Dedicated to V. F. Mironov on His 60th Anniversary

Modification of Silica Nanoparticles with Stereisomers of *p-tert*-Butylthiacalix[4]arene Containing Four 2-Oxo-2-{[3-(triethoxysilyl)prop-1-yl]amino}ethoxy Substituents at the Lower Rim

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Abstract—Three stereoisomers (*cone*, *partial cone*, and 1*,3-alternate*) of *p-tert*-butylthiacalix[4]arene bearing four anchor propyltriethoxysilane substituents at the lower rim were synthesized for the first time. Surface modification of silica nanoparticles ($d = 12$ nm) with the synthesized macrocycles gave novel hybride thiacalix [4]arene–SiO₂ particles. The obtained nanostructured adsorbents were found to efficiently extract nitroaromatic compounds from aqueous solutions. The *partial cone* and 1*,3-alternate* thiacalix[4]arene–SiO₂ hybrid particles showed affinity to nitrophenols.

Agricultural, tannin, food, and textile industries are known as the main sources of such pollutants as phenol and aniline [1]. About 280,000 tons of textile dyes are annually released to the environment with wastewater [2], which has a negative environmental impact because of the presence of the toxic nitro-phenols and nitroanilines [3–7]. Hazardous xenobiotics prevent insolation of natural waters, thereby slowing down plant photosynthesis and, on the last run, doing harm to aquatic life [8].

Many physicochemical and biological methods, including coagulation and flocculation, membrane processes and oxidative ozonation, have already been applied to remove dyes from wastewater [9–13]. However, there are some limitations preventing wide use of such methods, including high power consump-tion, high cost, as well as stability and high water solubility of dies and problems of their removal [14]. In this connection, sorption purification provides a good alternative as a simple, express, cost-effective, and repetitive process [15]. A great variety of sorbents were reported, including activated coal [16], pit [17],

chitin [18], silica [19], fly ash, and others, but they did not show a high sorption capacity and used on a limited scale [20]. Over the past years, new, recyclable, and efficient nanostructured sorbents for the removal of organic dyes from wastewater have been developed.

Macrocyclic compounds (calixarenes), the objects of supramolecular chemistry, are widely used in the host−guest chemistry as building blocks for molecular recognition [21–29]. The immobilization of thiacalix [4]arenes on the surface of mineral oxides makes it possible to obtain recyclable sorbents [30, 31]. Such sorbents demonstrated thermal, physical, and thermal stability in different experimental conditions. Silica-based materials exhibit, due to the presence of silanol groups, weakly acidic properties and very high reactivity. Silica surface-modified by calixarene derivatives can react with various organic substrates [32, 33]. Earlier we studied the sorption properties of a material on the basis of silica particles and *p-tert*-butylthiacalix[4]arene containing at the lower rim one anchor organosilicon substituent (γ-ureidopropyltri-

