Design and synthesis of multifunctional thiacalixarenes and related metal derivatives for the preparation of sol–gel hybrid materials with non-linear optical properties†

Cedric Desroches,[a] **Cesar Lopes,**[b] **Vadim Kessler**[c] **and Stephane Parola** *[a]

[a] *Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS, Université Claude Bernard-Lyon 1, F-69622 Villeurbanne, France. E-mail: Stephane.Parola@univ-lyon1.fr*

[b] *Swedish Defence Research Agency (FOI), Division of Sensor Technology, SE-581 11, Linköping, Sweden*

[c] *Division of Inorganic and Physical Chemistry, Institute of Chemistry, Swedish University of Agricultural Sciences, Box 7015, 750 07 Uppsala, Sweden*

Thiacalixarenes bearing phenylazo or ethynylic groups on the lower rims were prepared and fully characterized. The functional groups were chosen for their ability to increase the electron delocalisation over the molecule and to form metal complexes. The formation of complexes between phenylazothiacalixarenes and metal salts (Zn^{2+}, Ag^+...), and the synthesis of platinum acetylides from ethynylthiacalixarenes were investigated. Preliminary studies on optical limiting properties for both ligands and complexes is reported. Clamping levels of ~4 µJ at 532 nm, were observed for both tetra(pentylphenylethynyl)tetrapropoxythiacalix[4]arene (150 mM in THF, 99% transmission) and the platinum complex (30 mM in THF, 83% transmission). A second functionalisation (upper rims) with metal alkoxide groups has also been investigated in order to prepare hybrid materials incorporating the optically active molecule. The same macrocycle core was thus bifunctionalised, and used for its optical properties on one side and as a precursor of an inorganic network for hybrid materials on the other.

Introduction

Optical Power Limiting (OPL) materials have mainly been developed for the protection of optical sensors and eyes from intense lasers.[1–4] Previous investigations on several families of compounds evidenced that the optical limiting behaviour of a given molecule can be related to the delocalisation of π-electrons and may be improved by the formation of metal complexes.[5] We have been investigating thiacalixarenes on the basis that they display delocalised π-electrons, they can be easily functionalised selectively on the upper rims or the lower rims and are interesting species for the formation of metal complexes.[6–9] Moreover, the presence of electron donating sulfur bridges may play an important role regarding non-linear optical properties and functional groups can be chosen with the ability to increase the electron delocalisation over the molecule and to form metal complexes.

The functional groups were chosen for their ability to increase electron delocalisation over the molecule and to form metal complexes. Thiacalixarenes bearing phenylazo groups on the upper rims were previously prepared and the optical limiting measurements showed promising results.[10] In order to extend the electron delocalisation over the molecule and thus enhance the optical limiting power of the species, substitutions of the upper rims through ethynyl bonds were also investigated and will be presented here.

Because interactions between the organic species and heavy atoms may improve the non-linear properties, the formation of complexes between phenylazothiacalixarenes and metal salts (Zn^{2+}, Ag^+) were investigated and the synthesis of platinum complexes from alkynylthiacalixarenes are reported in this paper with their optical characterization.

We are also attempting to prepare solid state materials incorporating thiacalixarenes. Such organic–inorganic hybrid materials can be prepared using the sol–gel route. However, preparation of highly concentrated and stable xerogels can only be achieved through strong interactions between the matrix and the organics. The functionalisation of the lower rims of the thiacalixarenes with a silicon alkoxide group is reported.[11,12] Class II hybrid materials where the optically active molecule is covalently linked to the inorganic network can thus be prepared.

Results and discussion

### Modification of the upper rims of the thiacalix[4]arenes

Synthesis of ligands with non-linear optical activity. Phenylazo moieties and alkynyl groups are both supposed to increase the electron delocalisation over the molecule through respectively N=N and C≡C bonds. Moreover, the formation of metal adducts or metal acetylides with specific cations (Ag^I, Hg^I, Hg^{II}, Pt^{II}, Pd^{II}) can be achieved through such groups which can thus be used as ligands.[13–17]

p-Tetrakis(4-nitrophenylazo)tetrahydroxythiacalix[4]arene (**1**), *p*-tetrakis(phenylazo)tetrahydroxythiacalix[4]arene (**2**) were prepared following the previously described procedures (Scheme 1).[9,10]

In our attempts to prepare alkynylthiacalix[4]arenes derivatives with several R groups, we started by investigating the formation of halothiacalixarenes. As previously reported by Lhoták *et al.*, the classical reactions used for the calixarenes failed.[18] However, the reaction between *N*-bromosuccinimide and the tetrahydroxythiacalix[4]arene, using acetone instead of 2-butanone as solvent gave, after 24 hours stirring, the 5,11,17,23-tetrabromo-25,26,27,28-tetrahydroxythiacalix[4]-arene. In the further functionalisations, protection of the hydroxyl groups was necessary in order to prevent reactions
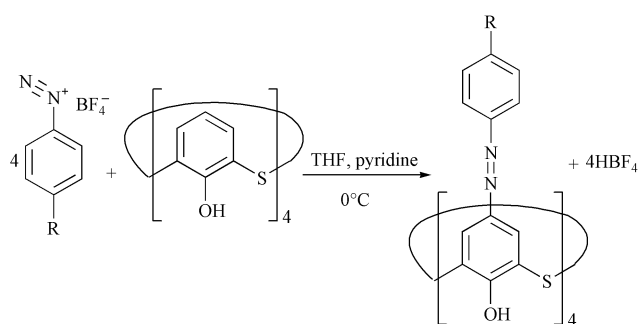
Scheme 1 Synthesis of the azothiacalixarenes **1** (R = NO$_2$) and **2** (R = H).

between the catalysts and the hydroxyl groups. The synthesis of 5,11,17,23-tetrabromo-25,26,27,28-tetrapropoxythiacalix[4]-arene was performed by reacting the tetrabromotetrahydroxy-thiacalix[4]arene with 1-iodopropane in acetone in the presence of caesium carbonate. The reactions were conducted under a nitrogen atmosphere.

The tetraethynylthiacalixarene (**3**), which was used for the synthesis of the platinum alkynyl complexes, was prepared by reacting the trimethylsilylacetylene with the tetrabromo-tetrapropoxythiacalix[4]arene in triethylamine under nitrogen. The reaction was catalysed by palladium(II) dichlorobis-tri-phenylphosphine and copper(I) iodide. The final compound **3** was obtained by elimination of the trimethylsilyl groups with tetrabutylammonium fluoride in THF at room temperature (Scheme 2). The ^{1}H NMR spectrum of **3** in CDCl$_3$ showed a singlet at 7.53 ppm for the phenolic units of the calixarene crown, one triplet at 3.91 ppm for the O–CH$_2$ group, one singlet at 3.02 ppm for the ethynylic proton, and the signals for the protons of the CH$_2$–CH$_3$ groups at 1.34 and 0.75 ppm.
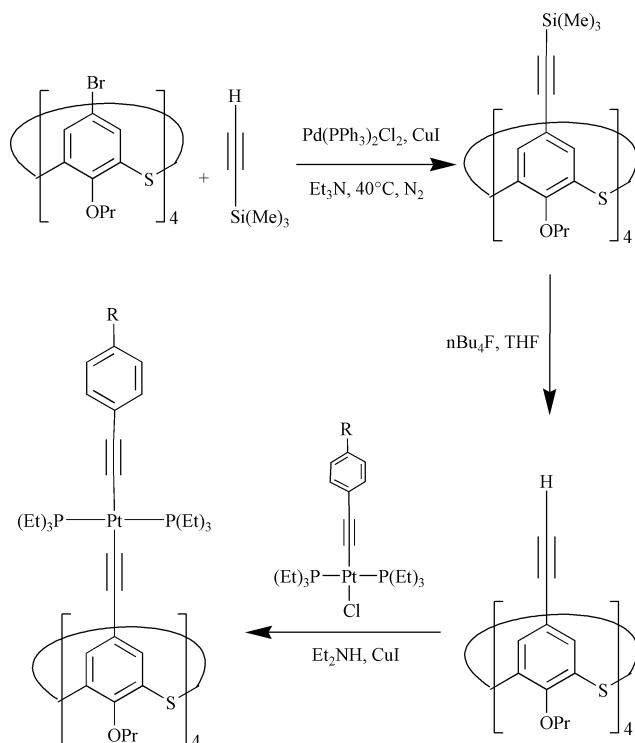
Scheme 2 Synthesis of the alkynylplatinum complexes **9** (R = H) and **10** (R = pentyl).

