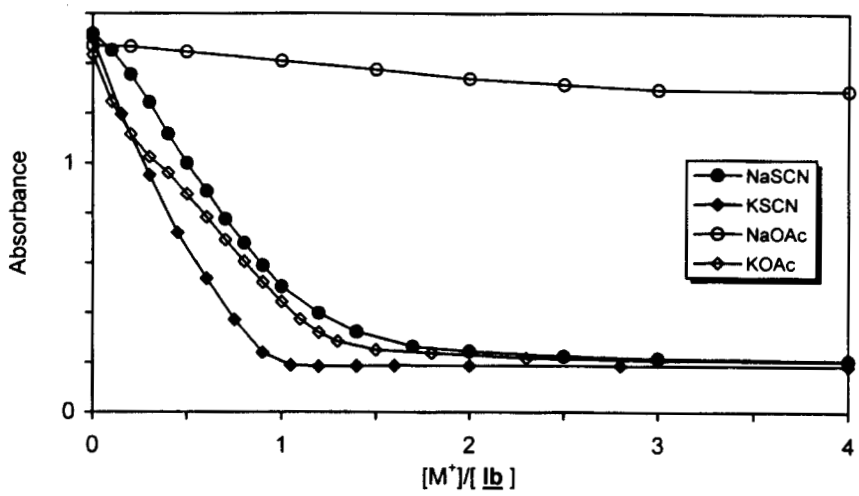


FIGURE 4 Variation of the intensity of the Q-band (λ = 700 nm) of compound **1b, H_2** by addition of $Na^+ X^-$ or $K^+ X^-$(X^- = AcO^-, SCN^-): (solvent: $CHCl_3$; the salts have been added in a solution $CHCl_3$ / MeOH: 90/10). (The contribution of aggregated species has been removed: the absorbance is proportional to the concentration of unaggregated **1b, H_2**.)

whereas SCN^- yields to a steep decrease of the Q-band up to the stoichiometry 1 Na^+ / 1 **1b, H_2**

On the other hand, both KSCN and KOAc lead to a decrease of the Q- band up to ratios in the range 1- 1.5 K^+ *per* **1b, H_2**. These observations are in agreement with the results obtained with four crown-ether substituted phthalocyanine derivatives[13]. The titration of **1b, H_2** with KSCN and KOAc may be followed by plotting:

$$\frac{C_a}{C_o} = \frac{A_m - A}{A_m - A_a}$$

where

C_a : Concentration of aggregated phthalocyanine

C_o: initial concentration of phthalocyanine; $C_o = C_a + C_m$

A_m: absorbance at λ_o (maximum of the Q-band) of the pure monomeric phthalocyanine; $A_m = \varepsilon_m l C_o$

A: absorbance experimentally observed at λ_o; $A = \varepsilon_m l C_m + \varepsilon_a l C_a$

A_a: absorbance at λ_o for the solution of pure aggregates; $A_a = \varepsilon_a l C_o$

The curve obtained by titration with KOAc shows three distinct regions:

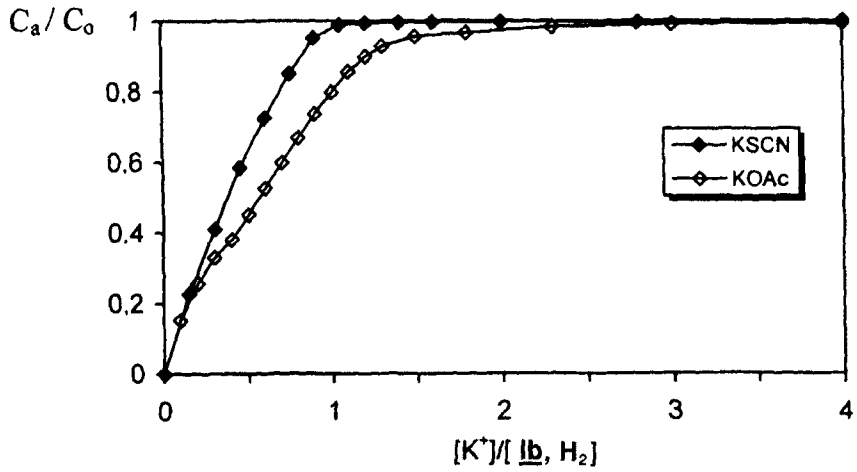


FIGURE 5 Percentage of aggregated phthalocyanine (C_a/C_o) as a function of the ratio $[K^+]$ / [**1b**, $\mathbf{H_2}$]

- for a ratio $[K^+]$ / [**1b**, $\mathbf{H_2}$] < 0.5, a concave curve is seen which is characteristic of a 2 ligands *per* one cation complexation (Fig. 6A).
- in the range 0.5 < $[K^+]$ / [**1b**, $\mathbf{H_2}$] < 1, the curve is approximately a straight line, this probably indicates[2] that the second complexation constant to form 2 K^+, 2 **1b**, $\mathbf{H_2}$ is larger than the first one (Fig. 6 B) (see references 2 and 3).
- finally, for $[K^+]$ / [**1b**, $\mathbf{H_2}$] > 1, a classical titration curve shape is obtained indicating a poor positive cooperativity for the third complexation (Fig. 6 C).

The equilibria involved can be written:

$$2L + M \rightleftharpoons L_2M \quad \beta_1 = \frac{[L_2M]}{[L]^2[M]}$$

$$L_2M + M \rightleftharpoons L_2M_2 \quad \beta_2 = \frac{[L_2M_2]}{[L_2M][M]}$$

$$L_2M_2 + M \rightleftharpoons L_2M_3 \quad \beta_3 = \frac{[L_2M_3]}{[L_2M_2][M]}$$

The complexation constants β_i cannot be compared directly since they are, in the general case, expressed in different units. It can be written instead:

$$\beta'_1 = L^2{}_o\beta_1 \quad \beta'_2 = L_o\beta_2 \quad \beta'_3 = L_o\beta_3$$

Where L_0 is the initial concentration of ligand **1b**, $\mathbf{H_2}$.

