



Detection of sulfate surface-active substances *via* fluorescent response using new amphiphilic thiacalix[4]arenes bearing cationic headgroups with Eosin Y dye

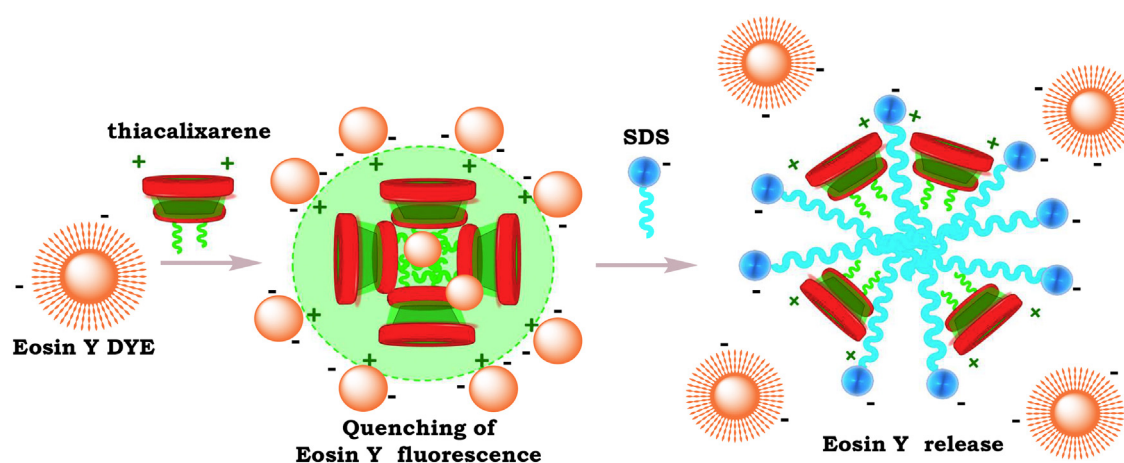


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GRAPHICAL ABSTRACT



HIGHLIGHTS

- Synthesis of new *p*-*tert*-butylthiacalix[4]arene ammonium amphiphiles in *1,3*-*alternate* stereoisomeric form.
- Supramolecular associates of new *p*-*tert*-butylthiacalix[4]arene ammonium amphiphiles with Eosin Y dye.
- New fluorescent probe for sodium lauryl and laureth sulfates with response from 3.5 μM of SAS.

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ABSTRACT

New ammonium-containing derivatives of *p*-*tert*-butylthiacalix[4]arene in *1,3*-*alternate* stereoisomeric form were synthesized *via* copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction of corresponding azides with *N*-propargyl-*N,N,N*-triethylammonium bromide. Critical aggregation concentration (CAC) of new amphiphilic thiacalixarenes **1-3** (with butyl, octyl and tetradecyl substituents) determined by pyrene micellization method are 91, 59 and 33 μM , respectively. According to DLS data the diameter of these aggregates is around 130 nm. Anionic dye Eosin Y (EY) forms the associates with positive charged thiacalixarenes **1-3**, shifts CAC to the low concentration region (2 μM) and decreases nanoaggregates size up to 90 nm. Thiacalixarene/EY associates were investigated as fluorescent probe for the determination

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Macrocyclic
Amphiphiles
Fluorescent sensing
sodium dodecyl sulphate

of different surface active substances (SAS) in the solution. It was found that only sodium dodecyl sulfate (SDS) and sodium laureth sulfate (SLES) causes EY release, while other anionic, cationic and zwitterionic SAS form only mixed aggregates. Fluorescent response of thiacalixarene/EY associates is considerable from 3.5 μM concentration of SDS.

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1. Introduction

The formation of the nanoscale objects by the self-assembly of small molecules is an attractive strategy that brings with it the challenge of controlling the size and structure of the assemblies through interactions on the molecular scale. Thus, design of new amphiphilic synthetic receptors with high affinity to specific guests attracts a great attention since its can be used in molecular recognition, drug delivery, catalysis, cell mimics, gene transfer and many other applications [1–5]. Calix[n]arenes are macrocyclic oligomers composed of phenolic units linked by methylene groups at meta-positions, forming a unique basket shape. It has been widely used to construct macrocyclic amphiphiles [6,7] due to their unique structure, variety of stereoisomeric forms and facile functionalization of both upper and lower rims. Their ability to form host-guest complexes and to bind both organic molecules and metal ions is successfully used in extraction, recognition of different substrates and as components of molecular devices [8–10]. Furthermore, these macrocycles are indispensable in the design of biomimetic systems – artificial systems modeling at the molecular level or mimic the reaction and the processes occurring in living organisms [11]. Firstly reported by Miyano [12], *p*-butylthiacalix-*tert*-butylthiacalix[n]arenes became a very attractive class of calixarene family with key features as larger cavity size and ability of sulfur bridge to take part in metal ions binding [13]. Recently [14] we synthesized an universal “clickable” platform based on thiacalix[4]arene adopting 1,3-*alternate* stereoisomeric form. Stepwise functionalization of the macrocycle lower rim by Mitsunobu reaction allows to design on the thiacalixarene platform two molecular domains with quite different properties located on opposite sides of the macrocycles plane. One of them has lipophilic properties whereas the other side of the macrocycle contains the binding sites easily varied by CuAAC reaction [15].