The 5,11,17,23-tetra(4-pentylphenylethynyl)-24,25,26,27-tetrapropoxythiacalix[4]arene (**4**) was also prepared in order to compare the optical properties with the similar platinum derivative (Scheme 3).

The reaction of 4-pentylphenylacetylene with tetrabromo-tetrapropoxythiacalix[4]arene, under the same catalytic condi-
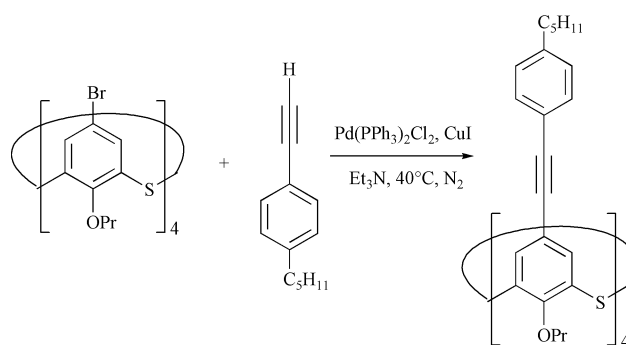
Scheme 3 Synthesis of the tetra(pentylphenylethynyl)tetrapropoxy-thiacalix[4]arene (**4**).

tions as for **3**, led to compound **4**. The ^{1}H NMR spectra of **4** in CDCl$_3$ showed a singlet at 7.57 ppm for the phenolic units of the calixarene crown, two doublets at 7.41 and 7.17 ppm for the aromatic rings, and the signals for the protons of the propyl and pentyl groups between 3.95 and 0.78 ppm. The structure of compound **4** could be determined using single crystal X-ray diffraction (Figs. 1 and 2) and selected bond lengths and angles are reported in Table 1. The conformation of the macrocycle
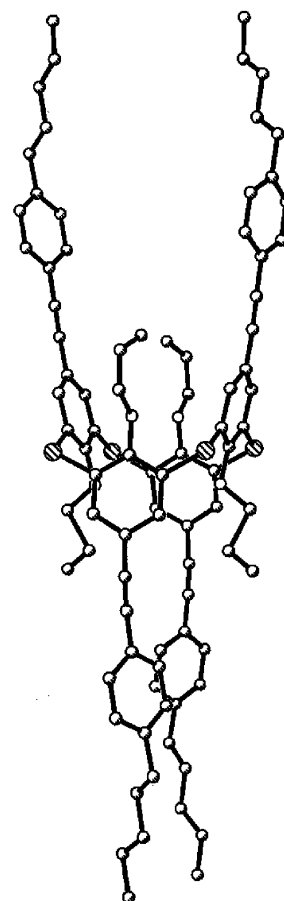

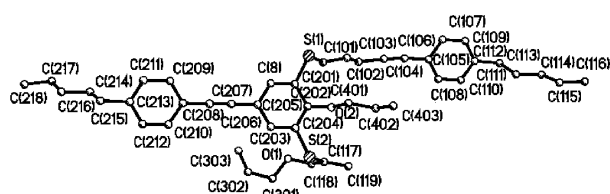**Fig. 1** Molecular structure of thiacalixarene **4**.

Fig. 2 Asymmetric unit of compound **4** showing the atom numbering scheme.

**Table 1** Selected bond lengths (Å) and angles (°) for compound **4**

S(1)–C(202)	1.766(5)	S(1)–C(101)	1.760(5)
S(2)–C(118)	1.751(5)	S(2)–C(204)	1.748(5)
O(1)–C(117)	1.380(5)	O(1)–C(301)	1.429(6)
O(2)–C(201)	1.364(5)	C(201)–C(204)	1.398(6)
C(201)–C(202)	1.400(6)	C(202)–C(8)	1.378(6)
C(102)–C(101)	1.369(6)	C(102)–C(103)	1.395(7)
C(205)–C(8)	1.385(7)	C(205)–C(203)	1.387(7)
C(205)–C(206)	1.437(7)	C(203)–C(204)	1.387(6)
C(117)–C(118)	1.402(7)	C(105)–C(108)	1.338(9)
C(105)–C(107)	1.363(8)	C(105)–C(106)	1.415(8)
C(104)–C(106)	1.192(8)	C(206)–C(207)	1.173(7)
C(202)–S(1)–C(101)	104.1(3)	C(118)–S(2)–C(204)	105.5(2)
C(117)–O(1)–C(301)	116.0(4)	C(201)–O(2)–C(401)	113.8(4)
O(2)–C(201)–C(204)	119.6(5)	O(2)–C(201)–C(202)	120.9(5)
C(8)–C(202)–S(1)	117.5(5)	C(201)–C(202)–S(1)	122.8(4)
C(8)–C(205)–C(203)	117.3(5)	C(8)–C(205)–C(206)	121.4(6)
C(201)–C(204)–S(2)	123.8(4)	C(203)–C(204)–S(2)	117.0(5)
C(119)–C(118)–S(2)	118.6(5)	C(117)–C(118)–S(2)	122.6(5)
C(106)–C(104)–C(103)	175.2(7)	C(207)–C(206)–C(205)	176.8(7)

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, y, −z + 3/2.

was found to be the 1,3 alternated one, supposedly to permit better packing of the long fragments to the calixarene ring. This was actually expected since the bromo derivative adopts the same conformation.[18]

Formation of metal complexes with the phenylazothiacalixarenes. Several complexes with various stoichiometries were prepared by simply mixing metal salts with phenylazothiacalixarenes. Compounds **1** and **2** gave two different adducts with AgSO$_3$CF$_3$, respectively with ratios of 2 : 5 (**5**) and 2 : 7 (**6**) between the thiacalixarenes and the cations. Reaction of **1** and **2** with ZnCl$_2$ led to similar species in a ratio 2 : 1 (**7** and **8**). The low solubility of those adducts precluded the formation of single crystals. Compounds **5–8** were characterized using FT-IR, UV-visible spectroscopy and elemental analysis. The exact complex formulae remain indeterminate since the experimental values of elemental analysis slightly differ from the calculated ones, probably due to the presence of solvent. As previously investigated by Hosseini *et al.*,[19] the coordination of Zn was probably done through metal–oxygen and metal–sulfur interactions in the cavity of the thiacalixarene core, although a possible coordination mode through the N=N bonds cannot be excluded. Knowledge of the exact coordination mode of the cations would require further investigations such as single crystal X-ray diffraction.