The first stage of the complexation of **1b**, $\mathbf{H_2}$ with KOAc can be modelled using a single constant β'_1; the fitting to the experimental curve leads to

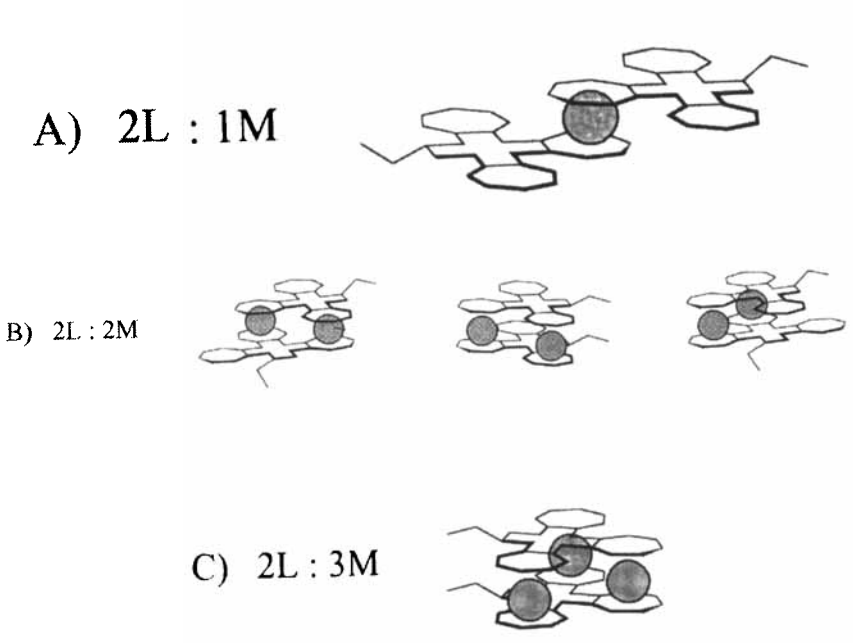


FIGURE 6 Schematic representation of cation/ligand complexes of various stoichiometries: A: 2L: 1M; B: 2L: 2M; C: 2L: 3M

$\beta_1 = 2.5 \times 10^{10} l^2$ mol^{-2}. This is in agreement with the corresponding constant found in the case of (15-crown-5)$_4$ PcM ($(6 \pm 2) \times 10^9$ l^2 mol^{-2} according to ref. 13).

For the second and third stage of the complexation, $[K^+]/[\underline{\mathbf{1b}}, \mathbf{H_2}] > 0.5$, three successive equilibria have been considered and fitted to the experimental curve to determine β'_2 and β'_3; in this way, it is found:

$$\beta'_1 = 2.5 \quad (\beta_1 = 2.5 \times 10^{10})$$
$$\beta'_2 = 500$$
$$\beta'_3 = 7$$

A strong positive cooperative effect is found when the second complexation is compared to the first one:

$$\beta'_2/\beta'_1 = 200$$

The third cation is more difficultly bound; this is very probably due to the fact that for the complexes of stoichiometry 2L: 2M (see Fig. 6B), some of the arrangements do not permit the complexation of the third potassium in sandwich

between two macrocycles. This phenomenon must not occur for the phthalocyanine derivative bearing four crown ether moieties.

The same type of studies and calculations has been carried out with KSCN. In this case, only two complexation equilibria have been taken into account:

$$\beta'_1 = 1\,000$$

$$\beta'_2 = 2\,000$$

A cooperative effect is still observed but its magnitude is smaller than in the case of KOAc. Due to the weaker ion pair energy interaction occuring in the case of KSCN, the first complexation constant (β'_1) is three orders of magnitude larger than for KOAc.

The complexation in the presence of NaOAc or NaSCN is more complicated to treat since the type of aggregated species formed during the addition of salt is not known with certainty. In consequence, no attempt to rationalize the complexation processes has been made.

4. COMPLEXATION PROPERTIES OF COMPOUND 2

The complexation properties of **2** have been compared with those of [(15-crown-5)$_4$ Pc]$_2$ Lu previously described[2,3]. In this last case, a fairly regular decrease of the absorption band is observed until a ratio [K^+] / [(15-crown-5)$_4$ Pc]$_2$ Lu = 4 is reached (Fig. 7).

In the case of **2**, the plateau value is reached for a stoichiometry in the range 2.5–3 and the absorbance decrease is significantly less than for [(15-crown-5)$_4$ Pc]$_2$ Lu. A dimer of **2** with the fully substituted phthalocyanine macrocycles facing each other would lead to a stoichiometry of 4 K^+: 2 L (2 : 1). Since a higher value is found, some aggregation must take place. However this process is not facilitated by the presence of only three crown-ether macrocyclic substituents on one of the phthalocyanine ring. Light scattering experiments have been carried out and they indeed show some light diffusion but the scattered intensity is two orders of magnitude lower in the case of **2** than for [(15-crown-5)$_4$ Pc]$_2$Lu, under similar conditions.

