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Synthesis, characterization and optical power limiting behaviour of phenylazo- and 4-nitrophenylazo-tetrahydroxytetrathiacalix[4]arene

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p-Tetrakis(4-nitrophenylazo)tetrahydroxytetrathiacalix[4]arene and *p*-tetrakis(phenylazo)tetrahydroxytetrathiacalix[4]arene were prepared and fully characterized using ^{1}H and ^{13}C NMR, mass spectroscopy, thermogravimetric analysis and differential scanning calorimetry. The solid-state structure of *p*-tetrakis(4-nitrophenylazo)tetrahydroxytetrathiacalix[4]arene was investigated by single crystal X-ray diffraction. It crystallized in the triclinic system (space group: $P\bar{1}$). *z*-Scan experiments were performed on the *p*-tetrakis(4-nitrophenylazo)tetrahydroxytetrathiacalix[4]arene showing non linear absorption due to two photon absorption with a TPA cross-section of about 50×10^{-50} cm^4 s per photon. Optical power limiting measurements on the *p*-tetrakis(phenylazo)tetrahydroxytetrathiacalix[4]arene at 532 nm (48% linear transmission) was found to limit the energy to ~9 μJ.

1. Introduction

Second order non-linearity has mostly been studied for applications in the fields of lasers, computer science and telecommunications.[1] Third-order non-linearity, on the other hand, is interesting for application in optical power limiting (OPL) devices. These optical limiters can be very useful for the protection of eyes or electro-optical sensors against intense laser aggressions.[2–4] The optical limiting behaviour of a given molecule is closely related to the presence of strong π-delocalisation and may be enhanced by the formation of metallic complexes. For these reasons, calixarenes and, thus, thiacalixarenes are of great interest, both displaying delocalised π-electrons through the aromatic rings.[5–7] Furthermore, they also exhibit complexing properties for neutral or ionic species, especially in their cone conformation.[8–12] Reinhoudt and coworkers have developed calix[4]arenes for second-order nonlinear optical applications,[13–15] but no data are available in the literature concerning third-order nonlinear properties of such molecules. Finally, these NLO active species have to be introduced into a matrix in order to prepare optical devices for the protection of eyes or sensors.

In our work, thiacalixarenes were chosen for application as optical limiters not only on the basis of their electronic delocalisation and their complexing properties, but also for their thermal stability allowing harsh treatment and therefore easy inclusion in a glass matrix. Moreover, thiacalixarenes can be easily functionalised *via* substitution either on the upper rims or on the lower rims permitting a kind of molecular engineering. Phenylazo moieties were selected as substituting groups because they might increase the electron delocalisation over the molecule and induce a complexing tendency toward specific cations (Ag^{I}, Hg^{I}, Hg^{II}) through the diazo functionality.[16,17] They were also easy to prepare and, despite their colour, can contribute to evaluation of the potential of such species for optical limiting.

2. Experimental

2.1 Measurements

^{1}H and ^{13}C NMR spectroscopy were performed on a Bruker AM300 spectrometer, and mass spectra were collected on a MAT 95 XL Finnigan spectrometer. Thermal analysis data were recorded using a DSC820 and a TGA/SDTA851^{e} Mettler Toledo systems.

Optical characterizations of the compounds were performed with different techniques using pyridine as solvent. Transmission spectra were collected for the different samples. A frequency doubled Nd : YAG laser and a Ti : sapphire laser were used in the different experiments for characterisation of the nonlinear properties. The Nd : YAG and the Ti : sapphire lasers delivered respectively 5 ns pulses at 532 nm and 170 fs pulses at 796 nm. The doubled Nd : YAG laser was used to perform optical limiting experiments and *z*-scans,[18,19] while the Ti : sapphire laser was used to perform *z*-scans and transient absorption experiments with a pump and probe technique. The transmission spectra were collected with the samples in solution in cells with 2 mm path-length. The 2 mm cells were used in the transmission measurements in order to reproduce the same conditions as the optical limiting experiments. Optical power limiting experiments at 532 nm were made in an f/5 configuration with a Q-switched Nd : YAG laser with 5 ns long pulses. This test-bed has been described elsewhere and is shown in Fig. 1.[20–22] A 2 mm quartz cell containing the filtered sample was put with the focus centred in the cell.