Synthesis of platinum complexes with alkynylthiacalixarene (9, 10). The reaction between **3** and *trans*-chlorophenylethynyl-bis(triethylphosphine)platinum(II) or *trans*-chloropentyl-phenylethynylbis(triethylphosphine)platinum(II) in the presence of copper(I) iodide gave respectively the platinum complexes **9** and **10**. The ^{1}H and ^{13}C NMR spectra with heteronuclear multiple bond correlation for compounds **9** and **10** in CD$_2$Cl$_2$ were consistent with tetra-substitution of the thiacalixarene. The ^{1}H NMR spectrum showed a singlet at 7.21 ppm for the phenolic units of the calixarene, two doublets at 7.12 and 7.01 ppm for the protons of the aromatic groups, two triplets at 3.79 and 2.52 ppm for respectively the O–CH$_2$ and the Ar–CH$_2$, a multiplet at 2.14 ppm for the P–CH$_2$ groups, a multiplet between 1.51 and 1.21 ppm for the CH$_2$ of the pentyl groups, and three triplets at 1.21, 0.87 and 0.64 ppm for the methyl groups. The ^{31}P NMR in CD$_2$Cl$_2$ showed a singlet at 12.78 ppm for the phosphine. The solid-state structure of compound **9** was determined using X-ray diffraction (Figs. 3 and 4) and selected bond lengths and angles are reported in Table 2. The conformation was also 1,3 alternated, being probably the most thermodynamically stable one for our experimental conditions.
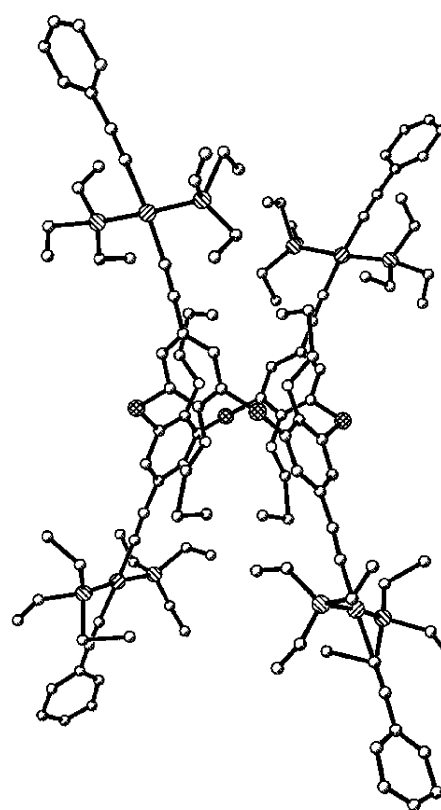
Fig. 3 Molecular structure of complex **9**.
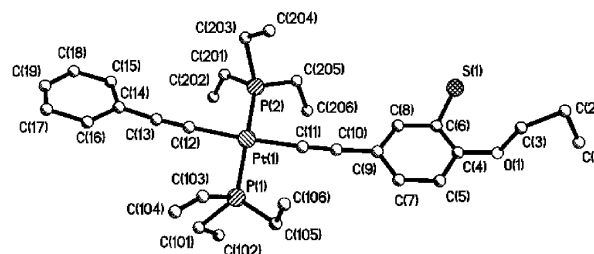
Fig. 4 Asymmetric unit of thiacalixarene **9** showing the atom numbering scheme.

Thermal analysis. TGA and DSC experiments showed high thermal stability for the thiacalixarenes compared to the single units (diphenylazo, dialkynylplatinum derivatives). Compound

Table 2 Selected bond lengths (Å) and angles (°) for compound **9**

|			
Pt(1)–C(11)	1.96(2)	Pt(1)–C(12)	2.07(2)
Pt(1)–P(1)	2.258(6)	Pt(1)–P(2)	2.287(6)
S(1)–C(5)#1	1.75(2)	S(1)–C(6)	1.79(2)
P(1)–C(105)	1.72(5)	P(1)–C(103)	1.83(12)
P(1)–C(101)	1.81(5)	P(2)–C(205)	1.69(2)
P(2)–C(201)	1.61(4)	P(2)–C(203)	1.85(4)
O(1)–C(4)	1.38(2)	O(1)–C(3)	1.52(4)
C(9)–C(10)	1.43(3)	C(10)–C(11)	1.20(2)
C(12)–C(13)	1.15(2)	C(13)–C(14)	1.38(3)
C(11)–Pt(1)–C(12)	175.9(7)	C(11)–Pt(1)–P(1)	90.6(5)
C(12)–Pt(1)–P(1)	91.8(5)	C(11)–Pt(1)–P(2)	90.5(5)
C(12)–Pt(1)–P(2)	87.5(5)	P(1)–Pt(1)–P(2)	173.2(3)
C(5)#1–S(1)–C(6)	108.8(9)	C(105)–P(1)–C(103)	80(3)
C(105)–P(1)–C(101)	115(2)	C(103)–P(1)–C(101)	103(2)
C(105)–P(1)–Pt(1)	119.9(17)	C(103)–P(1)–Pt(1)	116(4)
C(101)–P(1)–Pt(1)	116.1(16)	C(205)–P(2)–C(201)	106(2)
C(205)–P(2)–C(203)	106.2(14)	C(201)–P(2)–C(203)	77.7(16)
C(205)–P(2)–Pt(1)	118.7(9)	C(201)–P(2)–Pt(1)	125.5(18)
C(203)–P(2)–Pt(1)	114.8(12)	C(4)–O(1)–C(3)	111(2)
C(4)–C(6)–S(1)	124.0(16)	C(8)–C(6)–S(1)	116.1(18)
C(7)–C(9)–C(10)	120.5(17)	C(11)–C(10)–C(9)	174(2)
C(10)–C(11)–Pt(1)	175.8(17)	C(13)–C(12)–Pt(1)	178(2)
C(12)–C(13)–C(14)	175(2)	C(16)–C(14)–C(13)	123(2)
C(15)–C(14)–C(13)	123(2)		

Symmetry transformations used to generate equivalent atoms: #1 −y + 3/4, x + 3/4, −z − 1/4; #2 y − 3/4, −x + 3/4, −z − 1/4.

1 started to decompose at 210 °C while compound **2** showed high stability up to 310 °C. Compound **10** showed a melting point at 266 °C followed by a rapid decomposition. The thiacalixarene **4** melted at 238 °C and started to decompose at 290 °C. The thermal stability of these species has been an important parameter in the choice of this family of thiacalixarenes for optical applications. Indeed the stability upon heating allows easier inclusion in an inorganic matrix (thermal treatment).

