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Synthesis and complexation study of two dicalix-dipyrene

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INTRODUCTION

Calixarenes^[1] have been exploited in all areas of supramolecular chemistry^[2] over the past four decades and many recent developments have concerned their applications in the production of chemical entities with the dimensions of nanometres as in 'nanochemistry'^[3]. One of the most important use of calixarenes is the treatment of nuclear wastes^[4].

In a recent publication^[5] we have investigated the fluorescence-sensing properties of pyrenyl-appended calixarenes. The fluorescence behaviour of these product was investigated in acetonitrile in the presence of various cation perchlorate (Li⁺, K⁺, Cs⁺, Ag⁺, Al³⁺, Ba²⁺, Cd²⁺, and In³⁺). Only tren-N-tricalix[4]arene with three appended pyrenyl groups showed enhanced fluorescence in the presence of Al³⁺, and to a lesser extend, with In³⁺. This was interpreted by the need of a tren core to capture metal cations and give a fluorescent signal, the calixarenic unit having no important role in the complexation process.

In this paper we described the synthesis of two dicalix-diamidopyrene and investigated the binding properties in order to evidence some other feature of these ligands in the presence of lanthanide and Co²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Al³⁺ cations.

Synthesis part

Synthesis of 1

The synthesis of derivative 1 was conducted at the beginning of the compound (1). In the latter, one adds 5 equivalents K₂CO₃, 2.5 equivalents N-PCA and

excessive KI and door-to reflux under nitrogen in acetonitrile for 2 days. The derivative 1 is purified on silica column (CH₂Cl₂/acetone: 85/15), it is obtained in the form of a yellow powder with a yield of 28%. Mass spectrometry MALDI-TOF showed that the derivative 1 is m/z = 1980.72 (C₁₃₂H₁₄₆N₄O₁₂).

Synthesis of iii

The iii derivative is obtained by reacting mono methyle ester calix[4]arene (ii) with 0.33 equivalents 2,2'-(ethylenedioxy) bis (ethylamine) (commercial) in a mixture of methanol/toluene: (1/1). It brings to reflux under nitrogen for 24 hours. The product iii is purified by column chromatography on silica (CH₂Cl₂/acetone: 90/10) and is obtained in the form of white powder with a yield of 38%. Mass spectrometry FAB⁺ showed that the derivative iii is m/z = 1526.0 (C₉₈H₁₂₈N₂O₁₂).