Herein we report the synthesis of new amphiphilic thiacalix[4]arene derivatives containing ammonium groups and their supramolecular aggregates with EY dye and some SAS.

2. Material and methods

All reagents were purchased from either Acros or Sigma-Aldrich and used without further purification. Solvents were purified by standard methods [16]. Parent *p*-*tert*-butylthiacalix[4]arene [17], 5,11,17,23-tetra-*tert*-butyl-25,27-bis[butyloxy]-26,28-bis[3-(4-phenyl-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene, 5,11,17,23-tetra-*tert*-butyl-25,27-bis[octyloxy]-26,28-bis[3-(4-phenyl-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene, 5,11,17,23-tetra-*tert*-butyl-25,27-bis[tetradecyloxy]-26,28-bis[3-(4-phenyl-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene [18] and *N*-propargyl-*N,N,N*-triethylammonium bromide [19] were synthesized according to the previous published procedures.

TLC was done using “Merck UV 254” plates with UV lamp VL-6.LC (6W – 254 nm tube). Elemental analysis was performed with automated CHNS/O analyzer «Perkin Elmer PE 2400 series 2». NMR experiments were recorded at Bruker Avance 400 Nanobay with CDCl_3 (δ :H 7.26 ppm) as internal standard. MALDI-TOF mass-spectra were recorded at UltraFlex III TOF/TOF with PNA matrix,

laser Nd: YAG, $\lambda = 355$ nm. Cellu Sep H1 dialysis membranes with molecular-weight cutoff (MWCO) limits near 1000 Da were used.

2.1. UV-vis absorbance spectra

The UV/Vis-spectra were recorded on Lambda 35 UV/Vis spectrophotometer (Perkin Elmer Instruments) in the optical cell with 1.0 cm light pass at 298 K. The stoichiometry of the complex was determined by the Job's method in TRIS buffer (pH 7.4) with the total concentration of components 2 or 70 μM .

2.2. Dynamic light scattering (DLS) measurements

Dynamic light scattering (DLS) experiments and zeta-potential measurements were carried out on Zetasizer Nano ZS instrument (Malvern Instruments, USA) with 4 mW 633 nm He-Ne laser light source and the light scattering angle of 173°. The data were treated with DTS software (Dispersion Technology Software 5.00). The solutions were filtered through Millex HV 0.45 μM filter before the measurements to remove dust. The experiments were carried out in the disposable plastic cells DTS 0012 (Sigma-Aldrich, USA) at 298 K with at least three experiments for each system. Statistical data treatment was done using t-Student coefficient and the particle size determination error was <2%. The prepared samples were ultra-sonicated within 30 min before measurements.

2.3. Fluorescence spectroscopy

Fluorescence experiments were performed in 1.0 cm quartz cuvettes and recorded on a Fluorolog FL-221 spectrofluorimeter (HORIBA Jobin Yvon) in the range of 350–430 nm and excitation wavelength 335 nm with 2.5 nm slit for the pyrene and at the range of 500–600 nm and excitation wavelength 480 nm with 2 nm slit for EY. All studies were conducted in buffered aqueous solution (TRIS buffer, pH 7.4) at 298 K.

2.4. General procedure for synthesis of compounds 1–3

Corresponding alkylazide derivative (0.188 mM), *N*-propargyl-*N,N,N*-triethylammonium bromide (0.124 g, 0.566 mM), triethylamine (1 ml), copper(I) iodide (0.0035 g, 0.0188 mM) were dissolved in 10 ml of dry toluene-DMF mixture (1:1). The reaction mixture was stirred at 60 °C for 12 h, and then solvent was evaporated in *vacuo*. Crude product was dissolved in 10 ml of deionized water and purified by dialysis for 3 days using Cellu Sep H1 dialysis membrane. After water evaporation in *vacuo* compound was dried in a vacuum desiccator over P_2O_5 to give **1–3** as white powder.

5,11,17,23-Tetra-*tert*-butyl-25,27-dibutyloxy-26,28-bis[3-(4-methylene-*N,N,N*-triethylammonium bromide)-1,2,3-triazol-1-yl]propyloxy]-2,8,14,20-tetrathiacalix[4]arene **1**

$m = 0.202$ g (75%). Mp: 190 °C (decomp.); MALDI-TOF (m/z): 1249 [M-Et-2Br]⁺; 1463 [M+Na]⁺; IR (KBr) ν_{max} cm⁻¹: 3422 (C–H), 1607 (C–C_{Ar}), 1239 (=C–O), 1133 (C–N).

¹H NMR (400 MHz, CDCl_3 , 298 K) δ_{H} , ppm: 0.79 (t, $J = 7.2$ Hz, 6H, CH₃), 0.87–0.96 (m, 4H, CH₂), 1.01 (s, 18H, CMe₃), 1.06–1.16 (m, 4H,

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