5. CONCLUSION

The synthesis and the studies of two crown-ether substituted phthalocyanine derivatives permitted us to determine, by UV – visible absorption spectra, the

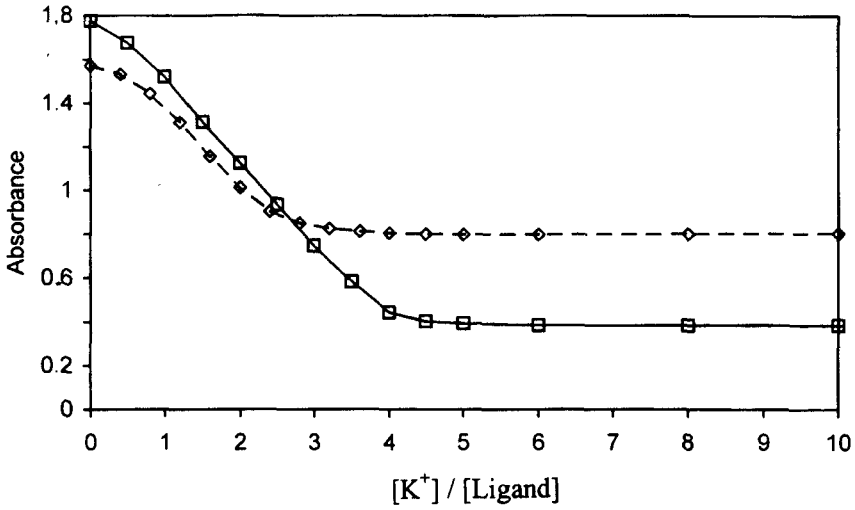


FIGURE 7 Decrease of the Q – absorption band of [(15-crown-5)$_4$ Pc]$_2$ Lu (full line) and **2** (dashed line) in a chloroformic solution by addition of KSCN in MeOH (at the end, the methanol amount does not exceed 5 %)

effect of the preorganization of the macrocyclic crown-ether subunits on the formation of sandwich complexes of stoichiometry 2 Ligands / 1 cation, 2 Ligands / 2 cations and 2 Ligands / 3 cations. A strong positive cooperative effect has been noticed for the complexation of the second cation (β'_2= 500) relatively to the complexation of the first one (β'_1 = 2.5) with the couple **1b, H_2** / KOAc in $CHCl_3$. Studies are in progress to link the functionalized products on polymeric chains and more detailed analyses of the complexation processes are under way[19].

6. EXPERIMENTAL SECTION

6.1 Generalities

Thin film chromatographies have been carried out on silica (Merck 60 F_{254}) or neutral alumina (Merck 60 F_{254} type E). Column chromatographies have been carried out using as stationary phases silica 60 (Merck, 63 – 200μm or 15 – 40μm for the flash chromatography) or alumina 90 neutral (Merck, 63 – 200μm,

Activity I). Preparative thin film chromatographies were carried out on silica 60 $F_{254+366}$ (Merck) or neutral alumina (Merck, 60 F_{254}).

Melting points have been measured with an optical microscope equipped with a heating plate (Mettler FP 82). IR spectra were recorded with a Fourier Transform Perkin-Elmer 1600 apparatus in the range 4 000 – 400cm^{-1} (KBr pellet) and 4 000 – 650cm^{-1} (NaCl cell). UV spectra were obtained with a Uvikon 860. NMR spectra were recorded at 300MHz(^{1}H) or 75MHz (^{13}C) with a Bruker AM 300 apparatus. Gas chromatography coupled with Mass Spectrometry (GCMS) was used to characterize all the compounds (Hewlett Packard Ultra 1, EIMS 5971). The temperature variations are indicated as follows: 140/2/16/270/5-Inj250; this means 2min at 140°C, then a temperature increase of 16°C/min, 5 min at 270°C; the ionization chamber in which injection is carried out is maintained at 250°C. Several mass spectrometry techniques have been used depending on the compounds:

- Chemical ionisation (in collaboration with Mrs Morin, Ecole Normale Supérieure) using NH_3 (M_w < 2 000g/mole).
- Fast Atom Bombardment (FAB) in collaboration with A. van Dorsselaer (Université L. Pasteur) (matrix: m – nitrobenzyl alcohol)
- Field Desorption (R. Polley, K. Haberroth, Institut für Org. Chemie, Tübingen)
- Matrix Assisted Laser Desorption Ionization (MALDI) – Time of flight (TOF) method used together with Mr. G. Bolbach (Université P. & M. Curie, Paris VI).

The microanalyses have been carried out by Mr C. Keyser at Institut C. Sadron in Strasbourg.

6.2 Syntheses

The synthesis of the 15-crown-5 substituted phtalonitriles has been described in the literature and the procedures have been followed without significant modifications[5,7,13,15–18]

4,5 – dibromo – 2 methoxyphenol (5)

This is the starting material for the preparation of the compound **4**.

In a dried (300°C under argon) vessel, 300 ml of CH_2Cl_2, 50ml guaiacol (0.44 mole; 1 eq.), 200mg iron powder and 3 iodine crystals are introduced. The reaction mixture is cooled down to 0°C and 50ml Br_2 (0.97mole; 2.2 eq.) in solution in 100ml CH_2Cl_2 are added dropwise for 4 hours. After completion of the addition, the mixture is stirred at room temperature for 20 hours. The bromine in

excess is neutralized with an aqueous solution of $Na_2S_2O_3$. 5 H_2O (42g; 0.17mole). The organic extract is rinsed with water (3 × 300ml) and dried over $MgSO_4$. The crude product is filtered over silica (eluent CH_2Cl_2) and recrystallized from 200ml of cyclohexane / toluene (95/5) (Yield: 67%).

m.p. = 93–94°C.

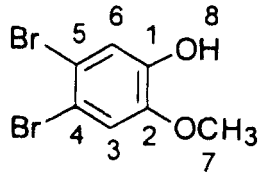
GCMS (m/z): t_{ret} = 4.7mn (θ_{ramp}: 140/2/16/270/5-Inj250)

280,282,284 (M^+); 265,267,269 (M^+-CH_3); 237,239,241 (M^+-CH_3-CO); 160,162 (MH^+-CH_3-CO-Br).

