



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

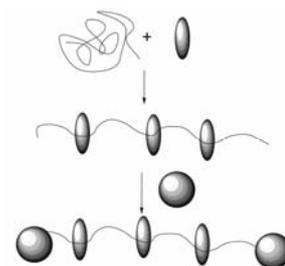
POLYROTAXANE BASED ON POLYDIMETHYLSILOXANE AND LOWER RIM MODIFIED CALIX[8]ARENE DERIVATIVE

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Polyrotaxane composed of epoxy-terminated polydimethylsiloxane/octaallyloxy-*para*-tert-butylcalix[8]arene inclusion complex and *para*-tritylaniline, as bulky stopper at the end-chains is reported. The chemical structure of the polyrotaxane was proved by FTIR and ¹H-NMR spectroscopy. The average number of macrocyclic encapsulation of polymer chain determined by ¹H-NMR indicated 12% coverage. A unimodal molecular weights distribution was proved by SEC analysis, which clearly evidenced the rotaxane formation and not a physical mixture between components. The thermal properties evaluated by TGA and DSC measurements revealed improvements of the thermal stability of polyrotaxane compared with non-rotaxane ones. The fluorescence spectra of polyrotaxane exhibited well resolved blue emission bands arisen from the calixarene derivative chromophore units.



INTRODUCTION

Currently, in the field of supramolecular chemistry, rotaxane and polyrotaxanes are the most studied interlocked molecules.¹⁻⁵ A rotaxane is an assembly in which the macrocyclic molecule (host) encircles an axle (guest) through non-covalent interactions.¹ To prevent dethreading of the host from the axle, bulky functions (also known as stoppers) are attached at the ends of the axle. The role of hosts is played by cyclic molecules, whereas guests include inorganic/organic small molecules or polymers. Most of the polyrotaxanes already reported contain as macrocyclic compounds cyclodextrins,⁵⁻¹¹ crown ethers,¹² or calixarenes.^{2,13-21}

Due to the hydrophobic cavities, calixarenes are able to accommodate various neutral and charged

inorganic/organic guest molecules which allow their use in molecular recognition.¹³⁻¹⁹ Intensive studies have been performed not only because of their capacity of the inclusion complexes formation, but also because of ease functionalization on the upper rim (*para*-positions) and the lower rim (the hydroxyl phenol groups), which could improve their affinity for guest molecules.²² In spite of the extended use of host compounds for polyrotaxanes formation, calixarenes and their derivatives have received less attention compared with other macrocyclic molecules. To date, complexation studies have been limited and a few supramolecular architectures with neutral small molecules or polymers were reported.^{14,17,18} We have recently reported interlocked molecules with modified polydimethylsiloxane, as a linear component

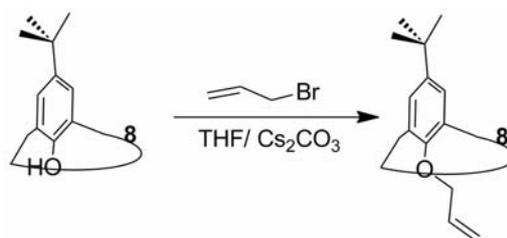
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threaded by *para*-tertbutylcalix[6]arene, as host molecules and we exemplified such improvements on the thermal as well as morphological properties of the non-complexed polydimethylsiloxane.¹⁸

Herein, we report the synthesis and characterization of a polyrotaxane composed of octaallyloxy-*para*-tertbutylcalix[8]arene (**2**), as new host compounds with better solubility in organic solvents than most of the other calixarenes, and epoxy-terminated polydimethylsiloxane with molecular weights of about 1500 g·mol⁻¹ (neutral guest molecule) (**3**). To the best of our knowledge, the present study is the first example where macrocycle **2** was used in the synthesis of polyrotaxane with neutral polymers. The chemical structure, thermal and optical properties of the polyrotaxane **5** was investigated and compared with the non-rotaxane **3** polymer.