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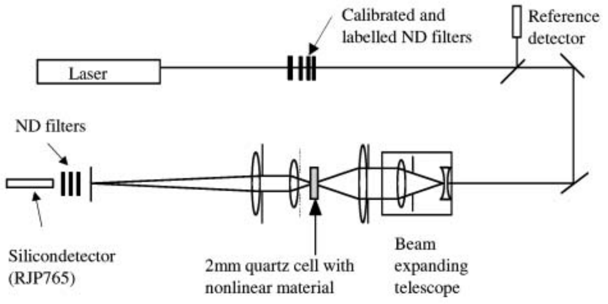


Fig. 1 The optical power limiting test-rig.

2.2 X-Ray crystal structure determination

Data were collected on a Kappa CCD Nonius diffractometer. The crystal was mounted on a glass capillary and bathed in a cold nitrogen stream during the collection. The cell parameters were calculated from 10 frames with 1° steps. Then all reflections data were collected. The hypothesis was found by direct methods using the SHELXS program.[23] The structure was refined using SHELXL-97[24] with anisotropic temperature factors for all non-H atoms. Hydrogen atoms were calculated at theoretical positions and refined riding on C or O atoms. Due to the space group, the asymmetric unit is represented by a half macrocycle and by three half pyridine molecules. Table 1 summarizes the crystal parameters and the experimental details. Selected bond lengths and angles are given in Table 2. CCDC reference number 139879. See http://www.rsc.org/suppdata/jm/b1/b105034f/ for crystallographic files in .cif or other electronic format.

2.3 Preparation of *p*-tetrakis(4-nitrophenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene 1

Tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (0.5 g, 1 mmol) and *p*-nitrobenzenediazonium tetrafluoroborate (1.42 g, 6 mmol) were dissolved in 20 mL of THF. The reaction was initiated by addition of pyridine (1 mL) at 0 °C. The reaction mixture turned orange and a slow precipitation occurred. After two days, the precipitate was filtered and washed successively with cold THF and MeOH. The product was recrystallized from pyridine to give red crystals of **1** (0.78 g, 71%). ^{1}H NMR (C_5D_5N) δ 8.60 (s, 8H, ArH), 8.29 and 7.86 (2d, both 8H, ArH in the 4-nitrophenyl moieties, $J = 9.12$ Hz), 8.17 (s, 4H, ArOH); ^{13}C NMR (C_5D_5N) δ 168.13 (s, Ar*C*-OH), 156.43 (s, Ar*C*-NO_2), 149.10, 148.42 (s, Ar*C*-N=N), 144.65 (s, Ar*C*-S-Ar), 133.56, 125.18, 123.43 (Ar*C*-H); MS (FAB, negative mode, Thy.) *m*/*z*: calcd $M = 1092.24$; $[M-H]^- = 1091.2$.

Table 1 Crystallographic data for **1**

Empirical formula	$C_{83}H_{63}N_{19}O_{12}S_4$
Formula weight	1646.76
Temperature	123 K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a	10.7076(5) Å
b	13.6925(5) Å
c	15.3195(6) Å
α	65.773(2)°
β	70.237(2)°
γ	88.749(2)°
Volume	1909.62(14) Å^3
Z, calculated density	1, 1.432 mg m^{-3}
Absorption coefficient	0.203 mm^{-1}
F(000)	854
Crystal size	0.56 × 0.20 × 0.05 mm
θ range	2.71 to 27.81°
Reflections collected/unique	14905/8717 [R(int) = 0.0464]
Goodness-of-fit on F^2	1.012
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0764$, $wR_2 = 0.1906$
R indices (all data)	$R_1 = 0.1571$, $wR_2 = 0.2409$

Table 2 Selected bond lengths (Å) and angles (°) for **1**

S1–C13	1.771(3)	S2–C17	1.769(4)
S1–C5	1.770(4)	S2–C1	1.769(4)
O1–C6	1.345(4)	O4–C18	1.289(4)
O2–N3	1.216(5)	O5–N6	1.224(5)
O3–N3	1.219(5)	O6–N6	1.224(5)
N1–N2	1.253(5)	N4–N5	1.263(4)
N1–C3	1.416(5)	N4–C15	1.425(5)
N2–C7	1.433(5)	N5–C19	1.438(5)
N3–C10	1.471(5)	N6–C22	1.474(5)
C13–S1–C5	100.53(17)	C1–S2–C17	111.94(17)
N2–N1–C3	114.3(3)	N5–N4–C15	114.3(3)
N1–N2–C7	112.7(3)	N4–N5–C19	112.7(3)
O2–N3–O3	123.3(4)	O6–N6–O5	122.6(4)
O2–N3–C10	118.0(4)	O6–N6–C22	118.8(4)
O3–N3–C10	118.7(4)	O5–N6–C22	118.6(4)
C2–C1–S2	113.7(3)	C14–C13–S1	119.4(3)
C6–C1–S2	125.9(3)	C18–C13–S1	118.6(3)