Scheme 1.
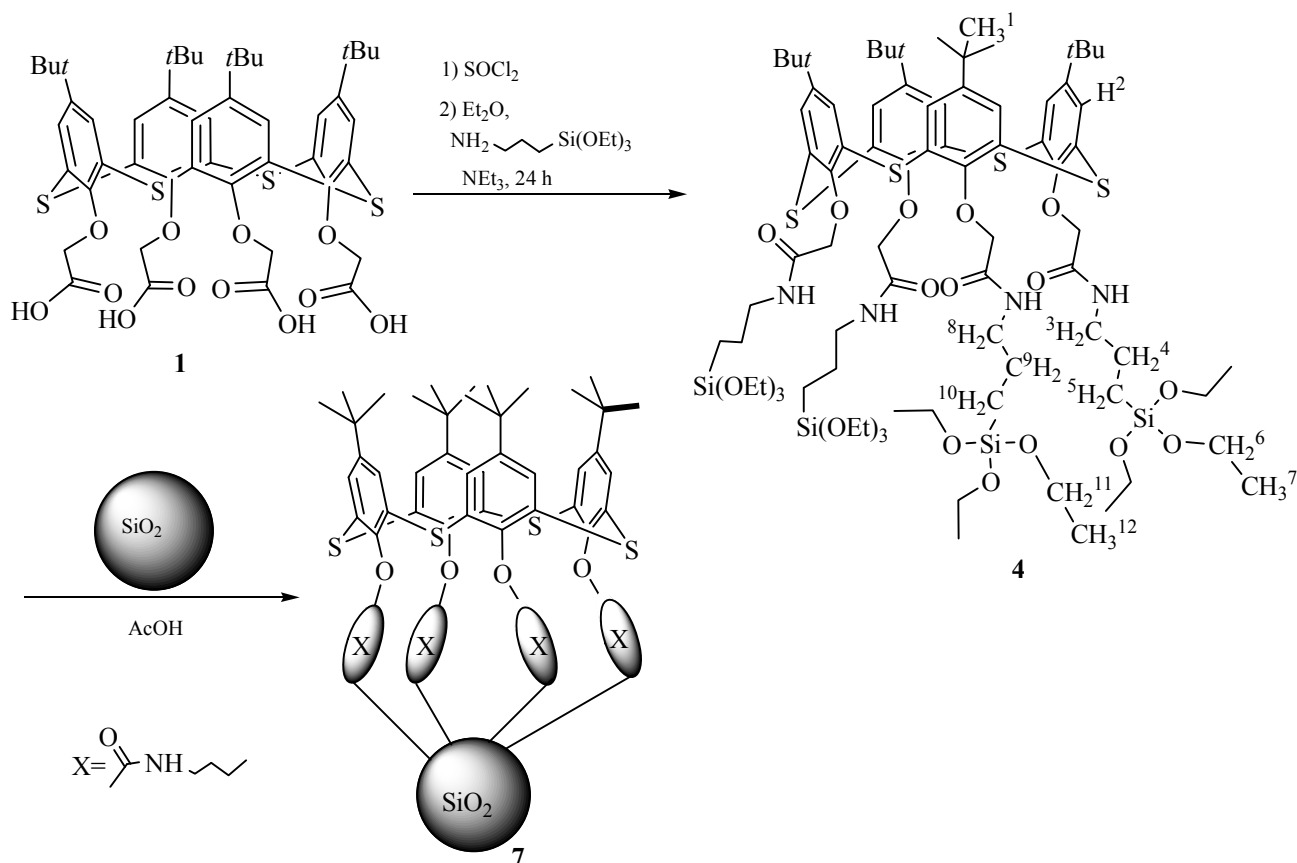
ethoxysilyl group) which allowed binding the macro-cycle of substrate, as well as three benzyl substituents which imparted hydrophobicity to the synthesized material. This *p-tert*-butylthiacalix[4]arene derivative was found to preferentially adsorb nitro derivatives of aniline (2-nitroaniline and 2,4-dinitroaniline) and 2,4-dinitrophenol [21].