Optical characterization. Linear transmission and optical limiting experiments were performed at 532 nm. The optical limiting behaviour was not measured on compound **1** because of low linear transmission at 532 nm (1 mM/pyridine, 1%). The silver complex **5** (0.26 mM/pyridine) showed a clamping level at ~7 μJ but with a very low linear transmission at 532 nm (6%), while the Zn complex **7** had a limiting value of 22 μJ (5 mM/pyridine) with a transmission of 50%. The tetraphenylazothiacalixarene **2** (6 mM in pyridine, ~50% transmission at 532 nm) was found to limit the energy to ~9 μJ (Figs. 5 and 6). The silver complex **6** (7.8 mM/pyridine) showed a clamping level at 8 μJ with a transmission of 40% at 532 nm. The Zn complex **8** (7.5 mM/pyridine) presented a clamping level at 6 μJ with a linear transmission of ~40% at 532 nm. The formation of adducts between the thiacalixarenes and a metal salt did not seem to improve the optical limiting behaviour as significantly as expected.
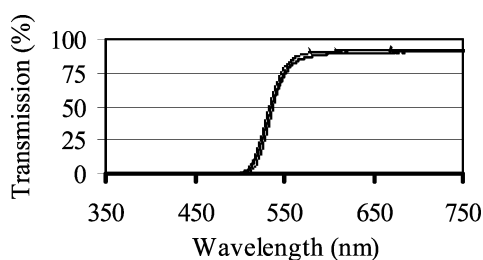

Fig. 5 Linear transmission for the phenylazothiacalixarene derivatives **2**, **6** and **8**.

It is also important to notice that the similar calixarenes, with CH$_2$ bridges instead of sulfur, did not show any optical limiting behaviour under the same conditions. This evidenced the
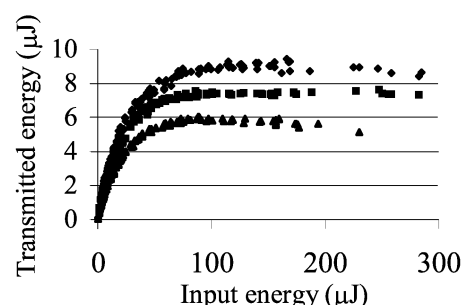
Fig. 6 OPL measurements at 532 nm for the phenylazothiacalixarene derivatives **2** (◆), **6** (■) and **8** (▲).

important role of the sulfur atoms on the optical properties of these macrocycles.

The tetra(pentylphenylethynyl)tetrapropoxythiacalix[4]arene (**4**) (0.15 M in THF) showed very high transmission in the visible wavelengths (>90% between 400–700 nm) and a clamping level of about 3.5 μJ at 532 nm for an internal transmission of nearly 100% (Figs. 7 and 8).
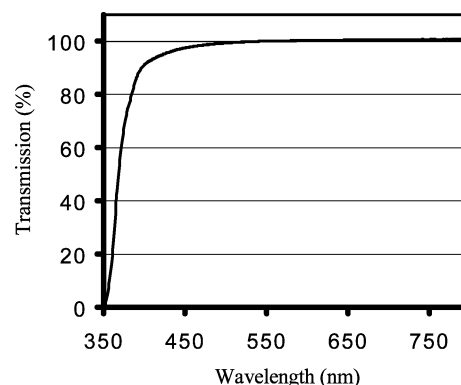
Fig. 7 Linear transmission for the thiacalixarene **4**.
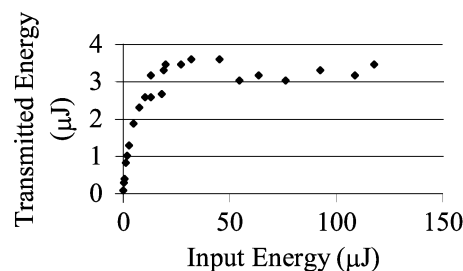
Fig. 8 OPL measurements at 532 nm for compound **4**.

The linear transmission at 532 nm for compound **10** (0.03 M in THF) was 93%. The transmission in the visible area was not as high as for compound **4**, however clamping values of ~4 μJ were observed with a five-fold reduction in concentration. It is a well known fact that heavy atoms such as Pt can increase the spin–orbit coupling and thereby enhance the non-linear absorption in molecules. The organometallic compound **10** is therefore expected to give better absorption than the organic compound **4**. This observation evidenced the influence of the insertion of the platinum in the organic species on the optical properties since increasing the concentration of the Pt-complex would probably lead to a lower clamping value. Thus, even if the alkynylthiacalixarenes showed interesting behaviour concerning non-linear absorption, their use as ligands for the formation of metal complexes should be of even higher interest.

Modification of the lower rims

Synthesis of precursors for class II sol–gel hybrid materials. Optical limiting molecules need to be incorporated into a solid-

state matrix in order to be useful for real applications. It is well known that the sol–gel routes allow easy insertion of organic dyes into an oxide network because of the low temperature of the process. Two major classes of the so-called organic–inorganic hybrids can be considered. In class I hybrids the organic molecules have weak chemical interactions with the inorganic network (van der Waals, hydrogen bonds). In class II hybrids the organics are strongly bonded to the inorganic network (covalent).

In the class I materials, the optically active molecules can be introduced into the oxides simply by mixing together a solution of the thiacalixarene in THF or formamide with the solution of the precursor (TMOS) in ethanol. Hydrolysis of the tetra-alkoxysilane was performed by adding water in acidic conditions (HNO_3). Gelation and careful drying of the gels were then performed at room temperature within several weeks. Homogeneous and transparent hybrid monoliths with concentrations of about 10 mM in thiacalixarene were obtained.[20] When the concentration of the organics was increased, precipitation or crystallization occurred during the gelation process whatever the conditions. In order to prevent these defects in the final xerogels, class II hybrids were considered. In this case the thiacalixarenes have to be functionalised with a trialkoxysilane group to create the organic–inorganic covalent link at a very early step in the elaboration of the material, in the precursor.

Acylation reactions between a hydroxyl group of an organic dye and a metal alkoxide bearing isocyanate groups were previously investigated and permitted the synthesis of hybrid precursors.[11,12] The same reaction on the phenolic hydroxyl groups of the thiacalixarenes was unsuccessful. Because of the low reactivity of the phenolic hydroxyls of the thiacalixarene it was necessary to introduce a spacer bearing primary alcohol functions on the phenolic units.

The tetrabromotetra(2-*tert*-butyldimethylsiloxyethoxy)thiacalix[4]arene was prepared by reacting the tetrabromotetrahydroxythiacalix[4]arene with 1-iodo-2-(*tert*-butyldimethyl)-siloxyethane (Scheme 4). Then functionalisation of the upper rim was performed. The formation of alkynylthiacalixarene is described in detail here but this can be extended to other functionalities. 4-Pentylphenylacetylene was reacted with the tetrabromotetra(2-*tert*-butyldimethylsiloxyethoxy)thiacalix[4]arene in the presence of a catalyst, using the same procedure as for compound **4**. Then N(Bu)$_4$F was added to remove the protection and obtain the primary alcohol group on the spacer. The acylation reaction was then achieved by adding the 3-isocyanatopropyltriethoxysilane as described in Scheme 4 and compound **11** was obtained. The ^{1}H NMR spectrum of **11** was consistent with the tetra-functionalisation. It showed for example a triplet at 0.47 ppm for the CH$_2$–Si, a triplet at 0.65 ppm for the CH$_3$ of the pentyl, a triplet at 1.15 ppm for the CH$_3$ of the ethoxy groups in the expected ratio for a tetra-substitution. The acylation reaction was also confirmed by the presence in the final species of a signal corresponding to NH groups at 5.24 ppm.

11 could either be used as a single source precursor for hybrid organic–inorganic materials or together with another inorganic precursor using the same procedure as for the elaboration of class I xerogels.