2.4 Preparation of *p*-tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene 2

Tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (0.5 g, 1 mmol) and benzenediazonium tetrafluoroborate (6 mmol) were dissolved in 20 mL of THF. The reaction was initiated by addition of pyridine (1 mL) at 0 °C. The mixture was stirred for 16 hours at 0 °C and the yellow product was precipitated by addition of methanol (50 mL). **2** was successively washed with MeOH and diethyl ether and recrystallized from a pyridine–methanol solution (0.58 g, 64%). ^{1}H NMR (C_5D_5N) δ 14.6 (s, 4H, ArOH), 8.54 (s, 8H, ArH), 7.90 (d, 8H, ArH of the phenylazo moieties, $J = 7.6$ Hz), 7.41 (t, 8H, N_2-ArH, $J = 7$ Hz), 7.32 (t, 4H, N_2-ArH, $J = 7$ Hz); ^{13}C (C_5D_5N) δ 166.77 (Ar*C*-OH), 153.25, 144.63 (Ar*C*-N=N), 124.1 (Ar*C*-S-Ar), 132.89, 130.73, 129.59, 123.08 (Ar*C*-H) ; MS (FAB, negative mode, Thy.) *m*/*z* :calcd $M = 912$, $[M-H]^- = 911$.

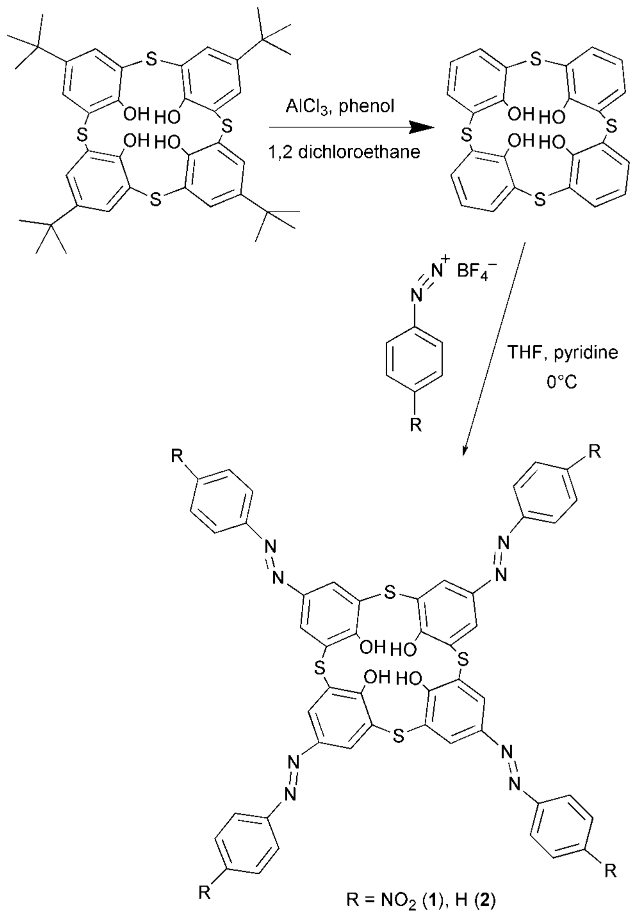
3. Results and discussion

3.1 Synthesis

The two modified thiacalixarenes, namely *p*-tetrakis(4-nitrophenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (**1**) and *p*-tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]-arene (**2**), were prepared following the modified procedure reported by Bouoit.[25] The synthetic procedure for **1** and **2** is shown in Scheme 1. They were prepared by reacting the respective benzenediazonium tetrafluoroborate salts with the tetrahydroxytetrathiacalixarene in THF, in the presence of pyridine. The formation of compounds **1** and **2** was confirmed by ^{1}H NMR, mass spectroscopy and by X-ray structural analysis for **1**. The ^{1}H NMR spectrum of **1** shows one singlet at 8.60 ppm attributed to the aromatic protons of the tetrathiacalixarene cycles and two doublets at 8.29 and 7.86 ppm corresponding to the aromatic protons of the nitrophenyl moieties. The spectrum of **2** displays one singlet at 8.54 ppm for the aromatic protons of the tetrathiacalixarene cycles, one doublet at 7.9 ppm for the aromatic hydrogen atoms located in the α position of the diazo group, and, finally two triplets centred at 7.41, 7.32 ppm for the hydrogen atoms located in the *meta* and *para* positions. Red single crystals of **1** were slowly grown from a pyridine solution.