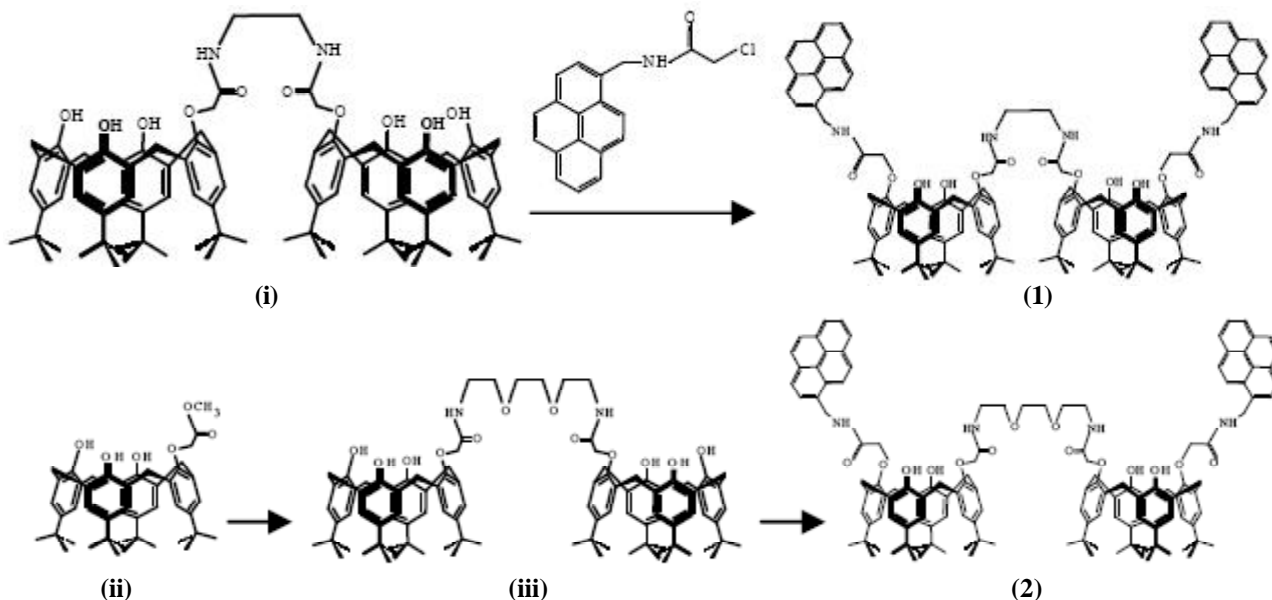
Synthesis of 2

We introduce 0.500 g (0.327 mmol) of derivative iii, 0.220 g (1.63 mmol) of K₂CO₃ and 10 ml of acetonitrile. We gave a stirring under room temperature for 1 hour. Then we add 0.250 g (0.819 mmol) N-PCA and excessive KI and door to reflux under nitrogen for 3 days. After extraction, the residue is solubilized in the minimum dichloromethane and purified on silica column (CH₂Cl₂/acetone: 85/15). The derivative 2 is obtained in the form of a yellow powder with a yield of 33%.

Preparation of i:

i (300 mg ,0.208 mmol), K₂CO₃ (144 mg ,1.04 mmol), N-PCA (160 mg ,0.521 mmol) and an excess

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of KI, acetonitrile (4 mL) were refluxed for 2d. After evaporation under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with aqueous 1N HCl. The organic layer was dried over Na_2SO_4 , filtrated and evaporated. Chromatography on a SiO_2 column (85:15 CH_2Cl_2 /acetone) gave pure 1. White solid. Mp 165-166 °C $^1\text{H NMR}$ (CDCl_3): 9.06 (t, 2H, $J = 3.3$ Hz, NHCO), 8.98 (s large, 2H, NHCO-pyrenyl), 8.17-7.70 (m, 18H, pyreneH), 6.87 (s, 4H, ArOH), 6.78-6.53 (m, 16H, ArH), 5.07 (d, 4H, $J = 3.0$ Hz, OCH_2CO -pyrenyl), 4.88 (s, 4H, OCH_2CO), 4.20 (d, 4H, $J = 13.2$ Hz, AB system, ArCH_2Ar), 4.11 (s, 4H, $\text{NHCH}_2\text{pyrenyl}$), 3.87 (q, 4H, $J = 3.9$ Hz, CH_2CH_2), 3.29 (d, 4H, $J = 15.0$ Hz, A'B' system, ArCH_2Ar), 2.96 (d, 4H, $J = 13.2$ Hz, AB system, ArCH_2Ar), 2.71 (d, 4H, $J = 15.0$ Hz, A'B' system, ArCH_2Ar), 1.09 (s, 36H, tert-butyl), 0.93 (s, 18H, tert-butyl), 0.87 (s, 18H, tert-butyl). MW = 1980.63 calculated for $\text{C}_{132}\text{H}_{146}\text{N}_4\text{O}_{12}$, (MALDI-TOF) $m/z = 1980.72$. Yield 28 %.

Preparation of iii

ii (500 mg, 0.69 mmol), 2,2'-(ethylenedioxy)bis(ethylamine) (34 mg, 0.23 mmol), 5 mL méthanol/toluène : (1/1) were refluxed for 24h. After evaporation under reduced pressure, the residue was dissolved in CH_2Cl_2 . Chromatography on a SiO_2 column (90:10 CH_2Cl_2 /acetone) gave pure iii. White solid. Mp 212-214°C $^1\text{H NMR}$ (CDCl_3): 10.06 (s, 2H, ArOH), 9.39

(s, 4H, ArOH), 9.24 (t, 2H, $J = 4.71$ Hz, NHCO), 7.11 (s, 4H, ArH), 7.09 (s, 8H, ArH), 7.04 (s, 4H, ArH), 4.59 (s, 4H, OCH_2CO), 4.27 (d, 4H, $J = 13.2$ Hz, AB system, ArCH_2Ar), 4.17 (d, 4H, $J = 13.2$ Hz, A'B' system, ArCH_2Ar), 3.76-3.71 (m, 12H, CH_2CH_2), 3.37 (d, 4H, $J = 13.2$ Hz, AB system, ArCH_2Ar), 3.36 (d, 4H, $J = 13.2$ Hz, A'B' system, ArCH_2Ar), 1.27 (s, 18H, tert-butyl), 1.25 (s, 36H, tert-butyl), 1.20 (s, 18H, tert-butyl). MW = 1526.1 calculated for $\text{C}_{98}\text{H}_{128}\text{N}_2\text{O}_{12}$, (MALDI-TOF) $m/z = 1526.0$. Yield 38 %.