Conclusion

Thiacalixarene and related metal complexes have shown interesting potential for non-linear optical applications. Optical limiting properties were promising compared to similar calixarenes which showed no or poor limiting behaviour. The use of the thiacalixarene macrocycles gave lower clamping values than for the single isolated units (diphenylazo, diphenylacetylene...). Moreover, this is a way to achieve higher stability for the azo and alkynyl species compared to isolated units. Functionalisation of the lower rim with the trialkoxysilane groups, which
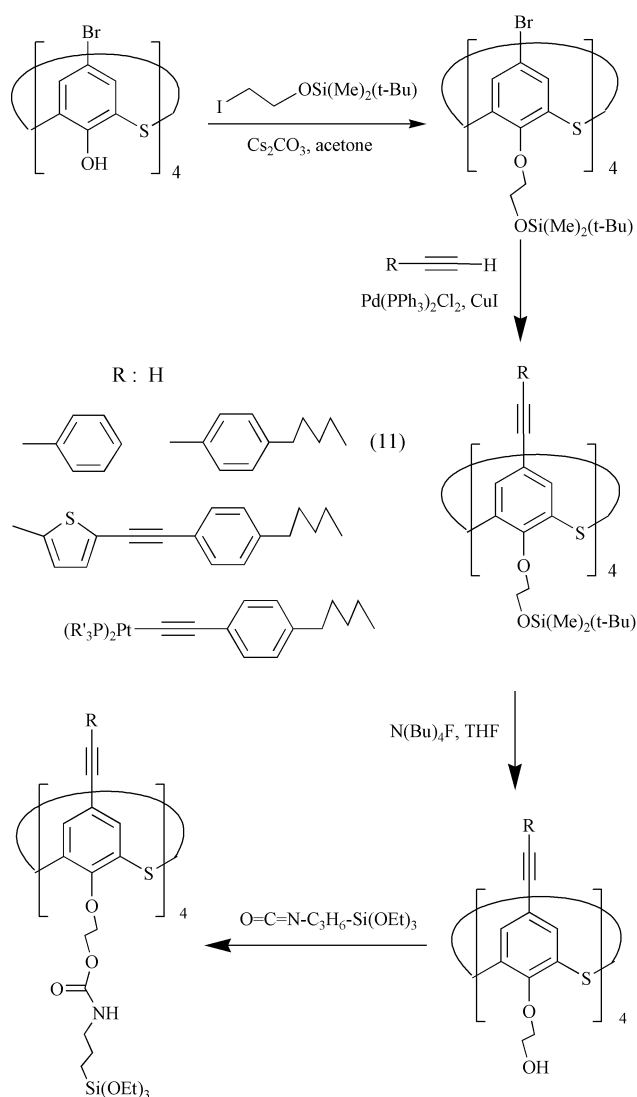
Scheme 4 General procedure for the synthesis of the trialkoxysilane derivatives.

can be extended to other metal alkoxides, was possible and allowed the elaboration of xerogels with high concentrations of optically active molecules using the sol–gel process. The same macrocycle can thus act as a ligand for the formation of metal complexes on one side, and as a precursor of inorganic polymerisation for the formation of hybrid materials on the other.

Experimental

^{1}H and ^{13}C NMR spectroscopy was performed on a Brüker AM300 spectrometer. Thermal analysis data were recorded using a DSC820 Mettler Toledo systems.

Linear transmission was measured on a Varian Cary 5G spectrophotometer with background correction for cell and solvent. The optical limiting experiments were performed in a *f*/5 set-up, using 2 mm quartz cells and a frequency doubled Nd-YAG laser operating at 10 Hz, delivering 5 ns pulses at 532 nm.[21,22]

X-Ray crystallography

Crystallographic data were collected using a Bruker SMART CCD 1k diffractometer to $2\theta \leq 40°$ (data are summarized in Table 3). The structures were solved by direct methods, the majority of the non-hydrogen atoms were obtained from the initial solution, the others being obtained from the difference Fourier syntheses. All non-hydrogen atoms were refined first in isotropic and then in anisotropic approximations (except for the

Table 3 Crystal data for compounds **4** and **9**

Compound	**4**	**9**
Empirical formula	$C_{88}H_{96}O_4S_4$	$C_{124}H_{176}O_4P_8Pt_4S_4$
Formula weight	1345.89	2887.01
Temperature/K	295(2)	295(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal
Space group	$C2/c$	$I4(1)/a$
$a/Å$	23.009(4)	21.6628(17)
$b/Å$	23.370(4)	21.6628(17)
$c/Å$	17.968(3)	28.045(3)
$\beta/°$	125.796(15)	90
$V/Å^3$	7837(2)	13161(2)
Z	4	4
μ/mm^{-1}	0.170	4.446
Reflections collected	11922	19835
Independent reflections	3655 [R(int) = 0.0619]	3055 [R(int) = 0.0698]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0595$, $wR2 = 0.1514$	$R1 = 0.0589$, $wR2 = 0.1561$
R indices (all data)	$R1 = 0.1195$, $wR2 = 0.1702$	$R1 = 0.1083$, $wR2 = 0.1836$

carbon atoms of the pentyl chains of **4** subjected to partial disorder due to the thermal vibration and the ethyl groups in the phosphine ligands of **9**, subjected to partial rotational disorder). The positions of all the hydrogen atoms were calculated geometrically and included into the final cycles of refinement in isotropic approximation. All the calculations were performed on an IBM PC using the SHELXTL-NT program package.[23]

CCDC reference numbers 193184 and 193185.

See http://www.rsc.org/suppdata/dt/b2/b210252h/ for crystallographic data in CIF or other electronic format.

Syntheses

***p*-Tetrakis(4-nitrophenylazo)tetrahydroxythiacalix[4]arene (1) and *p*-tetrakis(phenylazo)tetrahydroxythiacalix[4]arene (2).** Compounds **1** and **2** were prepared following the previously reported procedure.[9,10]

5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxythiacalix[4]arene. Tetrahydroxythiacalix[4]arene (1 g, 2 mmol) was suspended in acetone (50 ml). *N*-Bromosuccinimide (1.43 g, 8 mmol) was added to the solution. After 24 hours stirring, the tetrabromotetrahydroxythiacalix[4]arene was filtered off and washed with CH_2Cl_2 and methanol. Yield: 0.99 g, 61%. ¹H NMR (C_5D_5N): δ 7.83 (s, 8H, Ar), 12.34 (s, 4H, OH). ¹³C NMR (C_5D_5N): δ 108.2 (Ar–C–Br), 124.9 (Ar–C–S), 140.0 (Ar–CH), 163.1 (Ar–C–O).

5,11,17,23-Tetrabromo-25,26,27,28-tetrapropoxythiacalix[4]arene. 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxythiacalix[4]arene (0.5 g, 0.62 mmol) was suspended in acetone (30 ml) and caesium carbonate (1.6 g, 1.23 mmol) was added. The suspension was refluxed for 20 min and 1-iodopropane (1 ml, 6.9 mmol) was added to the solution. The reflux was maintained for 24 hours under nitrogen and the solvent was evaporated to dryness. The powder was dissolved in CH_2Cl_2 and treated with HCl (1 M) and water (30 ml). The organic phase was evaporated after drying on Na_2SO_4. The tetrabromotetrapropoxythiacalix[4]arene was recrystallized from a mixture $CHCl_3$–methanol. Yield: 0.49 g, 80%. ¹H NMR (CDCl₃): δ 0.77 (t, 12H, CH_2–CH_3), 1.15 (m, 8H, CH_2–CH_3), 3.88 (t, 8H, O–CH_2), 7.70 (s, 8H, Ar).