3.2 X-Ray structure

The molecular structure of **1** was determined in the solid state by single crystal X-ray diffraction analysis (Fig. 2a and 2b). The macrocycle **1** crystallizes with four pyridine molecules



Scheme 1 Synthesis of *p*-tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arenes (R = NO_2, H).

and adopts a 1,2-alternate conformation stabilized through hydrogen bonds between O(1)···O(4) (2.662(4) Å), O(4)···S(2) (3.128(4) Å), S(1)···O(4) (2.965(3) Å) and S(1)···O(1) (3.058 (3) Å). The four bridging sulfur atoms are coplanar. Usually calix[4]arene[5,6] or thiacalix[4]arene[26] derivatives with four free hydroxy groups adopt a cone conformation which is stabilized by a cycle of four strong intramolecular H-bonds. Here a pyridine molecule interrupts this cycle. In fact, a bifurcated H-bond is observed between O(4)–H(4) and the two acceptor atoms N(40) and S(2) with interatomic distances of 2.550(5) Å for O(4)···N(40), 3.128(4) Å for O(4)···S(2), 2.057(5) Å for H(4)···N(40) and 2.859(2) Å for H(4)···S(2). A second bifurcated H-bond connects between the other hydroxy groups O(1)–H(1) and O(4)···S(1) atoms, with interatomic distances of 2.662(4) Å for O(1)···O(4), 3.058 Å for O(1)···S(1), 1.855(3) Å for H(1)···O(1) and 2.591(1) Å for H(1)···S(1). Another short contact is noted between S(1) and O(4) (2.965(3) Å). The angles between the plane containing the four sulfur atoms and the aromatic rings are quite different, 47.6(1)° for the C(1)–C(6) ring and 63.9(1)° for the C(13)–C(18) ring.

3.3 Thermal analysis

Thermal stability of both compounds was investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA of **1** shows a two-step process between 80 and 170 °C corresponding to the elimination of the solvated pyridine molecules. The DSC endothermic peak at 230 °C corresponds to the melting of **1** followed instantaneously by its decomposition. **2** shows a better thermal stability than **1**. It starts to decompose at 310 °C, which is quite high for a diazo-containing species.

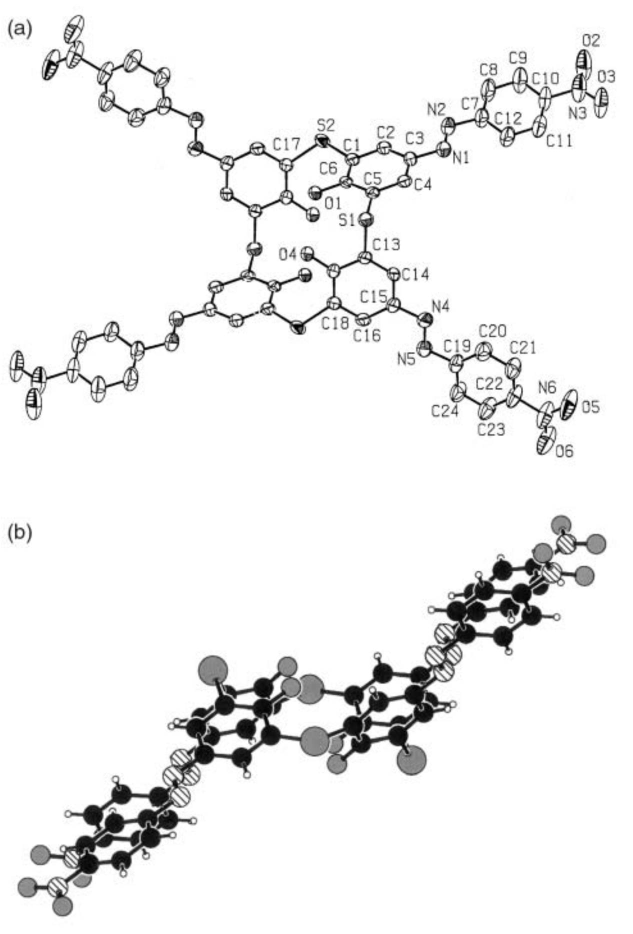


Fig. 2 ORTEP drawing of *p*-tetrakis(4-nitrophenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (**1**) (a) and side view of the molecule (b). The solvent molecules have been removed for clarity.