IR: ν (cm^{-1}) (KBr pellet)

3381 (OH); 3100,3050,3029 (C_{ar}-H); 2977,2931 (CH_3); 2833 (CH_3); 1601,1576,1494 (C_{ar}=C_{ar}); 1456,1450 (CH_3); 1400; 1382; 1329 (OH + C_{ar}-OH); 1266 (C_{ar}-OCH_3); 1251: 1224; 1204 (C_{ar}-H); 1170,1148,1103; 1028 (C_{ar}O-CH_3); 902; 875; 865 (C_{ar}-H); 839; 792; 652; 607; 561; 522; 448.

NMR ^1H: δ (ppm), $CDCl_3$



SCHEME 4

7.18 (s, 1H, H_3 or H_6); 7.06 (s, 1H,H_3 or H_6); 5.58 (s, broad, 1H, H_8); 3.88 (s, 3H, H_7).

NMR ^{13}C: δ (ppm), $CDCl_3$, (H - decoupling)

146.5, 145.6 (C_1, C_2); 119.2, 115.4 (C_3, C_6); 115.5, 113.7 (C_4, C_5); 56.4 (C_7).

Microanalysis: ($C_7H_6O_2Br_2$, 281.9 $g.mol^{-1}$)

calculated: C, 29.82; H, 2.15; Br. 56.68

found: C,29.63; H,1.99; Br.55.85

4,5 – dicyano – 2- methoxyphenol (6)

In a dry vessel, 5g of **5** (17.7mmoles; 1 eq.), 4.76g CuCN (53.1mmoles; 3 eq.) and 100ml freshly distilled DMF are introduced. The reaction mixture is heated under reflux in nitrogen for 8 hours. After cooling down to room temperature, the mixture is poored into 1 l of aqueous hydrochloric acid (5%) containing $FeCl_3$ (8.7g; 53.6 mmoles). The reaction mixture is heated at 80°C and the organic compounds are extracted with 2x600ml ethyl acetate. The organic extracts are

washed with distilled water, dried over $MgSO_4$, filtered through paper and evaporated to dryness. The brown viscous oil is filtrated over silica with CH_2Cl_2, CH_2Cl_2 / AcOEt (80/20 %), AcOEt and then purified by chromatography (silica: 200g; eluent: CH_2Cl_2 and then CH_2Cl_2 / AcOEt, 95/5 and 90/10). A first fraction contains the monobromo-monocyano derivative. The compound **6** is recrystallized from methanol (yield: 59%).

m.p. = 232.5 ± 1°C.

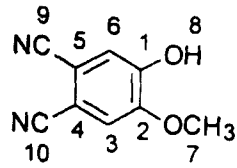
GCMS (m/z): t_{ret} = 9mn (θ_{ramp}: 100/2/16/250/5-Inj220)

174 (M^+): 159 (M^+-CH_3); 131 (M^+-CH_3-CO).

IR: ν (cm^{-1}) (KBr pellet)

3260 (OH); 3061 (C_{ar}-H); 2951 (CH_3); 2858 (CH_3); 2241, 2229 (CN); 1600, 1572, 1518 (C_{ar}=C_{ar}); 1468, 1450 (CH_3); 1374 (OH + val. OH); 1307 (C_{ar}-OCH_3); 1282; 1240; 1218; 1177; 1095 (O-CH_3); 1009; 896 (C_{ar}-H); 836; 736; 709; 636; 541.

NMR ^1H: δ (ppm), acetone-d_6



SCHEME 5

9.52 (s, broad, 1H, H_8); 7.58 (s, 1H, C_3 or C_6); 7.38 (s, 1H, C_3 or C_6); 4.04 (s, 3H, H_7).

NMR ^{13}C: δ (ppm), acetone-d_6, (H-decoupling)

152.9, 152.6 (C_1, C_2); 121, 117.7 (C_3, C_6); 117.5, 117.3 (C_9, C_{10}); 110.1, 108.5 (C_4, C_5); 57.8 (C_7).

Microanalysis: ($C_9H_6O_2N_2$, 174.2 $g.mol^{-1}$)

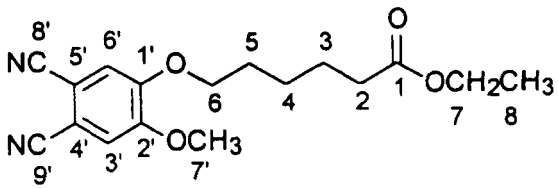
calculated: C, 62.07; N, 16.08; H, 3.47

found: C, 62.00; N, 15.75; H, 3.56

6-(4',5'-dicyano-2'-methoxy benzoxy) ethyle hexanoate. (7)

550mg (3.16mmoles, 1 eq.) of **6** are in suspension in 8ml distilled DMSO. 360mg (6.41mmoles, 2 eq.) of KOH are added. After 30min, 2 g of ethyl 6-bromohexanoate (8.96mmoles, 2.8 eq.) are introduced and the solution is stirred overnight. The reaction mixture is diluted with 60ml CH_2Cl_2, washed with distilled water; the organic phase is dried over $MgSO_4$, filtrated and evaporated to dryness. The excess of ethyl 6-bromohexanoate is separated by chromatography