In the present work, we synthesized hybrid organic–inorganic materials comprising silica and *p-tert*-butyl-thiacalix[4]arene with four anchor propyltriethoxysilyl substituents and studied their sorption properties with respect to a series of nitrophenols and nitroanilines.
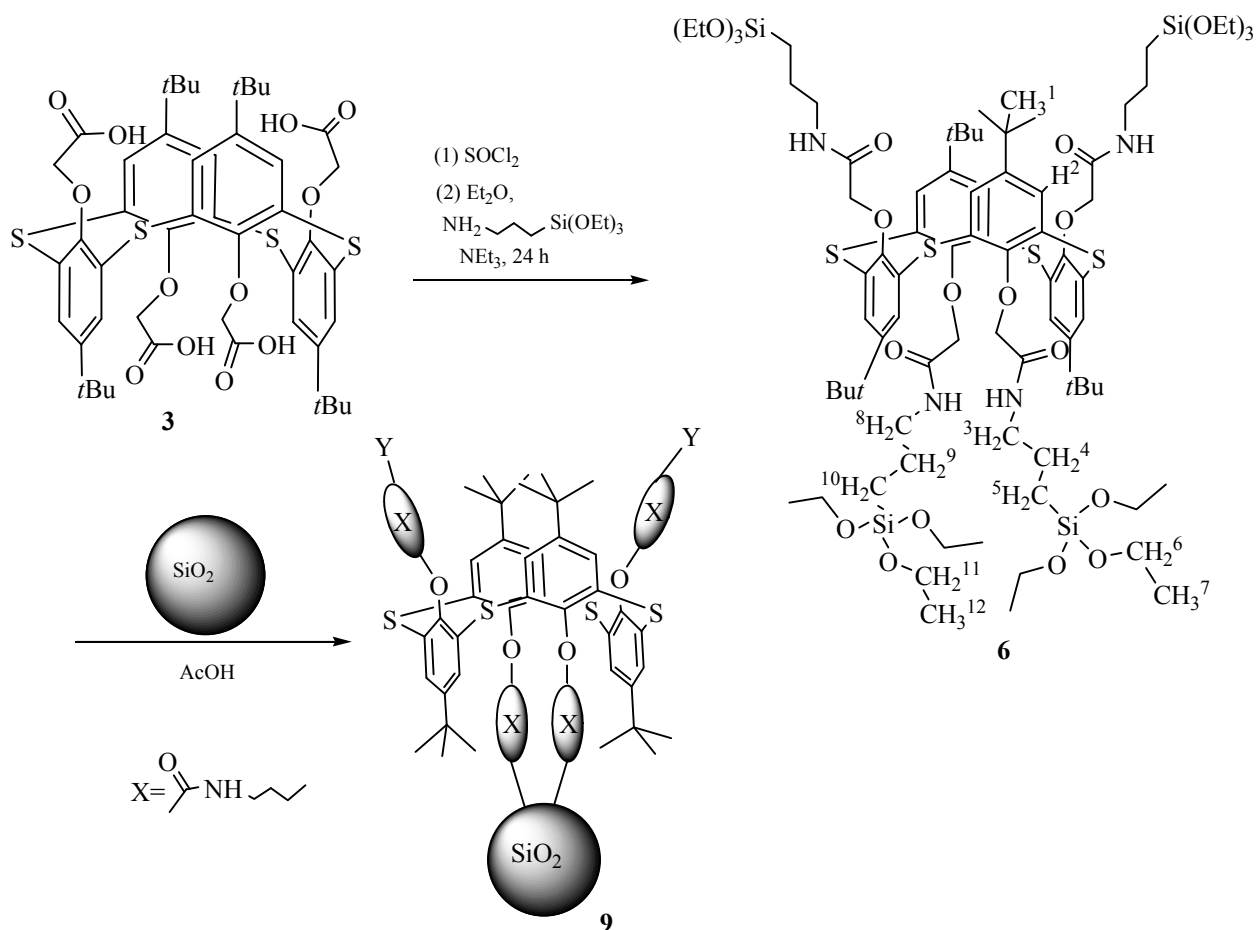
The immobilization of calixarene derivative on the surface of silica nanoparticles (NPs) is based on the block synthesis, specifically, functionalization of the silanol groups on the silica surface with trialkoxysilyl derivatives of *p-tert*-butylthiacalix[4]arene. We pre-viously found [22] that, the surface modification of silica NPs with trimethoxysilyl-substituted *p-tert*-butylthiacalix[4]arenes in an active medium takes path of oligocondensation to form silsesquioxane structures

[22]. Therefore, we synthesized macrocycles contain-ing the less reactive triethoxysilyl groups.