RESULTS AND DISCUSSION

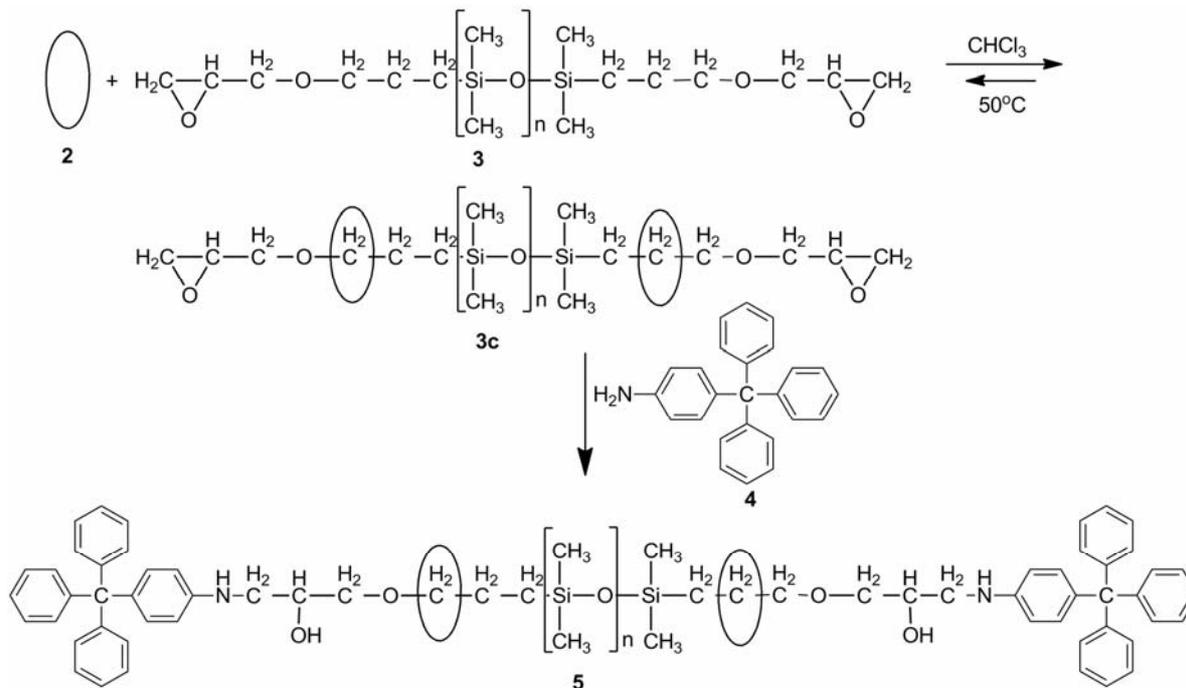
In order to gain a deeper understanding of the expansion of the cavity, after lower rim modification of *para*-tertbutylcalix[8]arene (**1**),¹⁸ octaallyloxy-*para*-tertbutylcalix[8]arene **2** was obtained by slightly modified previously reported conditions,²³ by lower rim modification of the parent monomer (**1**), using a weak base (Cs₂CO₃), in THF and an excess of allyl bromide, Scheme 1.



Scheme 1 – Synthesis of octaallyloxy-*para*-tertbutylcalix[8]arene by lower rim modification of *para*-tertbutylcalix[8]arene.

Polyrotaxane **5** containing macrocycle molecules **2** threaded onto neutral guest molecule (epoxy-terminated polydimethylsiloxane with molecular weights of about 1500 g mol⁻¹) (**3**), was obtained by mixing an excess of host **2** with guest **3** in CHCl₃ resulting in a polypseudorotaxane **3c**, and finally 4-tritylaniline (**4**) was added, as a monofunctional end-capping reagent to react with the epoxy groups present at the end chains, Scheme 2.

The chemical structures of macrocycle **2** and polyrotaxane **5** was proved by FTIR and ¹H-NMR spectroscopy. The ¹H-NMR spectrum, of compound **2** indicated complete lower rim substitutions (the absence of protons from phenol groups from 9.62 ppm (not shown).



Scheme 2 – Synthesis of a polyrotaxane composed of octaallyloxy-*para*-tertbutylcalix[8]arene (**2**) and epoxy-terminated polydimethylsiloxane (**3**).