5,11,17,23-Tetra(trimethylsilylethynyl)-25,26,27,28-tetra-propoxythiacalix[4]arene. 5,11,17,23-Tetrabromo-25,26,27,28-tetrapropoxythiacalix[4]arene (0.98 g, 1 mmol) was dissolved in triethylamine (30 ml) and the dichloro-bis(triphenylphosphine)-palladium(II) (0.07 g, 0.10 mmol), CuI (10 mg, 0.05 mmol) and trimethylsilylacetylene (1.13 ml, 8 mmol) were added. The mixture was heated to 40 °C under nitrogen. The black powder was dissolved in CH_2Cl_2 (40 ml) and treated with HCl (1 M) and

water (30 ml). The organic phase was dried over Na_2SO_4 and filtered. The solution was concentrated and methanol was added until crystallization started. The solution was then cooled down to 4 °C to achieve the crystallization. Yield: 0.75 g, 72%. ¹H NMR (CDCl₃): δ 0.24 (s, 36H, Si–$(CH_3)_3$), 0.76 (t, 12H, CH_2–CH_3), 1.26 (m, 8H, CH_2–CH_3), 3.90 (t, 8H, O–CH_2–), 7.50 (s, 8H, Ar). ¹³C NMR (CDCl₃): δ 0.3 (Si–CH_3), 10.2 (propoxy-CH_3), 22.9 (propoxy-CH_2), 71.7 (O–CH_2), 94.7 (C≡C), 103.8 (C≡C), 118.6 (Ar–C–C≡), 129.9 (Ar–C–S), 136.3 (Ar–CH), 160.6 (Ar–C–O).

5,11,17,23-Tetraethynyl-25,26,27,28-tetrapropoxythiacalix-[4]arene (3). 5,11,17,23-Tetra(trimethylsilylethynyl)-25,26,27,28-tetrapropoxythiacalix[4]arene (1 g, 1 mmol) was dissolved in THF (40 ml). N(Bu)₄F·3H₂O (2.41 g, 8 mmol) were added to the solution. The mixture was stirred for 4 h at room temperature and evaporated to dryness. The powder was dissolved in CH_2Cl_2 (40 ml) and treated with HCl (1 M) and water (30 ml). The organic phase was dried over Na_2SO_4 and concentrated. The product, **3**, crystallized on addition of methanol. Yield: 0.65 g, 85%. ¹H NMR (CDCl₃): δ 0.75 (t, 12H, CH_2–CH_3), 1.34 (m, 8H, CH_2–CH_3), 3.02 (s, 4H, C≡C–H), 3.91 (t, 8H, O–CH_2), 7.53 (s, 8H, Ar). ¹³C NMR (CDCl₃): δ 10.2 (propoxy CH_3), 22.4 (propoxy CH_2), 71.7 (O–CH_2), 77.6 (C≡C–H + solvent) 82.3 (C≡C), 117.6 (Ar–C–C≡), 129.0 (Ar–C–S), 136.2 (Ar–CH), 160.8 (Ar–C–O). FTIR (cm⁻¹): ν(≡C–H) 3273, 2089 and 801.

5,11,17,23-Tetra(4-pentylphenylethynyl)-25,26,27,28-tetra-propoxythiacalix[4]arene (4). Dichloro-bis(triphenyl-phoshine)palladium(II) (0.14 g, 0.20 mmol), CuI (0.02 g, 0.1 mmol) and 4-pentylphenylacetylene (1.55 ml, 8 mmol) were added to a solution of 5,11,17,23-tetrabromo-25,26,27,28-tetrapropoxythiacalix[4]arene (0.979 g, 1 mmol) in triethylamine (30 ml). The mixture was heated to 40 °C for 24 h under nitrogen and evaporated to dryness. The black powder was dissolved in CH_2Cl_2 (40 ml) and treated with HCl (1 M) and water (30 ml). The solution was concentrated before addition of methanol until crystallization started. The solution was cooled down to 4 °C to achieve the crystallization. Yield: 0.9 g, 67%. ¹H NMR (CDCl₃): δ 0.78 (t, 12H, ethoxy CH_3), 0.92 (t, 12H, pentyl CH_3), 1.63–1.17 (m, 24H, CH_2), 2.64 (t, 8H, Ar–CH_2), 3.95 (t, 8H, O–CH_2), 7.17 (d, 8H, Ar), 7.41 (d, 8H, Ar), 7.57 (s, 8H, Ar). ¹³C NMR (CDCl₃): δ 10.4 (propoxy CH_3), 14.4 (pentyl CH_3), 22.9 (pentyl CH_2 + propoxy CH_2), 31.7 (pentyl CH_2), 36.3 (pentyl CH_2), 71.7 (O–CH_2), 87.5 (C≡C), 89.9 (C≡C), 119.2 (Ar–C), 120.7 (Ar–C), 129.0 (Ar–CH pentyl + Ar–C–S), 131.8 (Ar–CH), 135.5 (Ar–CH), 143.8 (Ar–C), 160.28 (Ar–C–O).

Ag_5[1]₂(SO_3CF_3)₅·13C_5H_5N (5). **1** (0.15 g, 0.14 mmol) was dissolved in pyridine (20 ml). AgSO_3CF_3 (0.1 g, 0.39 mmol)

was added and the mixture was stirred for 24 h, protected from light. Methanol was added to precipitate a purple powder, which was washed with methanol and diethyl ether. Yield: 0.15 g, 60%. Found: C, 46.07; N, 12.62; H, 2.38; S, 9.22; Ag, 12.14. Calc. for $C_{166}N_{37}H_{121}S_{13}Ag_5$ C, 44.30; N, 11.52; H, 2.69; S, 9.24; Ag, 11.99%. FTIR (cm^{-1}): ν(OH) 3471, ν(NO$_2$ asym.) 1516, ν(NO$_2$ sym.) 1340; ν(C=C) 1569.

Ag$_7$[2]$_2$(SO$_3$CF$_3$)$_7$ (6). **2** (0.1 g, 0.1 mmol) was dissolved in chloroform (10 ml). AgSO$_3$CF$_3$ (0.2 g, 0.778 mmol) was added and the mixture was stirred for 12 h protected from light. After filtration, the red powder was washed with methanol and diethyl ether. Yield: 0.08 g, 60%. Found: C, 34.07; N, 6.20; H, 1.82; S, 12.49; Ag, 22.41. Calc. for $C_{103}N_{16}H_{32}S_{15}Ag_7$ C, 34.12; N, 6.18; H, 1.76; S, 13.25; Ag, 20.84%. FTIR (cm^{-1}): ν(OH) 3446, 3384, ν(C=C) 1628, 1574, ν(C–O) 1259.

Zn[1]$_2$Cl$_2$ (7). **1** (0.1 g, 0.092 mmol) was suspended in THF (10 ml). ZnCl$_2$ (0.1 g, 0.73 mmol) and H$_2$O (0.9 ml) were added and the mixture was stirred for 70 h. The suspension was filtered and methanol added to precipitate a purple powder, which was washed with methanol, water and diethyl ether. Yield: 0.129 g, 54%. Found: C, 48.09; N, 12.63; H, 2.68; S, 9.14; Zn, 3.29. Calc. for $C_{96}N_{24}H_{56}S_8Zn$ C, 49.60; N, 14.47; H, 2.41; S, 11.00; Zn, 2.81%. FTIR (cm^{-1}): ν(OH) 3460, 3308, ν(NO$_2$ asym.) = 1519, ν(NO$_2$ sym.) 1337.