First we accomplished a two-stage synthesis of *p-tert*-butylthiacalix[4]arenes substituted at the lower bearing at the lower rim four 2-oxo-2-[3-(triethoxy-silyl)propylamino]ethoxy groups. At the first stage, three isomeric acids **1**–**3** were converted into the corresponding chlorides by boiling in SOCl₂. At the second stage, 3-(triethoxysilyl)propan-1-amine was acylated with acid **1**–**3** chlorides in diethyl ether to obtain in yields of 51–92% the *cone*, *partial cone*, and *1,3-alternate* stereoisomers of *p-tert*-butylthiacalix[4]-arenes **4**–**6** which have four (triethoxysilyl)propyl-amino]ethoxy substituents at the lower rim (Schemes 1–3).

The composition and structure of *p-tert*-butyl-thiacalix[4]arenes **4**–**6** were confirmed by elemental analysis and physicochemical methods (¹H and ¹³C NMR and IR spectroscopy and mass spectrometry). The conformation of the macrocycle was established by 1D (¹H) and 2D (¹H–¹H NOESY) NMR spectroscopy.

Scheme 2.

The ^{1}H NMR spectra of the *cone* and *1,3-alternate* *p-tert*-butylthiacalix[4]arenes with four triethoxysilyl substituents at the lower rim (compounds **4** and **6**, respectively) contain singlets of the *tert*-butyl groups at 1.10 and 1.21 ppm, respectively. The oxymethylene protons appear as singlets at 4.82 (**4**) and 4.04 ppm (**6**) an the aromatic protons, as singlets at 7.32 (**4**) and 7.54 ppm (**6**). The proton signals of the methylene groups on the amide nitrogen atoms give a multiplet at 3.33–3.38 ppm (**4**) or a doubled triplet at 3.27 ppm, $^2J_{HH} = 14.5$, $^3J_{HH} = 6.5$ Hz (**6**), and the proton signals of the methylene groups on the silicon atom appear as an upfield AA'XX' system at 0.62–0.67 (**4**) and 0.61–0.65 ppm (**6**). The ethoxy methyl protons are registered as triplets at 1.20 (**4**) and 1.21 ppm (**6**), the ethoxy methylene protons, as quartets at 3.79 (**4**) and 3.81 ppm (**6**), and the amide protons, as a broadened singlet at 7.91 ppm (**4**) and a triplet at 7.89 ppm (**6**).

In the ^{1}H NMR spectrum of compound **5** (*partial cone*), the *tert*-butyl proton signals appear as three singlets (1 : 1 : 2) at 1.33, 1.30, and 1.04 ppm, the

oxymethylene protons, as two singlets at 4.96 and 4.42 ppm and AB doublet at 4.84 and 4.38 ppm ($^2J_{HH} = 14.7$ Hz) and aromatic protons, as two singlets at 7.61 and 7.80 ppm and AB doublet at 7.04 and 7.47 ppm ($^4J_{HH} = 2.4$ Hz). The methylene groups on the amide nitrogen atom give multiplets at 3.10–3.52 ppm, and the methylene groups on the silicon atom, as multiplets at 0.37–0.42 and 0.66–0.72 ppm. The ethoxy methyl protons are registered as multiplets in the range 1.17–1.21 ppm, the ethoxy methylene protons, as multiplets at 3.73–3.83 ppm, and the amide protons, as triplets at 7.31, 7.94, and 8.66 ppm.

The successful synthesis of macrocycles **4–6** allowed us to pass to the next stage, specifically, the synthesis of hybrid particles by surface functionalization of silica with the synthesized macrocycles. The surface modification of silica NPs ($d = 12$ nm) was performed in an active medium for which we used acetic acid. Experiments showed that the surface functionalization of silica NPs in acetic acid is complete in 3 h, whereas polycondensation under the

Scheme 3.

same conditions takes 24 h, as was detected by a change in the turbidity of solutions of macrocycles **4**–**6** in acetic acid in the absence of silica NPs and gel formation. Compounds **4**–**6** all gave monodisperse colloid systems **7**–**9**, respectively (Schemes 1–3).