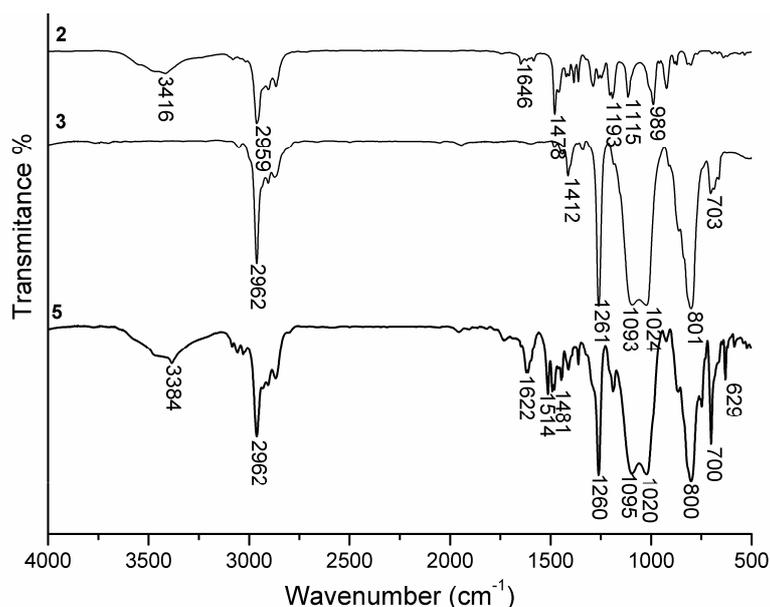


Fig. 1 – FTIR spectra of **2**, **3** and polyrotaxane **5**.

FTIR spectra of the non-rotaxane **3**, macrocycle **2** and rotaxane **5**, indicated that the vibration bands near 1024 and 1095 cm^{-1} of the polymer **3** (strong Si-O-Si stretching absorption characteristic of siloxane backbone) is shifted to 1020 and 1095 cm^{-1} in the spectrum of polyrotaxane **5**. In addition, the vibration located at 3416 cm^{-1} in the macrocycle **2** is 32 cm^{-1} shifted to lower frequencies in the polyrotaxane spectrum, Fig. 1.

$^1\text{H-NMR}$ spectrum of polyrotaxane **5**, Fig. 2, presents different resonance peaks of methyl protons linked to the silicon atoms, compared to the corresponding peaks of the non-complexed **3** polymer (not shown). These signals appear at 0.02 ppm in the non-rotaxane **3** and at 0.05 ppm in the polyrotaxane **5**. The peaks corresponding to the epoxy groups from 3.13-2.58 ppm, corresponding to the non-rotaxane **3**, disappeared due to the ring opening reaction with end-capping **4**. The peaks of CH-OH and CH₂-NH groups obtained after blocking reaction are situated at 3.71 and 3.43 ppm, respectively. The $^1\text{H-NMR}$ analysis was used to determine the coverage of the polymer **3** with macrocycle, *i.e.*, the average number of macrocycle **2** per repeating unit. The molar ratio incorporation of the macrocycle **2** has been calculated using the ratio of the integrated area of the signal assigned of the *tert*-butyl protons (1.25 ppm), labeled “g”, and the methyl protons linked to the silicon atoms labeled “a” from **5** (0.05 ppm). The average number of macrocycle **2** per repeat units, calculated as $(I_g/72) / (I_{\text{Ha}}/6)$, was found to be 0.12 (*i.e.*, ca. 12% coverage), denoting weak hydrophobic interactions between macrocycle

and polysiloxane units under the reaction conditions.

To gain further insight into the complexation ability of macrocycle **2** towards polymer **3**, the stability constant (K_s) was determined by $^1\text{H-NMR}$ titration (not shown). The value of K_s in CDCl_3 was found to be $(21 \pm 3) \text{ M}^{-1}$, and can be attributed either to conformational changes of the macrocycle molecule upon inclusion of the guest molecule inside of the cavity or lower hydrophobic interactions between them.