on silica (150g; eluent: CH_2Cl_2 and CH_2Cl_2 / AcOEt, 1.2%). The product is recrystallized from 30ml of heptane / toluene (75/25 %) (yield: 79.5%).
m.p. = 102.5 ± 1°C.
GCMS: (m/z): t_{ret} = 10.8 min (θ_{ramp}: 140/2/16/270/5-Inj250)
316 (M^+); 271 (M^+-OEt); 229 (M^+-OEt-CO-CH_2); 215 (M^+-OEt-CO-$(CH_2)_2$);
201 (M^+-OEt-CO-$(CH_2)_3$); 187 (M^+-OEt-CO-$(CH_2)_4$); 174 (MH^+-OEt-CO-$(CH_2)_5$);
159 (MH^+-OEt-CO-$(CH_2)_5$-CH_3); 143($^+(CH_2)_5CO_2Et$).
IR: ν (cm^{-1}), (KBr pellet)
3127, 3068 (C_{ar}-H); 2930 (CH_2, CH_3); 2862 (CH_2, CH_3);
2229 (CN); 1729 (C=O); 1593, 1566, 1520 (C_{ar}=C_{ar});
1472,1455,1451 (CH_2, CH_3); 1414; 1400; 1391; 1373 (CH_3);
1360 (C_{ar}-O-C_{al}); 1288, 1236 (C_{ar}-OC_{al}); 1223; 1200 (C-O ester); 1162;
1094; 1047 (C_{ar}O-C_{al}); 1026; 1007; 959; 926 (C_{ar}-O-C_{al});
892, 858 (C_{ar}-H); 815; 538.
NMR ^1H: δ (ppm), $CDCl_3$



SCHEME 6

7.14 (s, 1H, H_3 or H_6); 7.13 (s, 1H, H_3 or H_6); 4.13 (q, 2H, H_7); 4.07 (t, 2H, H_6);
3.95 (s, 3H, H_7'); 2.35 (t, 2H, H_2); 1.9 (m, 2H, H_5); 1.72 (m, 2H, H_3);
1.42 (m, 2H, H_4); 1.26 (t, 3H, H_8).
^{13}C: δ (ppm), $CDCl_3$ (H-decoupling)
173.4 (C_1); 152.7, 152.1 ($C_{1'}$, $C_{2'}$); 115.8, 115.7 ($C_{8'}$, $C_{9'}$); 115.5, 114.8 ($C_{3'}$, $C_{6'}$); 108.8, 108.6 ($C_{4'}$, $C_{5'}$); 69.5 (C_6); 60.3 (C_7); 56.5 ($C_{7'}$); 34 (C_2); 28.4 (C_5); 25.4 (C_4); 24.5 (C_3); 14.2 (C_8).
Microanalysis: ($C_{17}H_{20}O_4N_2$, 316.3g.mol^{-1})
calculated: C, 64.54; H, 6.37; N, 8.85
found: C, 64.75; H, 6.43; N, 8.75

2-[5-(hexyloxycarbonyl) pentyloxy]-3-methoxy; 9,10; 16,17; 24-tris-(3,6,9 trioxaundecan-1,11-diyloxy) dihydrophthalocyanine (1b, H_2)

Synthesis of **1b, Mg**.

In a dry vessel are introduced: 115mg $MgCl_2$ (1.2mmole; 1.2 eq.), 955mg of phthalonitrile **3** (3mmoles; 3 eq.), 317mg of **4** (1mmole; 1 eq.) and 10ml distilled n-hexanol. The reaction mixture is heated under reflux and then 450µl (3mmoles; 3 eq.) of DBU are added. The heating is maintained during 5H30 and, after cooling, most of the n-hexanol is evaporated under vacuum. The substituted magnesium phthalocyanines are precipitated and washed with pentane.

Four different products corresponding to **1a, Mg** (Rf = 0.4), **1b, Mg** (Rf = 0.75), **1c, Mg** and **1d, Mg** (Rf= 0.9) and **1e, Mg** (Rf = 1) (see Figure 2) can be detected by TLC on alumina (eluent: $CHCl_3$ / MeOH: 94/6%). In further reactions, the mixture will be used. It is treated at 65–70°C in 40ml DMF containing 2.5 ml HCl (36%) for 2 hours. After cooling, 100ml $CHCl_3$ and 25ml MeOH are added. The organic phase is washed with 250ml distilled water. After evaporation, the crude phthalocyanine compounds are filtrated over 200 g alumina (eluent: $CHCl_3$ / MeOH: from 2 to 5% alcohol). In this way 980mg of green powder is obtained. The four products **1a, H_2** (Rf = 0.2), **1b, H_2** (Rf = 0.45), **1c, H_2** and **1d**, H_2 (Rf = 0.75) and **1e, H_2** (Rf = 1) can be detected by TLC on alumina (eluent: $CHCl_3$ / MeOH: 97/3).

The crude product is separated by preparative thin layer chromatography on alumina (eluent: $CHCl_3$ / MeOH: 97/3; Rf = 0.45). The product is recovered from the plate by using $CHCl_3$ / MeOH (90/10). **1b, H_2** is then solubilized in $CHCl_3$, filtrated over sand to remove traces of alumina and the impurities are further removed by a soxhlet extraction with methyl acetate (yield: 23.1 %).

The overall yield of preparation of **1a-f** is estimated to be around 64 %.

IR: ν (cm-1) (KBr pellet)

3386 (NH bound + OH, H_2O); 3296 (NH free); 3074 (C_{ar}-H); 2926 (CH_2, CH_3); 2863 (CH_2, CH_3); 1731 (C=O); 1670; 1609, 1484, 1448 (C_{ar}=C_{ar}, C_{ar}=N); 1404; 1380; 1360 (C_{ar}-O-CH_2); 1330; 1280 (C_{ar}-OCH_2); 1204 (C_{ar}-H); 1130, 1098 (C_{al}-O-C_{al}); 1057 (C_{ar}O-CH_2); 1024; 937 (C_{ar}-O-CH_2); 856 (C_{ar}-H); 794; 744; 705.