Zn[2]$_2$Cl$_2$ (8). **2** (0.1 g, 0.1 mmol) was dissolved in CHCl$_3$–THF (10 : 1). ZnCl$_2$ (0.1 g, 0.73 mmol) and pyridine (0.2 ml) were added and the mixture was stirred for 48 h. The suspension was filtered and the yellow powder was washed with water, methanol and diethyl ether. Yield: 0.053 g, 60%. Found: C, 57.06; N, 11.29; H, 3.39; S, 11.94; Zn, 3.57. Calc. for $C_{96}N_{16}H_{64}S_8Zn$ C, 58.75; N, 11.42; H, 3.26; S, 13.00; Zn, 3.34%. FTIR (cm^{-1}): ν(OH) 3469, 3328, ν(C=C) 1580.

5,11,17,23-Tetra[*trans*-(phenylethynyl)ethynyl-bis(triethylphosphine)platinum(II)]-25,26,27,28-tetrapropoxythiacalix[4]-arene (9). *Synthesis of trans*-chloro*(phenylethynyl)bis(triethylphosphine)platinum(II).* *trans*-Cl$_2$Pt(PEt$_3$)$_2$ (0.484 g, 0.553 mmol) was dissolved in toluene (80 ml). CuI (0.0014 mg, 0.007 mmol) and triethylamine (20 ml) were added. The mixture was cooled to 0 °C and a solution of phenylacetylene (0.028 g, 0.274 mmol) in toluene (20 ml) was slowly added. The solution was stirred for 1 h at 0 °C and 12 h at room temperature. The solvent was evaporated after filtration. The powder was dissolved in CH$_2$Cl$_2$ and treated with NH$_4$Cl (5%, 40 ml) and H$_2$O (20 ml). The organic phase was dried over MgSO$_4$ and evaporated to dryness. The product was purified using column chromatography (basic alumina, CH$_2$Cl$_2$–pentane, 3 : 7) to give the Pt salt. Yield: 0.15 g, 52%. ^{1}H NMR [(CD$_3$)$_2$CO]: δ 1.24 (m, 18H, CH$_2$–CH$_3$), 2.08 (m, 12H, P–CH$_2$–), 7.08 (d, 2H, Ar), 7.19 (t, 1H, Ar), 7.26 (t, 2H, Ar). ^{31}P NMR (CDCl$_3$): δ 15.99.

Synthesis of **9**. *trans*-chloro(phenylethynyl)bis(triethylphosphine)platinum(II) (0.10 g, 0.21 mmol) was dissolved in toluene (40 ml). CuI (0.5 mg, 0.0026 mmol) and triethylamine (10 ml) were added. The mixture was cooled to 0 °C and a solution of 5,11,17,23-tetraethynyl-25,26,27,28-tetrapropoxythiacalix[4]arene (0.039 g, 0.051 mmol) in toluene (10 ml) was added. The solution was stirred for 12 h at room temperature. After evaporation to dryness, the powder was dissolved in CH$_2$Cl$_2$ and treated with NH$_4$Cl (5%, 40 ml) and H$_2$O (20 ml). The organic phase was dried over MgSO$_4$ and evaporated. The product was purified using column chromatography (basic alumina, CH$_2$Cl$_2$–pentane, 2 : 8) to give compound **9**. Yield: 0.13 g, 87%. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.67 (t, 12H, propoxy CH$_3$), 1.25 (m, 80H, propoxy CH$_2$ + P–CH$_2$–CH$_3$), 2.18 (m, 48H, P–CH$_2$), 3.82 (t, 8H, O–CH$_2$), 7.15 (d, 8H, Ar), 7.22 (t, 4H, Ar), 7.30 (m, 16H, Ar). ^{31}P NMR (CDCl$_3$): δ 12.50.

5,11,17,23-Tetra[*trans*-(4-pentylphenylethynyl)ethynyl-bis(triethylphosphine)platinum(II)]-25,26,27,28-tetrapropoxy-thiacalix[4]arene (10). Compound **10** was prepared following exactly the same procedure as for **9** using 4-pentylphenylacetylene instead of phenylacetylene. Yield: 90%. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.64 (t, 12H, ethoxy-CH$_3$), 0.87 (t, 12H, pentyl CH$_3$), 1.21 (m, 72H, P CH$_2$–CH$_3$), 1.25 (m, 8H, O–CH$_2$–CH$_2$), 1.33 (m, 16H, pentyl CH$_2$–CH$_2$), 1.61 (m, 8H, pentyl CH$_2$), 2.14 (m, 48H, P–CH$_2$), 2.52 (t, 8H, pentyl CH$_2$), 3.79 (t, 8H, O–CH$_2$), 7.01 (d, 8H, Ar), 7.12 (d, 8H, Ar), 7.21 (s, 8H, Ar). ^{13}C NMR (CDCl$_3$) + HMBC: δ 8.4 (P–CH$_2$–CH$_3$), 10.7 (propoxy CH$_3$), 14.4 (pentyl CH$_3$), 16.7 (P–CH$_2$), 22.7 (pentyl CH$_2$ + propoxy CH$_2$), 31.7 (pentyl CH$_2$), 36.1 (pentyl CH$_2$), 71.0 (O–CH$_2$), 124.2 (Ar–C), 126.4 (Ar–C), 128.4 (Ar–C–pentyl + Ar–C–S), 131.1 (Ar–CH), 133.6 (Ar–CH), 140.2 (Ar–C), 157.6 (Ar–C–O) (4 C≡ do not appear due to low concentration). ^{31}P NMR (CDCl$_3$): δ 12.78.

Compound 11. *Synthesis of 1-iodo-2-(tert-butyldimethyl)-siloxyethane.* Iodoethanol (1 ml, 12.8 mmol) was dissolved in CH$_2$Cl$_2$. Imidazole (0.871 g, 12.8 mmol) and *tert*-butyldimethylsilyl chloride (1.92 g, 13 mmol) were added to the solution. After filtration, 1 M HCl (20 ml) and H$_2$O (20 ml) were added. The organic phase was dried over Na$_2$SO$_4$ and evaporated to dryness. Yield: 2.75 g, 75%. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.80 (s, 6H, Si–CH$_3$), 0.90 (s, 9H, Si–t-Bu), 3.19 (t, 2H, CH$_2$–I), 3.82 (t, 2H, CH$_2$–O).

Synthesis of 5,11,17,23-tetrabromo-25,26,27,28-(2-tert-butyl-dimethylsiloxyethoxy)*thiacalix[4]arene.* The tetrabromotetrahydroxythiacalix[4]arene (0.5 g, 0.615 mmol) was suspended in acetone AND Cs$_2$CO$_3$ (1.6 g, 1.23 mmol) was added. The mixture was refluxed until complete dissolution and 1-iodo-2-(*tert*-butyldimethyl)siloxyethane (1.4 g, 4.9 mmol) was added. The reaction medium was then refluxed for another 24 h under nitrogen. A white precipitate was formed which was dried under reduced pressure. The white powder was dissolved in CH$_2$Cl$_2$ and treated with 1 M HCl (60 ml) and H$_2$O (30 ml). The organic phase was dried over Na$_2$SO$_4$ and evaporated to dryness. The product was recrystallized in a mixture OF diethyl ether–methanol. Yield: 1.23 g, 69%. ^{1}H NMR (CDCl$_3$): δ 0.16 (s, 24H, Si–CH$_3$), 0.95 (s, 36H, Si–t-Bu), 3.64 (t, 8H, O–CH$_2$), 4.09 (t, 8H, O–CH$_2$), 7.64 (s, 8H, Ar).