Evidence for the modification of silica with thiacalixarene derivatives was obtained by means of dynamic light scattering, transmission and scanning electron microscopy, simultaneous thermogravimetry with mass spectrometry detection and differential scanning calorimetry, and IR spectroscopy.

Dynamic light scattering was used to determine the hydrodynamic particle diameter. In the case of silica particles **7** modified with a *cone* macrocycle **4**, where all substituents are located on the same side of the macrocyclic platform, colloid nanoparticles with the polydispersity index of 0.10 and the hydrodynamic diameter of 157 nm are formed.

Monodisperse systems **8** and **9** formed by the modification of silica with thiacalix[4]arene derivatives

in the *partial cone* (**5**) and *1,3-alternate* conformations (**6**), where the functional groups are located on both sides of the macrocyclic platform, have the polydispersity indices of 0.20 and 0.10 and the hydrodynamic diameters 169 and 225 nm, respectively. Transmission electron microscopy gave the size of individual organosilicate particles, 16 (*cone*), 15 (*partial cone*), and 13 nm (*1,3-alternate*), in the associates detected by dynamic light scattering. According to scanning electron microscopy data, the modification of silica NPs with *p-tert*-butylthiacalix[4]arenes **4**–**6** does not change the spherical shape of the nanoparticles.

Simultaneous thermogravimetry and differential scanning calorimetry with mass spectrometry detection (TG–DSC–MS) allowed us to establish the temperature dependence of the weight loss rate of silica NPs. The weight loss of 3–6% conformed the modification of silica NPs with the corresponding thiacalixarene.

To study the absorption capacity of the silicate sorbent with respect to low-molecular aromatic

Adsorption capacity of hybrid particles (adsorbents) **7–9** and **10** [21] with respect to nitroaromatic compounds[a]

Adsorbent	2,4,6-Trinitrophenol ($\lambda = 370$ nm)	2,4-Dinitrophenol ($\lambda = 375$ nm)	2,4-Dinitroaniline ($\lambda = 413$ nm)	2-Nitroaniline ($\lambda = 292$ nm)	3-Nitroaniline ($\lambda = 293$ nm)	4-Nitroaniline ($\lambda = 281$ nm)
10	–[b]	35	30	17	–	–
7	–	–	–	–	–	–
8	21	12	–	–	–	10
9	20	28	–	–	–	10

[a] For each compound, the analytical wavelength is given; the figures in the table are the percent recoveries (R, %).
[b] (–) No adsorption takes place.

compounds, we chose the most common pollutants of industrial wastewater: 2,4,6-trinitrophenol, 2,4-dinitrophenol, 2,4-dinitroaniline, and 2-, 3-, and 4-nitroanilines.

The sorption properties of hybrid silica particles **10** modified with *1,3-alternate* thiacalix[4]arene derivatives and containing three benzyl groups and one organosilicon group as an anchor function were studied in [21]. Sorbent **10** adsorbed preferentially nitroanilines (2-nitroaniline and 2,4-dinitroaniline) and 2,4-dinitrophenol, binding the structurally related guest molecules mainly by π–π stacking.

The adsorption capacity of new hybrid thiacalix[4]arene–SiO$_2$ particles **7–9** with respect to nitroanilines and nitrophenols was studied by the same procedure. The recoveries for all the studied aromatic guest compounds are listed in the table. As seen from the table, sorbents **7–9** selectively bound phenol and aniline derivatives. The following recoveries (R, %) were obtained for sorbents **8** and **9**: 2,4,6-trinitrophenol 21 and 20, 2,4-dinitrophenol 12 and 28, and 4-nitroaniline 10 and 10, respectively. Sorbent **7** did not adsorb the chosen guest molecules, probably, because all its substituents are located on the same side of the macrocyclic platform and, therefore, the amide groups cannot take part in binding nitrophenols. By contrast, the amide groups in sorbents **8** and **9** are involved in binding and act as proton acceptors.