UV-visible: λ, nm (ε, l. mol^{-1}. cm^{-1})

700 (153 000); 662 (124 000); 644 (51 000); 600 (2 700); 422 (36 000); 349 (84 000); 295 (56 000).

Microanalysis: ($C_{69}H_{84}O_{19}N_8$. H_2O, 1329.5 + 18 = 1347.5g.mol^{-1})

calculated: C, 61.50; H, 6.43; N, 8.32

found: C, 61.52; H, 6.27; N, 8.27

MS (FAB, m/z): matrix: m-nitrobenzyl alcohol

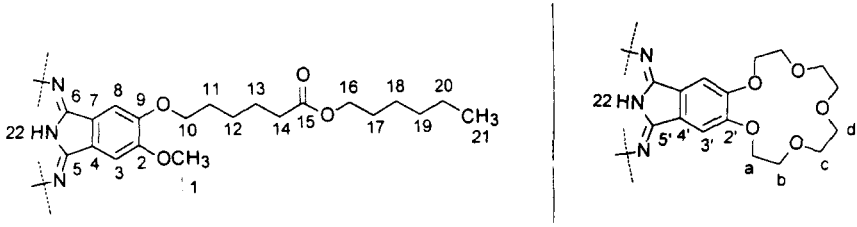
1351.4 ($M+Na^+$); 1329.4 (M^+); 1170.3 (MH^+-CO_2Hex-OCH_3).

MS (MALDI-TOF) matrix: α cyano-4-hydroxycinnamic acid

m/z = 1333.2 (M^+); 1355.5 (M + Na^+); 2663.5 $(M_2)^+$; 3999 $(M_3)^+$ – A systematic shift of 4 units is due to the use of standard calibration.

NMR ^{1}H and ^{13}C: (δ (ppm),

For **1b, H_2** the best experimental conditions were in $CDCl_3$ at 50°C. The NMR spectra have been shown to be sensitive to concentration: important chemical shifts are noticed between $3x10^{-3}$ M and $5x10^{-4}$ M.



SCHEME 7

TABLE I *^{1}H NMR Chemical shifts for* **1b, H_2** *and assignment of the peaks ($CDCl_3$, 3 10^{-3} M, 50°C)*

atoms	H_{14}	H_1	$H_{3,3',8}$	H_{10}	H_{11}	H_{12}	H_{13}
δ (ppm)	2.55	4.38	7.98–8.16	4.54	2.26	1.88	1.99
atoms		H_{16}	H_{17}	H_{18}	$H_{19,20}$	H_{21}	H_{22}
δ (ppm)		4.18	1.70	1.36	1.36	0.90	−3.35
atoms		H_a		H_b	H_c	H_d	
		4.60,4.54		4.23	3.98	3.98	

The assignment has been carried out by comparison with model compounds and COSY spectra of the corresponding 18-crown-6 derivative.

With the same numbering, the assignment of the ^{13}C NMR spectra has been carried out.

TABLE II *^{13}C NMR Chemical shifts for* **1b, H_2** *and assignment of the peaks ($CDCl_3$, 3 10^{-3} M, 50°C)*

atoms	C_1	C_2	$C_{2',9}$	$C_{3,3',8}$			$C_{4,4',7}$		$C_{5,5',6}$
δ (ppm)	56.9	152.2	151.4	105.6,105.4,105.3			130.2,129.8		148.4
atoms		C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}
δ (ppm)	69.6	29.7	26.2	25.2	34.5	not det.	64.6	28.8	25.7
atoms	C_{19}	C_{20}	C_{21}	C_a	C_b	C_c	C_d		
δ (ppm)	31.5	22.5	13.9	69.6	69.9	70.7	71.5		

Acetato {2-[5-(hexyloxycarbonyl) pentyloxy]-3-methoxy; 9,10; 16,17; 23,24 – tris – (3,6,9-trioxaundecan-1,11-diyloxy) phthalocyaninato}lutetium (1b, Lu OAc)

Two solutions are prepared separately:

- 120mg of lutetium triacetate (0.34mmoles; 3 eq.) are dried at 160°C under vacuum for 4H30, they then are dissolved in 2ml DMSO.
- 150 mg of **1b**, H_2 (0.113mmole; 1 eq.) are dried at 100°C for 4 hours in a stream of argon and then 8ml DMSO are added and heated up to 180°C until complete solubilization.

In the second solution 170µl (0.272mmole; 2.4 eq.) of a 1.6M solution of BuLi in hexane is introduced. After 20min of stirring at 180°C, 120mg lutetium triacetate in DMSO are added. After 30min at 190°C under argon, the reaction mixture is cooled down to room temperature and diluted with 30ml $CHCl_3$. The organic phase is washed with 20ml distilled water, and partly evaporated to dryness. The DMSO is removed by a strong air flow at room temperature during 24–48H. The crude product **1b, Lu OAc** is dissolved in a small amount of $CHCl_3$and precipitated by adding 100ml of a solution of Et_2O / AcOEt (90/10). 170 mg (yield: 96%) of **1b, Lu OAc** are obtained in this way.

N.B. **1b, LuOAc** cannot be purified by chromatography over alumina, it decomposes with the loss of the lutetium ion.

IR: ν (cm^{-1}), (KBr pellet)

3405 (OH, H_2O); 3077 (C_{ar}-H); 2924 (CH_2, CH_3);

2857 (CH_2, CH_3); 1719 (C=O, CO_2Hex + OAc);

1606, 1494, 1453 ($C_{ar} = C_{ar}$, $C_{ar} = N$); 1401; 1379; 1357 ($C_{ar} - O - CH_2$)

1277 (C_{ar}-OCH_2); 1202 (C_{ar}-H); 1128, 1085 (C_{al}-O-C_{al});

1055 ($C_{ar}O$-CH_2); 984; 936 (C_{ar}-O-CH_2); 862, 812 (C_{ar}-H); 769; 754; 734.