The formation of the polyrotaxane was also confirmed by SEC analysis by using THF as eluent, Fig. 3. The peak of free macrocycle **2** was not present in the chromatogram of polyrotaxane **5** and this point clearly evidenced that the rotaxane sample is not a physical mixture between components. However, the curve of the rotaxane copolymer situated at lower elution volumes could be attributed to the presence of the macrocycle **2** on the macromolecular chain, denoting higher hydrodynamic volume of the encapsulated polymer, Fig. 3.

The thermal properties were also evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC curves on the second heating scan of polyrotaxane **5** showed higher glass-transition temperature (T_g) as compared with the non-rotaxane **3** counterpart, Fig. 4. T_g increases from -113 °C to 13 °C in the polyrotaxane **5**. The higher T_g of polyrotaxane can be attributed to the encapsulation effect of the macrocycle **2**, which confers more rigidity to the polysiloxane **3** macromolecular chains.

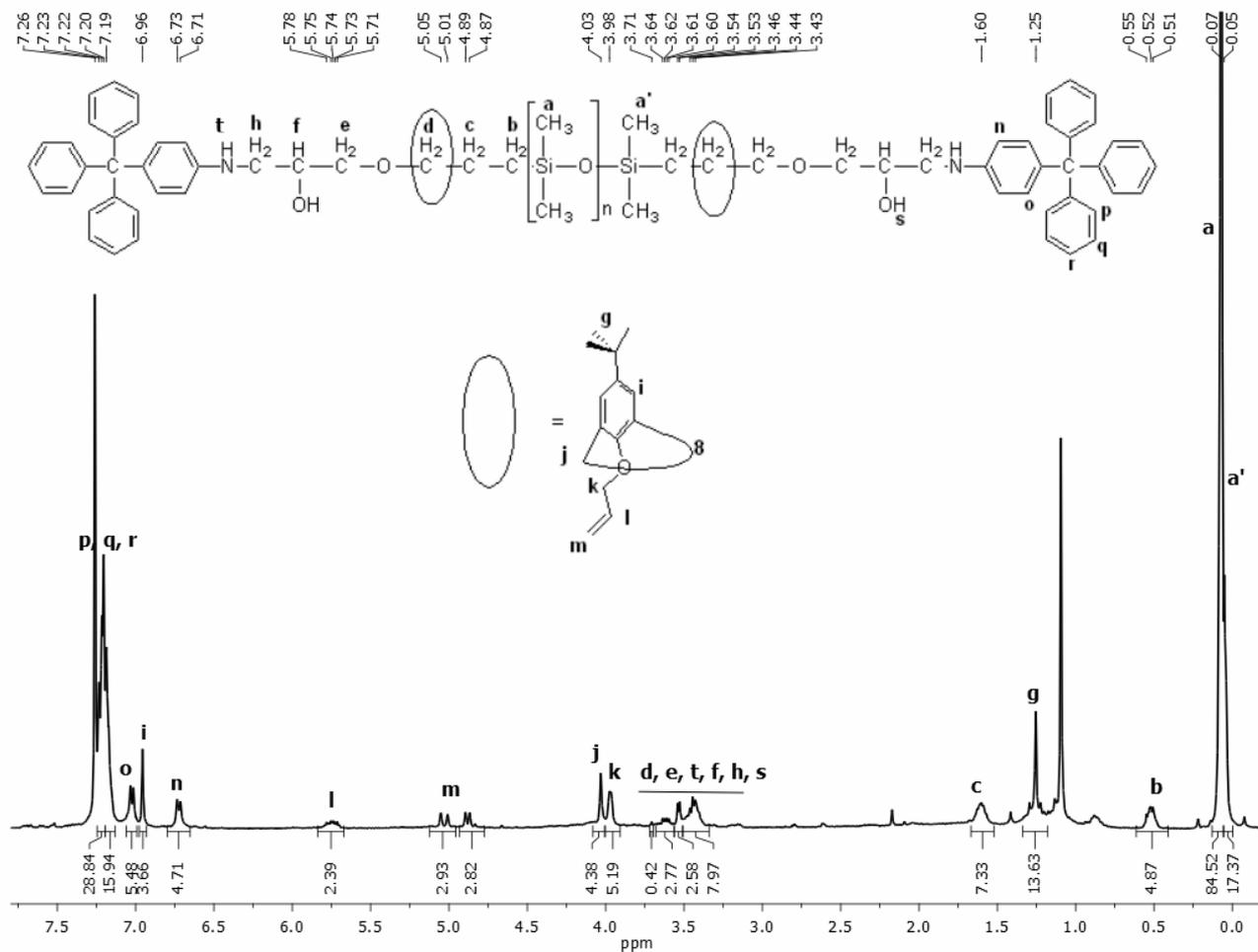


Fig. 2 – ^1H -NMR spectrum of polyrotaxane **5** in CDCl_3 .

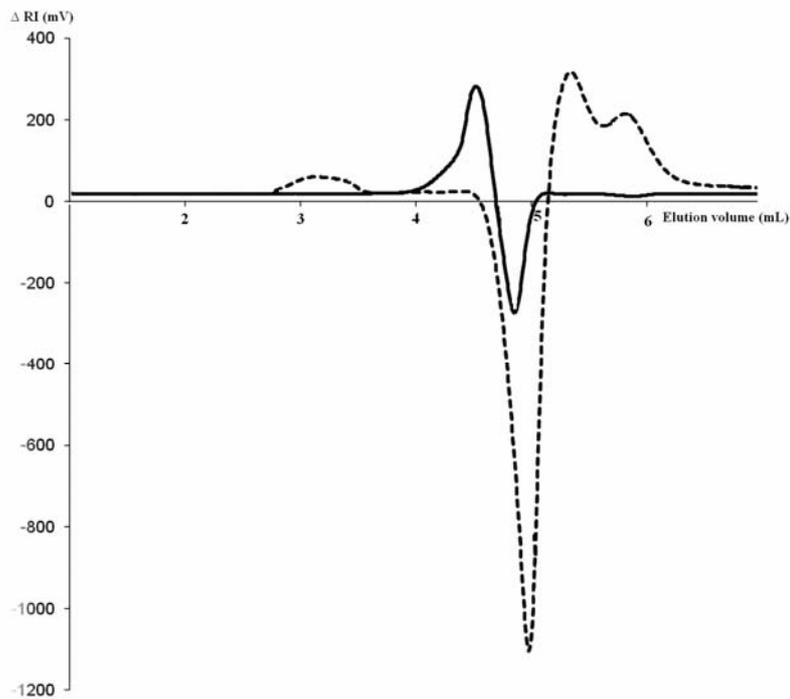


Fig. 3 – Size exclusion chromatography curves of the polyrotaxane **5** (dotted line) and macrocycle **2** (solid line).

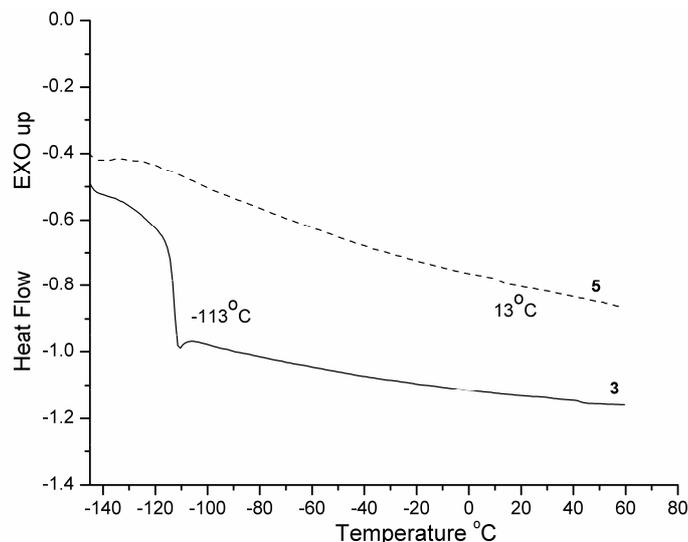


Fig. 4 – DSC traces on second heating scan of the non-rotaxane **3** (solid line) and polyrotaxane **5** (dotted line).