Sorbents **7–9** on the basis of silica functionalized with *p-tert*-butylthiacalix[4]arene derivatives having four organosilicon substituents are hydrophobic enough to adsorb nitrophenols and anilines, sorbent **10** on the basis of silica modified with *p-tert*-butylthiacalixarene with one organosilicon and three benzyl substituents.

Thus, we obtained and characterized three stereoisomers (*cone*, *partial cone*, and *1,3-alternate*) of *p-tert*-butylthiacalix[4]arene with four anchor propyltriethoxysilyl substituents at the lower rim. The surface modification of silica nanoparticles ($d = 12$ nm) with the synthesized macrocycles gave hybrid organic–inorganic thiacalix[4]arene–SiO$_2$ structures. The obtained nanostructured adsorbents selectively extracted aromatic nitroaromatic compounds from aqueous solutions. The *partial cone* and *1,3-alternate* thiacalix[4]arene–SiO$_2$ particles showed affinity to nitrophenols.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra in CDCl$_3$ were recorded on a Bruker Avance-400 spectrometer at 400 and 100 MHz, respectively. Elemental analysis was performed on a Perkin Elmer 2400 Series II instrument. The IR spectra were measured on a Perkin Elmer Spectrum 400 FTIR spectrometer. The electrospray ionization (ESI) mass spectra were obtained on a Bruker Daltonik AmazonX instrument. TThe melting points were measured on a Boëtius hot stage. Purity and reaction monitoring was performed by TLC on Silica G (200 μm, UV 254) plates.

Grade 1 deionized water (resistivity >18.0 MΩ cm at 25°C) was obtained from distilled water by purification on a Millipore-Q system.

The particle size in solution was determined by dynamic light scattering on a Malvern Zetasizer Nano ZS particle sizer equipped with a He–Ne laser (4 mV, $\lambda = 633$ nm), scattered light detection angle 173° with automatic control of the measurement position inside the cell). The electronic absorption spectra were registered on a Shimadzu UV-3600 spectrometer, cell thickness 1 cm. The samples were dispersed on a Sonics Vibracell VCX 500 instrument with a step microtip ($d = 3$ mm) immersed into a mixture of

solvent and undissolved material. Simultaneous thermogravimetry and scanning calorimetry (TG–DSC) was performed on a Netzsch Jupiter STA 449 C Jupiter analyzer in 40-μL platinum crucibles with a cap having a 0.5-mm hole at constant heating rates (10 and 4 deg/min; heating range 303–1173 K) in a dynamic argon atmosphere, flow rate 20 mL/min, at atmospheric pressure; sample weight 10–20 mg.