UV-visible: λ, nm (ε, $1.mol^{-1}.cm^{-1}$), $CHCl_3$.

679 (119 000); 614 (23 000); 356 (62 000); 291 (40 000).

Microanalysis: ($C_{71}H_{85}O_{21}N_8Lu$. $4H_2O$, 1561.5 + 72 = 1633.5 $g.mol^{-1}$, OAc included)

calculated: C, 52.20; H, 5.74; N, 6.86; Lu, 10.71

found: C, 52.11; H, 5.52; N, 6.98; Lu, 10.11

1) *MS (MALDI-TOF, m/z)*: matrix: α-cyano-4-hydroxycinnamic acid (M_w: 189.17 $g.mol^{-1}$) 1691.04 (M^+-OAc + 1 molecule of matrix, carboxylate form).

2) *MS (MALDI-TOF, m/z)*: C_{69} H_{82} O_{19} N_8 Lu (without OAc) M_w = 1502.43 (monoisotopic mass: 1501.51).

Main peaks observed (monoisotopic peak): 1501.63 (M^+); 1689.98 (M+ matrix)$^+$; 1713.93 (M+matrix+Na^+); 1729.14 (M+ matrix + K^+).

The analysis of the isotropic distribution at m/z = 1689.98 when compared to the calculated one shows the contribution of two ions, with and without H^+.

TABLE III *Assignment of the ^1H NMR spectra of* **1b, Lu OAc** *in $CDCl_3$ / CD_3OD (95/5 %) 3 10^{-3} M (reference taken: $CHCl_3$ δ=7.27 ppm) (notation as in Tables II and III)*

atoms	H_{14}	H_1	$H_{3,3',8}$	H_{10}	H_{11}	H_{12}	H_{13}
δ (ppm)	2.43	4.39	8.88	4.68	2.14	1.73	1.85
atoms		H_{16}	H_{17}	H_{18}	$H_{19,20}$	H_{21}	H_{22}
δ (ppm)		4.09	1.62	1.29	1.29	0.85	/
atoms		H_a	H_b	H_c	H_d		
		4.68	4.09	3.79	3.79		

{2-[5-(hexyloxycarbonyl)pentyloxy]-3-methoxy; 9,10; 16,17; 23,24-tris-(3,6,9-trioxaundecan-1,11-diyloxy)phthalocyaninato}[2,3;9, 10;16,17;23,24-tetrakis- (3,6,9-trioxaundecan-1,11-diyloxy) phthalocyaninato]lutetium (III) (2)

In a dry wessel, one introduces 160mg (0.102mmole; 1 eq) of phthalocyanine derivative **1b, Lu OAc**, 261mg (0.816mmole; 8 eq.) of crown-ether substituted phthalonitrile (**3**) and 6.5ml n-hexanol. The reaction mixture is heated at 160°C under argon until complete dissolution of **1b, Lu OAc** and **3** before adding 90µl (0.604 mmole; 6 eq.) of DBU. The reaction mixture is stirred under reflux for 8 hours. After cooling down to room temperature, the phthalocyanines are precipitated by adding of 80 ml n-hexane in the solution. The suspension is filtered over celite and rinsed successively with n-hexane, pentane / $CHCl_3$ (90/10 %), pentane / $CHCl_3$ (80/20%) and the product is finally extracted by a mixture $CHCl_3$/MeOH (95/5). The compound **2** is isolated by TLC (alumina;

eluent: $CHCl_3$ / MeOH: 97.5 / 2.5%; Rf = 0.7). The product is then filtrated twice over 40g of Bio-Beads® SX3 (eluent: $CHCl_3$) to remove the traces of remaining alumina (Yield: 21 %).

For UV-visible studies, **2** is further filtrated twice on Bio-Beads® SX3 the end fractions are discarded (green – yellowish colour). After redissolution in $CHCl_3$, the product is reprecipitated with Et_2O.

IR: ν (cm^{-1}) (KBr pellet)

3419 (OH, H_2O); 3074 (C_{ar}-H); 2927 (CH_2, CH_3);

2864 (CH_2, CH_3); 1730 (C=O);

1601,1499,1455 (C_{ar}=C_{ar},C_{ar}=N); 1399; 1376; 1357 (C_{ar}-O-CH_2); 1324;

1278 (C_{ar}-OCH_2); 1203 (C_{ar}-H); 1128, 1104, 1082 (C_{al}-O-C_{al});

1056 (C_{ar}O-CH_2); 982; 935 (C_{ar}-O-CH_2); 858, 810 (C_{ar}-H); 756.

UV-visible: λ, nm (ε.1.mol^{-1}. cm^{-1}), $CHCl_3$
666 (159 000); 603 (30 000); 476 (39 000); 367 (131 000); 291 (102 000).
Microanalysis: ($C_{133}H_{154}O_{39}N_{16}Lu$, 2775.7g.mol^{-1})
calculated: C, 57.55; H, 5.59; N, 8.07: Lu, 6.30
found: C, 57.37; H, 5.73; N, 7.54; Lu, 5.70
MS (MALDI-TOF, m/z): matrix: α-cyano-4-hydroxycinnamic acid (M_w = 189.17 g. mol^{-1})
M_w = 2775.38 g.mol^{-1} monoisotopic mass: 2773.997
Above approximately 1000, no other peak than the parent ion is observed (Figure 8).