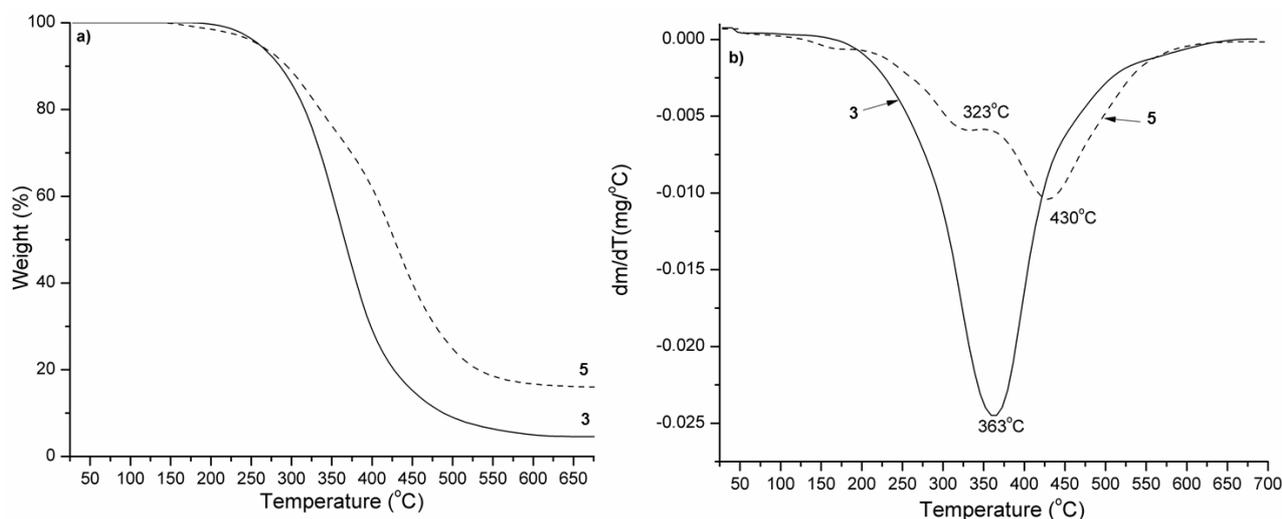


Fig. 5 – TGA spectra (a) and DTG thermograms (b) of the non-rotaxane **3** (solid line) and polyrotaxane **5** (dotted line).

The effect of encapsulation on the thermal stability was further supported by TGA and DTG measurements. As shown in Fig. 5a, the non-rotaxane **3** (solid line) shows a single step of degradation and higher decomposition temperature, as compared with polyrotaxane **5** (dotted line). The non-rotaxane **3** starts to decompose at about 281 °C, while its rotaxane homologue **5** shows the beginning of decomposition at about 267 °C, higher than the thermal decomposition temperature of macrocycle **2** molecule (259 °C), (not shown). DTG data revealed two weight loss stages for polyrotaxane **5** at 323 °C and 430 °C compared with non-rotaxane **3**, which degrades in a single step with a maximum temperature at 363 °C, Fig. 5b. It should be pointed that the rotaxane formation increases the thermal stability of the macrocycle **2** with about 8 °C. It

should be mention that a similar phenomenon was also previously reported for another polyrotaxanes.²⁴⁻²⁶

Recently, comparison of threaded and unthreaded systems has allowed significant insights on the optical properties.^{9-11,24-27} The optical properties of the polyrotaxane **5** and macrocycle **2** were investigated, as shown in Fig. 6. It should be pointed out that the non-rotaxane **3** polymer does not exhibit any electronic absorption and emission spectra.

Polyrotaxane **5**, revealed a distinct 55 nm hypsochromic shifts in UV-Vis, compared with macrocycle **2** host molecule, Fig. 6 a,b (solid line). The hypsochromic shifts could explain the presence of the $n-\pi^*$ transition only. Fluorescence emission (PL) of polyrotaxane **5** and macrocycle **2** appears at 454 and 438 nm, respectively, Fig. 6 a,b (dotted line).