Preparation of 2

iii (500 mg, 0.327 mmol), K_2CO_3 (220 mg, 1.63 mmol), N-PCA (250 mg, 0.819 mmol) and an excess of KI, acetonitrile (10 mL) were refluxed for 3d. After evaporation under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with aqueous 1N HCl. The organic layer was dried over Na_2SO_4 , filtrated and evaporated. Chromatography on a SiO_2 column (85:15 CH_2Cl_2 /acetone) gave pure 2. White solid. Mp 171-172°C $^1\text{H NMR}$ (CDCl_3): 10.04 (s, 1H, ArOH), 9.37 (s, 1H, ArOH), 9.18 (t, 2H, $J = 5.4$ Hz, NHCO), 9.11 (t, 2H, $J = 3.3$ Hz, NHCO-pyrenyl), 8.24-7.69 (m, 18H, pyreneH), 7.08 (s, 2H, ArOH), 6.77-6.50 (m, 16H, ArH), 5.28 (d, 4H, $J = 3.6$ Hz, OCH_2CO -pyrenyl), 4.72 (s, 4H, OCH_2CO), 4.05 (d, 4H, $J = 13.2$ Hz, AB system, ArCH_2Ar), 4.11 (s, 4H,

NHCH₂pyrenyl), 3.78 (q, 4H, J = 5.1 Hz, CH₂CH₂), 3.51 (t, 4H, J = 4.5 Hz, CH₂CH₂), 3.25 (d, 4H, J = 13.5 Hz, A'B' system, ArCH₂Ar), 3.18 (s, 4H, CH₂CH₂), 3.02 (d, 4H, J = 13.2 Hz, AB system, ArCH₂Ar), 2.65 (d, 4H, J = 13.5 Hz, A'B' system, ArCH₂Ar), 1.19 (s, 36H, tert-butyl), 0.93 (s, 18H, tert-butyl), 0.89 (s, 18H, tert-butyl). MW = 2068.73 calculated for C₁₃₆H₁₅₄N₄O₁₄, (MALDI-TOF) m/z = 2068.49. Yield 33 %. ¹³C-NMR (CDCl₃) : 168.748, 148.838, 148.110, 142.264, 132.120, 131.793, 130.519, 129.764, 128.205, 127.145, 126.439, 126.387, 125.987, 125.696, 125.454, 125.016, 124.825, 124.735, 122.410, 74.605, 69.950, 39.220, 33.966, 33.867, 33.653, 32.058, 31.571, 31.118, 30.831, 30.769.

EXPERIMENTAL

Instrumentation

Uncorrected melting points (Mps), Büchi 500. ¹H NMR, Bruker SY 200 (300 MHz, δ in ppm from tms, J in Hz in CDCl₃ or CD₃CN, TMS as standart). MALDI-TOF mass spectra, Biflex Bruker. All the reactions were run under N₂ atmosphere. SiO₂(Geduran 1.11567) was used for column chromatography. All reagents and solvents were commercial and used without further purification. The UV spectra were recorded on a Perkin Elmer Lambda (11) spectrophotometer. Conductance measurements were recorded on a conductimeter Tacussel CDM210 with cell constant 0.719.

Extraction studies

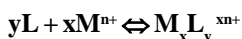
The extraction experiments of Ln³⁺ and transition metal picrates from water into dichloro methane were performed according to a procedure described in the literature^[6] Equal volumes (5 ml) of neutral aqueous solution of alkali metal picrate (2.5×10⁻⁴ M) and CH₂Cl₂ solution (5 ml) of calixarene derivatives (2.5×10⁻⁴ M) were mixed and magnetically shaken in a thermostated water bath at 20°C for 30 min and then left standing for 2 to 6 h in order to obtain a complete separation of the two phases. The concentration of metal picrate remaining in the aqueous phase was determined from the absorbance A at 355 nm. The percentage extraction (%E) was derived from the following

expression in which A₀ is the absorbance of the aqueous solution of a blank experiment without calixarene:

$$\%E = 100(A_0 - A)/A_0$$

Stability constant measurements

The stability constants β_{xy} being the concentration ratios [M_xL_y^{xn+}]/[Mⁿ⁺]^x[L]^y and corresponding to the general equilibrium:



(where Mⁿ⁺ = metal ion, L = ligand) were determined in acetonitrile by UV-absorption spectrophotometry at 25°C. The ionic strength was been maintained at 0.01 M using either Et₄NCIO₄ or Et₄NNO. The spectra of ligand solutions of concentrations ranging between 10⁻⁴ and 2×10⁻⁴ M and increasing concentration of metal ion were recorded between 250 nm and 350 nm. Generally the metal to ligand ratio R at the end of the titration did not exceed 20 and the equilibria were quasi-instantaneous for all the systems. Addition of the metal ion salts to the ligand induced in the spectra changes large enough to allow the analysis of the resulting data using the program "Letagrop"^[7]. Best values for the formation constants β_{xy} of the various complex species and their molar absorptivity coefficients for various wavelengths, are deduced from the best fit between the experimental and calculated UV spectra. The best fit is reflected by the lowest value of U (the sum of U values for all lambda given) corresponding to the square sum of a differences between experimental and calculated absorbances (U = Σ (A_{cal} - A_{exp})²). The β_{xy} values correspond to the arithmetic means of at least three independent experiments.

RESULTS AND DISCUSSION

Extraction properties of 1 and 2

The power extracting of derivatives 1 and 2 towards picrates cations lanthanides and transition metals is evaluated through the determination of the percentages of extraction %E latter of water to dichloromethane. The percentage extraction picrates metal of the two ligands studied are grouped in TABLES 1 and 2.

Based on these results, we have found that ligands behave very differently, in fact, a ligand have no affinity with all picrates studied (1) and a ligand with a power

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TABLE 1 : Pourcentages d'extraction %E des picrates de lanthanides de l'eau vers le dichlorométhane (α 20°C) par les dérivés 1 et 2

	La ³⁺	Pr ³⁺	Nd ³⁺	Eu ³⁺	Gd ³⁺	Er ³⁺	Yb ³⁺
1	<1	<1	<1	<1	<1	<1	<1
2	99	99	99	99	98	99	99

TABLE 2 : Pourcentages d'extraction %E des picrates de Al, Co, Zn, Cu et Cd de l'eau vers le dichlorométhane (α 20°C) par les dérivés 1 et 2

	Al ³⁺	Co ²⁺	Zn ²⁺	Cu ²⁺	Cd ²⁺
1	<1	<1	<1	<1	<1
2	99	99	99	99	99

TABLE 3 : Stability of complexes with derivatives 1 et 2 avec les lanthanides in acetonitrile : $\log \beta_{xy}$ ($I=10^{-2}M$, Et₄NNO₃, 25°C)

	ML	La	Pr	Nd	Eu	Gd	Er	Yb
1	2:1	8.57 ± 0.03	9.04 ± 0.05	9.34 ± 0.07	8.83 ± 0.09	8.61 ± 0.01	9.09 ± 0.02	9.62 ± 0.01
2	1:1	5.26 ± 0.09	5.36 ± 0.03	5.34 ± 0.01	6.77 ± 0.05	6.14 ± 0.20	5.56 ± 0.15	5.58 ± 0.18
	2:1				11.06 ± 0.19	10.03 ± 0.15	10.38 ± 0.19	10.35 ± 0.04

extracting absolute Towards all picrates studied (2). These results lead us to conclude that the nature and length of the bridge connecting the units calixaréniques are the only factors dominate the extraction since the two ligands that differ only by these two factors. Indeed elongation and the replacement of the bridge NHCH₂-CH₂NH (1) by NHCH₂CH₂OCH₂CH₂OCH₂CH₂NH (2) only gives the percentages of extraction from 0% to a total extraction of 100%. Furthermore, the magnitude of extraction observed percentages for each ligand was retained regardless of the nature of the cation considered.

Complexation properties of 1 and 2

Derivatives 1 and 2 are various (calix-amidopyrène) that differ by connecting the two units calixaréniques. The purpose of this study is to assess the role each of these gateways in the complexation properties of them.

Complexation of lanthanides

The complexation of this series of trivalent cations by the derivative 1 does generally not cause spectral fluctuations. One effect hypochrome which sometimes is accompanied points isobestiques are commonly observed. The stability constants of complex derivatives di-calixaréniques 1 and 2 with cations Ln³⁺ are collected in TABLE 3.