3.4 Optical power limiting measurements

z-Scans and optical power limiting experiments were performed in order to demonstrate the potential of these species as optical limiters. Since compound **1** absorbs significantly in the ground state at 532 nm it was not possible to perform any optical limiting experiment at this wavelength. However, with *z*-scans performed on **1** (18.5 mM in pyridine, Fig. 3), utilising the Ti : sapphire laser, the TPA cross-section was found to be $\sim 50 \times 10^{-50}$ cm^4 s per photon with peak irradiance between 33 GW cm^{-2} and 272 GW cm^{-2} (Fig. 4). This means that under the conditions used in these experiments, a pure two-photon absorption without any further absorption in the excited states can be considered to be responsible for the nonlinear absorption of **1**. This is consistent with the results

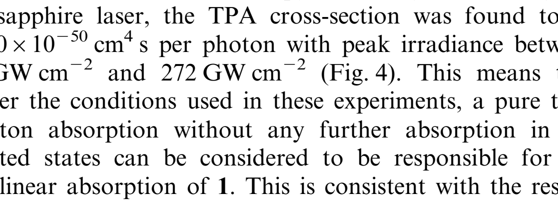


Fig. 3 *z*-Scans with compound **1** in 18.5 mM pyridine solution in 1 mm cells. The pulse length was 169 fs and the Rayleigh length 4 mm.

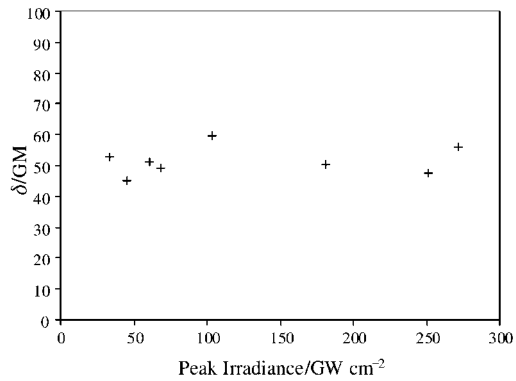


Fig. 4 Results from the *z*-scans on compound **1**. Each point in the graph results from a *z*-scan. δ is a measure of the two-photon absorption per molecule and photon (1 GM = 10^{-50} cm^4 s per photon molecule).

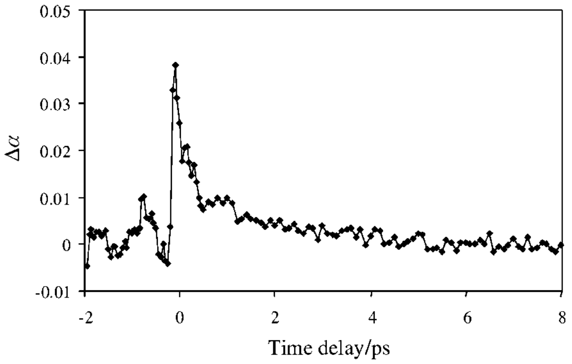


Fig. 5 Transient absorption of compound **1**. The pump energy was 3.5 μJ per pulse and the pulse length was 169 fs. The decay constant was found to be 1.7 ps.

from time resolved pump–probe absorption measurements. The transient absorption of compound **1** (Fig. 5) was found to have a very fast decay (<2 ps), which indicates that the nonlinear absorption is due to two-photon absorption and not related to excited state absorption. This is consistent with the results from the *z*-scans performed with different pulse-energies. Optical limiting at 532 nm was observed for compound **2** (6 mM in pyridine). It showed 48% linear transmission at 532 nm and was found to limit the energy to ~9 μJ (Fig. 6).

4. Conclusion

Although they absorb in the visible region and they do not limit enough to protect the eyes (below 1 μJ), these tetrathiacalixarenes have shown interesting potential for further optical power limiting developments. Other functionalities, as well as metal complexes, are currently under investigation in order to enhance the TPA cross-section, to improve the optical limiting behaviour and to increase the linear transmission in the visible.

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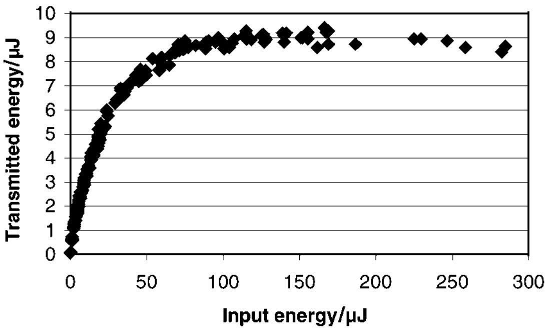

Fig. 6 Optical limiting for *p*-tetrakis(phenylazo)tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (**2**).

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