Synthesis of 5,11,17,23-tetra(4-pentylphenylethynyl)-25,26, 27,28-(2-tert-butyldimethylsiloxyethoxy)*thiacalix[4]arene.* The tetrabromo(2-*tert*-butyldimethylsiloxyethoxy)thiacalix[4]arene (0.276 g, 0.19 mmol) was dissolved in triethylamine (20 ml). Dichloro-bis(triphenylphosphine)palladium(II) (35 mg, 0.05 mmol), CuI (4.75 mg, 0.025 mmol) and 4-pentylphenylacetylene (0.3 ml, 1.52 mmol) were added to the solution. The reaction medium was heated to 40 °C for 36 h under nitrogen and then evaporated to dryness. The black powder was dissolved in CH$_2$Cl$_2$ and treated with 1 M HCl (90 ml) and H$_2$O (30 ml). The organic phase was dried over Na$_2$SO$_4$ and filtered. The product was purified using column chromatography (SiO$_2$, hexane). Yield: 0.2 g, 60%. ^{1}H NMR (CDCl$_3$): δ 0.09 (s, 24H, Si–CH$_3$), 0.85 (s, 36H, Si–t-Bu), 0.90 (t, 12H, pentyl CH$_3$), 1.34 (m, 16H, pentyl CH$_2$–CH$_2$), 1.63 (m, 8H, pentyl CH$_2$), 2.62 (t, 8H, pentyl CH$_2$), 3.48 (t, 8H, O–CH$_2$), 4.09 (t, 8H, O–CH$_2$), 7.15 (d, 8H, Ar), 7.40 (d, 8H, Ar), 7.61 (s, 8H, Ar).

Synthesis of 5,11,17,23-tetra(4-pentylphenylethynyl)-25,26, 27,28-(2-ol-ethoxy)thiacalix[4]arene. The tetra(4-pentylphenylethynyl)(2-*tert*-butyldimethylsiloxyethoxy)thiacalix[4]-arene (0.25 g, 0.138 mmol) was dissolved in THF (20 ml) and NBu$_4$F·3H$_2$O (0.33 g, 1.10 mmol) was added to the solution. The reaction medium was stirred for 4 h and evaporated to dryness. The powder was dissolved in CH$_2$Cl$_2$ and treated with 1 M HCl (60 ml) and H$_2$O (30 ml). The organic phase was dried over Na$_2$SO$_4$ and the white powder was precipitated by adding methanol. Yield: 0.12 g, 75%. ^{1}H NMR (CDCl$_3$): δ 0.90 (t, 12H, pentyl CH$_3$), 1.34–1.65 (m, 24H, pentyl CH$_2$–CH$_2$–CH$_2$), 2.64

(t, 8H, pentyl CH$_2$), 3.43 (t, 8H, O–CH$_2$), 4.14 (t, 8H, O–CH$_2$), 7.17 (d, 8H, Ar), 7.42 (d, 8H, Ar), 7.60 (s, 8H, Ar).

Synthesis of compound **11**. The tetra(4-pentylphenyl-ethynyl)(2-ol-ethoxy)thiacalix[4]arene (0.118 g, 0.087 mmol) was dissolved in toluene (20 ml). 3-Isocyanatopropyl-triethoxysilane (0.086 g, 0.087 mmol) and n-butyldiacetoxy tin(IV) (0.1 mg, 2.8×10^{-4} mmol) were added to the solution. The mixture was refluxed for 72 h and evaporated to dryness. A colourless liquid (**11**) was then obtained after extraction with THF. Yield: 0.14 g, 70%. ^{1}H NMR (CDCl$_3$): δ 0.47 (t, 8H, CH$_2$–Si), 0.65 (t, 12H, pentyl CH$_3$), 1.15 (t, 36H, Si–O–CH$_2$–CH$_3$), 1.20–1.68 (m, 24H, pentyl CH$_2$–CH$_2$–CH$_2$), 1.69 (m, 8H, NH–CH$_2$–CH$_2$), 2.61 (8H, pentyl CH$_2$), 3.18 (t, 8H, NH–CH$_2$), 3.85 (m, 24H, Si–O–CH$_2$), 3.98 (t, 8H, O–CH$_2$), 4.23 (t, 8H, O–CH$_2$), 5.24 (m, 4H, NH), 7.14 (d, 8H, Ar), 7.45 (d, 8H, Ar), 7.63 (s, 8H, Ar).

Acknowledgements

References

1 C. W. Spangler, *J. Mater. Chem.*, 1999, **9**, 2013.
2 A. A. Said, C. Wamsley, D. J. Hagan, E. W. Van Stryland, B. A. Reinhardt, P. Roderer and A. G. Dillard, *Chem. Phys. Lett.*, 1994, **228**, 646.
3 R. C. Hollins, *Nonlinear Opt.*, 2001, **27**, 1.
4 J. D. Bhawalkar, G. S. He and P. N. Prasad, *Rep. Prog. Phys.*, 1996, **59**, 1041.
5 J. D. Swalen and F. Kajzar, *Nonlinear Opt.*, 2001, **27**, 13.
6 C. Desroches, S. Parola, F. Vocanson, R. Lamartine, M. Perrin and J. Bouix, *New J. Chem.*, 2002, **26**, 651.
7 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971.
8 G. Mislin, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1345.
9 S. Parola, C. Desroches, F. Vocanson, R. Lamartine, J. Bouix, *Fr. Pat.*, WO 2 821 357, 2002.
10 C. Desroches, S. Parola, F. Vocanson, N. Ehlinger, P. Miele, R. Lamartine, J. Bouix, A. Eriksson, M. Lindgren and C. Lopes, *J. Mater. Chem.*, 2001, **11**, 3014.
11 D. Riehl, F. Chaput, Y. Lévy, J.-P. Boilot, F. Kajzar and P.-A. Chollet, *Chem. Phys. Lett.*, 1995, **245**, 36.
12 P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511.
13 E. Nomura, H. Taniguchi and Y. Otsuji, *Bull. Chem. Soc., Jpn.*, 1993, **66**, 3797.
14 E. Nomura, H. Tamiguchi and S. Tamura, *Chem. Lett.*, 1989, 1125.
15 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.
16 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.
17 V. Wing-Wah Yam, C.-H. Tao, L. Zhang, K. Man-Chung Wong and K.-K. Cheung, *Organometallics*, 2001, **20**, 453.
18 P. Lhoták, M. Himl, I. Stibor, J. Sykora and I. Cisarová, *Tetrahedron Lett.*, 2001, **42**, 7107.
19 A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. Mislin, B. W. Skelton, C. Taylor and A. H. White, *Eur. J. Inorg. Chem.*, 2000, 823.
20 C. Desroches, C. Lopes and S. Parola, to be published.
21 D. Vincent and J. Cruickshank, *Appl. Opt.*, 1997, **36**, 7794.
22 D. Vincent, *Nonlinear Opt.*, 1999, **21**, 413.
23 SHELXTL-NT reference manual, Bruker AXS, Madison, WI, 1998.