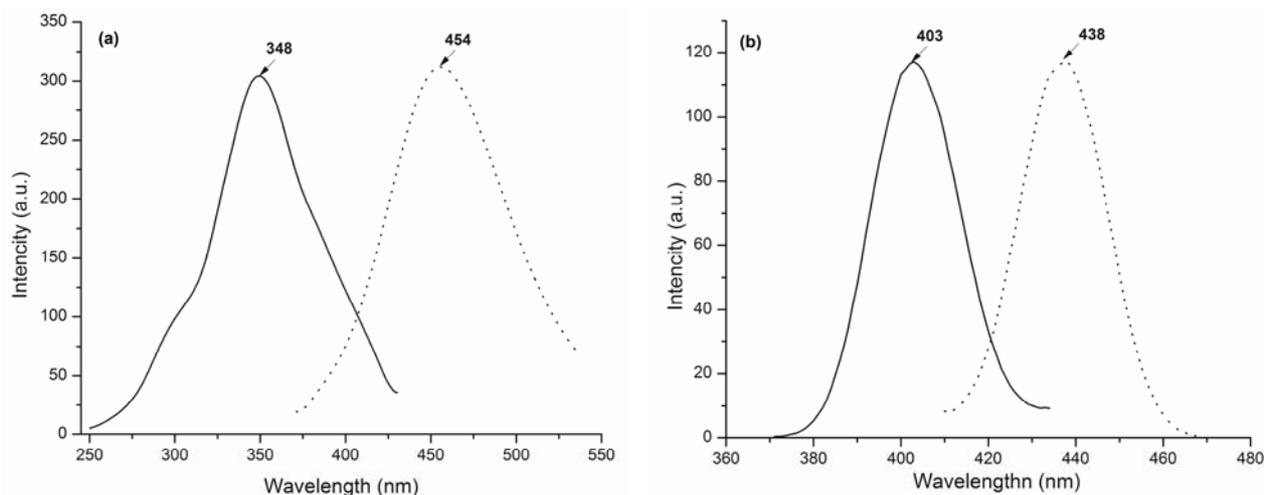


Fig. 6 – Absorption (solid line) and fluorescence emission (PL) (dotted line) spectra of polyrotaxane **5** (a) and macrocycle **2** (b) in 1.8×10^{-5} M CHCl_3 solutions.

The polyrotaxane **5** shows a larger emission band and higher fluorescence intensity compared to the macrocycle **2**, which suggests that aromatic groups of calixarenes absorb light and then transfer the energy to guest polymer **3**. The strongly increasing its optical response could be as a consequence of interactions between them. Nevertheless, the resulting fluorescence intensities are comparable with those of common fluorescent dyes.²⁷

EXPERIMENTAL

Macrocycle **2** was synthesized by modification on the lower rim of the parent *para*-tertbutylcalix[8]arene, using Cs_2CO_3 as base medium, THF as solvent instead NaH and DMF,²³ followed by recrystallisation from $\text{CHCl}_3/\text{CH}_3\text{OH}$ to give the compound **2** as a fine white powder in 72.8% yield.

$^1\text{H-NMR}$ (CDCl_3), δ : 6.95 (s, 16H, aromatic), 5.78-5.71 (m, 8H, $-\text{CH}=\text{}$), 5.05-4.87 (dd, 16H, $=\text{CH}_2$), 4.03 (s, 16H, Ar- CH_2), 3.98-3.96 (m, 16H, $-\text{O}-\text{CH}_2$), 1.09 (s, 72H, $-(\text{CH}_3)_3$).

FTIR (KBr), (cm^{-1}): 3416 and 2959 (stretching vibration of aliphatic and aromatic C-H), 1647 and 1479 (phenyl vibrations), 1204, 1115, and 989.

Polymer **3** was prepared through cationic equilibration of D_4 with TMDS, followed by the hydrosilation of the obtained Si-H terminated polydimethylsiloxanes (H-PDMS) with allyl glycidyl ether (AGE) in the presence of hexachloroplatinic acid catalyst, as previously reported.²⁸

$^1\text{H-NMR}$ (CDCl_3), δ : 0.02 (s, CH_3Si end), 0.05 (two s, CH_3Si chain), 0.50-0.54 (m, $\text{CH}_2\text{CH}_2\text{Si}$, β adduct), 1.55-1.64 (m, $\text{CH}_2\text{CH}_2\text{Si}$, β adduct), 2.58-2.78 (m, CH_2 epoxy), 3.10-3.33 (m, CH epoxy), 3.35-3.45 and 3.65-3.69 (m, $\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ and dd, $\text{O}-\text{CH}_2$ -epoxy), (not shown).