In acetonitrile, derivative 1 does shape than cash binucleaires with lanthanides cations. The values of the logarithms of stability constants are between 8.57 and 9.62 with an affinity for Yb³⁺ where stability of its complex is 10 times greater than that of complex La³⁺, Eu³⁺ and Gd³⁺. The absence of the mononuclear species with the ligand 1 can be explained by the length of the bridge ethylene diamide, considered too short to allow

for flexibility and a rearrangement of the molecule around a cation order to coordinate. A second argument which can be offered is the contribution of central atoms of oxygen, in the case of ligand 2, in the coordination of the metal in the mononuclear complex.

According to TABLE 3, we can see that the derivative 2 form ML species with all cations in the series Ln³⁺ studied, along with the species M₂L from europium indicating a size effect. ML complexes and M₂L trained with Eu³⁺ are the most stable in the series. However, mononuclear complexes formed with La³⁺, Pr³⁺ and Nd³⁺ are even suggesting stability coordination equivalent. But the stability of the complexes mono and binucleaires trained with cations size weaker showing a decrease from Eu³⁺ to Gd³⁺ then remains constant with Er³⁺ and Yb³⁺.

Complexation of transition metals and aluminium: Co, Cu, Cd, Zn and Al

Successive additions of metal solutions to the solution of the derivative 1 lead, in the case of Co²⁺, Zn²⁺ and Cu²⁺, an hypochrome effect with low spectral variations. All absorption spectra in UV related to the complexation of these cations by the derivative 2 have an effect hypochrome except in the case of Al³⁺ where there is the formation of two isobestiques points. The spectral variations are usually small and in all cases the points isobestiques correspond to a unique balance. The interpretation of these spectral variations leads us in TABLE 4:

TABLE 4 : Stability of complexes with 1 et 2 behavior of transition metals and Al³⁺ in acetonitrile : $\log \beta_{xy}$ ($I=10^{-2}M$, Et₄NClO₄ or Et₄NNO₃, 25°C)

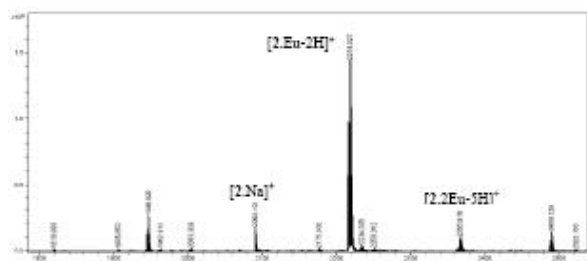
	ML	Al	Co	Zn	Cu	Cd
1	1:1	5.00±0.01	5.19±0.03	5.65±0.02	5.00±0.02	4.79±0.02
2	1:1	4.23±0.09	4.66±0.02	4.24±0.01	4.93±0.05	4.32±0.03

With this second serie of cations, derivatives 1 and 2 seem to be in agreement viewpoint stoichiometries they are formed mononuclear species in all cases. The complexes formed with the derivative 1 are more stable than those formed with the derivative 2. There is a selectivity of mild derivative 1 towards zinc and derivative 2 towards copper. In conclusion, and as a first observation, the replacement of the bridge CH_2CH_2 (in derivative 1) by $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ (in derivative 2) led the formation of the mononuclear species with trivalent lanthanides in agreement with the acidic nature of the latter lasts, which seem to prefer sites oxygenates. This has strengthened the stability of the complexes binucleaires.

Complexation study with mass spectroscopy: MALDI-TOF

Following the study by UV spectrophotometry and in order to confirm some stoichiometries harvested by it, we had resorted to the technique of mass spectrometry method MALDI-TOF once the end of the complexation is reached. The system studied by the latter is as follows: $2/\text{Eu}$.

Complexation of europium by derivative 2



Mass spectrum MALDI-TOF related to the complexation of Eu^{3+} by derivative 2

The results of mass spectrometry MALDI-TOF show the presence of signal on the mononuclear complex $[2.\text{Eu}-2\text{H}]^+$ at 2218.0 m/z as well as on the complex binucléaire $[2.2\text{Eu}-5\text{H}]^+$ at 2365.9 m/z. This is perfectly in line with the results obtained by UV spectrophotometry.

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