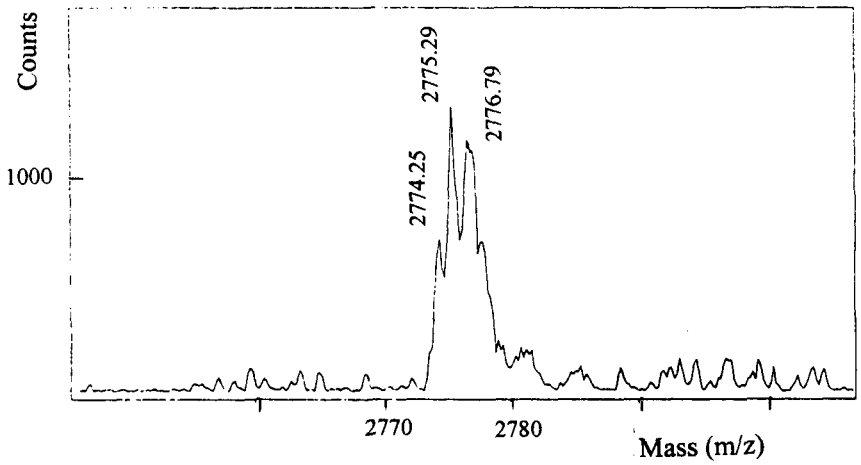


FIGURE 8 Isotopic distribution of the parent ion observed for **2** (apparatus: Vestec)

TABLE IV *Assignment of the* ^{1}*H NMR spectrum of* **2**

atoms	H_1	$H_{3,3',8}$	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}
δ (ppm)	3.78	broad 4.9–6.5	3.78	2.20	1.87	1.96	2.46
atoms	H_{16}	H_{17}	H_{18}	$H_{18'}$	H_{19-20}	H_{21}	H_{22}
	4.11	1.65	1.32	/	1.32	0.89	/
atoms	H_a	H_b	H_c	H_d		H_e	
	3.78	4.11	3.91	3.91		/	

6.3 Complexation properties

The complexation properties have been determined by adding solutions of salt ($2.5x10^{-3}$ M in MeOH or $CHCl_3$ / MeOH: 90/10) to chloroformic solutions (10^{-5} M) of mono or bisphthalocyanine lutetium derivatives. The solutions are stirred for 1–2 mn before UV-visible absorption measurements. The value of the absorbance is corrected by the variation of the volume.

The amount of aggregated species is given by the formula given in the section: « complexation properties of **1b**, H_2.

The calculation of the equilibrium constants has been partly explicited in the corresponding section. With the same notation, one can write:

$$x = [L]/L_o;\ y = [LM]/L_o;\ z = [L_2M_2]/L_o;\ t = [L_2M_3]/L_o;$$
$$u = [L_2M_4]/L_o;\ m = [M]/L_o;\ m_o = M_o/L_o$$

It then comes:

$$x + y + 2z + 2t + 2u = 1$$
$$m + y + 2z + 3t + 4u = M_o$$

These equations represent the conservation of the mass of ligand and cation. Further developments may be found in the literature in order to use them to calculate the binding constants.[20]

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References

(1) J. Simon, P. Bassoul and S. Norvez, *New J. Chem*, **13**, 13 (1989).
(2) T. Toupance, V. Ahsen and J. Simon, *J. Amer. Chem. Soc.*, **116**, 5352 (1994).
(3) T. Toupance, H. Benoit, D. Sarazin and J. Simon, *J. Amer. Chem. Soc.*, **119**, 9191 (1997).
(4) V. Le Berre, L. Angely, N. Simonet-Gueguen and J. Simonet, *J. Chem. Soc. Chem. Comm.*, **13**, 984 (1987).
(5) A.R. Koray, V. Ahsen and Ö. Bekâroglu, *J. Chem. Soc. Chem. Comm*, 932 (1986).
(6) N. Kobayashi and Y. Nishiyama, *J. Chem. Soc. Chem. Comm*, 1462 (1986).
(7) R. Hendriks, Ot. E. Sielcken, W. Drenth and R.J.M. Nolte, *J. Chem. Soc.*, 1864 (1986).
(8) J. Vacus, G. Memetzidis, P. Doppelt and J. Simon, *J. Chem. Soc. Chem. Comm.*, 697 (1994).
(9) D. Pernin, K. Haberroth and J. Simon, *J. Chem. Soc. Perkin Trans. 1*, 1265 (1997).
(10) N.B. Subbotin, L.G. Tomilova, N.A. Kostromina and E..A Luk'yanets, *J. Gen, Chem. USSR*, 345 (1986).
(11) H. Sugimoto, T. Higashi and M. Mori, *Chem. Lett.*, 801 (1982).
(12) H. Sugimoto, T. Higashi, A. Maeda, Y. Hirai, J. Teraoka, M. Mori, H. Masuda and T. Taga, *J. Less Common Met.*, **112**, 387 (1985).
(13) N. Kobayashi and A.B.P. Lever, *J. Amer. Chem. Soc*, **109**, 7433 (1987).
(14) Ot. E. Sielcken, M.M. van Tilborg, M.F.M. Roks, R. Hendriks, W. Drenth and R.J.M. Nolte, *J. Amer. Chem. Soc.*, **109**, 4261 (1987).

(15) C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
(16) V. Ahsen, E. Yilmazer, M. Ertas and O. Bekaroglu, *J. Chem. Soc. Dalton Trans.*, 401 (1988).
(17) J. Vacus, *Thèse de doctorat*, Paris, (1994).
(18) T. Toupance, *Thèse de doctorat*, Paris, (1995).
(19) L. Facchini, *La Nouvelle Scientifique / Science en situation*, (octobre/novembre 1999).
(20) R. Rosset, D. Bauer and J. Desbarres, *Chimie analytique des solutions et informatique* Masson, Paris (1991[2]).