FTIR (KBr), (cm^{-1}): 2962, 1261, 1093, and 1024.

Polyrotaxane (**5**) was synthesized as follows: to a solution of **2** (0.12 g, 0.25 mmol) in 2.5 mL of CHCl_3 was added (0.025 g, 0.16 mmol) polymer **3** and vigorously stirred at 55 °C temperature for 72 h. The epoxy groups located at the ends of siloxane chains were then reacted with blocking molecule **4** (0.011 g, 0.32 mmol) and the reaction was warmed to 70 °C

and continued for 8 h. The resulting brown color product, soluble in CHCl_3 was precipitated in methanol, filtered and dried. Then the solid was suspended in diethyl ether to remove uncomplexed polymer **3**, filtered and dried. Finally, a light yellow solid was obtained 0.042 g (yield of about 28 %).

$^1\text{H-NMR}$ (CDCl_3), δ : 7.23 – 7.19 (m, 30H from **4**), 7.03-7.01 (d, $J = 7.92$ Hz, 4H from **4**), 6.96 (s, 16H from **2**), 6.73-6.71 (d, $J = 7.92$ Hz, 4H from **4**), 5.78-5.71 (m, 8H from **2**), 5.05-4.87 (dd, $J = 16.72$ Hz, $J = 1.76$ Hz, 16H from **2**), 4.03 (s, 16H from **2**), 3.98 (d, 16 H from **2**), 3.64-3.43 (m, 12H from **3**), 1.6 (d, 4H from **3**), 1.25 (s, 72H from **2**), 0.55 -0.51 (m, 4H from **3**), 0.07 (s, 90 H from **3**), 0.05 (s, 6H from **3**).

FTIR (KBr), (cm^{-1}): 3384 (OH stretching vibration), 2962 (stretching vibration of aliphatic and aromatic C-H), 1622, 1514, 1418, 1260, 1095, 1020, 801.

Characterization

$^1\text{H-NMR}$ spectra were recorded on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and z-gradients. Spectra were recorded in CDCl_3 . The chemical shifts are reported as δ values (ppm) relative to the residual peak of the solvent. FTIR spectroscopic characterization of the samples was performed on a Specord Carl Zeiss Jena infrared spectrophotometer on KBr pellets. Size exclusion chromatography (SEC) was performed using a HR 5 E Styragel column (Waters) equipment, with flow rate of THF 0.3 mL min^{-1} with both UV ($\lambda=345 \text{ nm}$) and refractive index detectors; polyethylene oxide (PEO) standards was used for calibration curves. The thermal properties of the samples were studied on a DSC 200 F3 Maia calorimeter (Netzsch) in the range -150 to 60 °C at a scanning rate of $10 \text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) measurements have been performed on a Mettler Toledo TGA/DTA 851e at a heating rate of $15 \text{ }^\circ\text{C min}^{-1}$ under 20 mL min^{-1} nitrogen flow. The heating scanning rates were performed on 1.5 to 3 mg of the sample in the 25-800 °C temperature range. Absorption and fluorescence emission spectra of compounds were measured on a Shimadzu spectrophotometer.

CONCLUSIONS

A main-chain polyrotaxane consisting of octaallyloxy-*para*-tertbutylcalix[8]arene, as host

molecules and epoxy-terminated polydimethylsiloxane, as guest molecules has been synthesized. As much as 12% coverage is proved to thread onto each polymer chains. Thermal properties of the non-rotaxane counterpart were found to be significantly enhanced by the presence of macrocycle molecules onto polymer chains. This finding offers a significant contribution to the area of the encapsulation process, in spite of the extended use of lower-rim chemical modified calix[8]arene macrocycles, as hosts for neutral organic molecules or polymers.

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