Transmission electron microscopy was performed on a JEOL JEM 100CX II microscope. Before measurements, chloroform solutions ($c = 10^{-4}$ g/mL) were evaporated on a formvar-coated nickel (150 mesh) for 1 h.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{2-oxo-2-[3-(triethoxysilyl)propylamino]ethoxy}-2,8,14,20-tetrathiacalix[4]arenes 4–6 (*general procedure*). A mixture of 0.20 g (2.10×10^{-3} mol) stereoisomer **1–3** of (5,11,17,23-tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]arene-25,26,27,28-tetrayl)tetra(oxyacetic acid) and 5 mL (0.042 mol) of thionyl chloride was refluxed for 2 h. Excess thionyl chloride was removed by distillation and the residue was dried in a vacuum for 2 h using a tube filled with NaOH, after which a solution of 0.20 mL (8.61×10^{-4} mol) of 3-(triethoxysilyl)propan-1-amine and 0.12 mL (8.61×10^{-4} mol) of trimethylamine in diethyl ether was added. The resulting mixture was stirred for 24 h at room temperature, the precipitate that formed was removed by centrifugation, and the organic layer was evaporated and dried in a vacuum.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{2-oxo-2-[3-(triethoxysilyl)propylamino]ethoxy}-2,8,14,20-tetrathiacalix[4]arene (**4, *cone***). Yield 0.26 g (70%), brown powder, mp 220°C. IR spectrum, ν, cm^{-1}: 3290, 2969 (N–H), 1650 (C=O), 1165 (C–O–C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.62–0.67 m (8H, CH$_2$Si), 1.10 s [36H, (CH$_3$)$_3$C], 1.19 t (36H, CH$_2$CH$_3$, $^3J_{HH}$ = 7.0), 1.64–1.74 m (8H, CH$_2$CH$_2$CH$_2$), 3.33–3.38 m (8H, NHCH$_2$), 3.79 q (24H, CH$_2$CH$_3$, $^3J_{HH}$ = 7.0), 4.82 s (8H, OCH$_2$CO), 7.32 s (8H$_{Ar}$), 7.91 t (4H, NH). ^{13}C NMR spectrum, δ$_C$, ppm: 7.9, 18.6, 28.3, 31.2, 42.2, 58.6, 128.1, 134.8, 135.2, 147.5, 158.0, 168.3. Mass spectrum (ESI), *m/z*: 1788.8 [*M* + Na]$^+$. Found, %: C 56.85; H 7.26; N 3.64; S 7.88. C$_{84}$H$_{140}$N$_4$O$_{20}$S$_4$Si$_4$. Calculated, %: C 57.11; H 7.99; N 3.17; S 7.26. *M* 1765.3.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{2-oxo-2-[3-(triethoxysilyl)propylamino]ethoxy}-2,8,14,20-tetrathiacalix[4]arene (**5, *partial cone***).

Yield 0.34 g (92%), light brown powder, mp 118°C. IR spectrum, ν, cm^{-1}: 3290, 2969 (N–H), 1650 (C=O), 1165 (C–O–C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.37–0.42 m (2H, CH$_2$Si), 0.66–0.72 m (6H, CH$_2$Si), 1.04 s [18H, (CH$_3$)$_3$C], 1.17–1.21 m (36H, CH$_2$CH$_3$), 1.30 s [9H, (CH$_3$)$_3$C], 1.33 s [9H, (CH$_3$)$_3$C], 1.72–1.85 m (8H, CH$_2$CH$_2$CH$_2$), 3.10–3.15 m (2H, NHCH$_2$), 3.25–3.34 m (2H, NHCH$_2$), 3.40–3.52 m (4H, NHCH$_2$), 3.73–3.83 m (24H, CH$_2$CH$_3$), 4.38 d (2H, AB system, OCH$_2$CO, $^2J_{HH}$ = 14.7), 4.42 s (2H, OCH$_2$CO), 4.84 d (2H, AB system, OCH$_2$CO, $^2J_{HH}$ = 14.7), 4.96 s (2H, OCH$_2$CO), 7.04 d (2H$_{Ar}$, AB system, $^4J_{HH}$ = 2.4), 7.31 t (1H, NH, $^3J_{HH}$ = 5.8), 7.47 d (2H$_{Ar}$, AB system, $^4J_{HH}$ = 2.4), 7.61 s (2H$_{Ar}$), 7.80 s (2H$_{Ar}$), 7.94 t (2H, NH, $^3J_{HH}$ = 5.9), 8.66 t (1H, NH, $^3J_{HH}$ = 5.7). ^{13}C NMR spectrum, δ$_C$, ppm: 7.84, 8.16, 8.39, 18.5, 23.1, 23.3, 23.6, 31.2, 31.3, 31.4, 34.3, 34.4, 34.5, 41.9, 42.2, 42.3, 58.5, 58.6, 69.8, 74.3, 74.7, 125.8, 125.9, 127.4, 127.7, 133.5, 135.2, 135.3, 136.8, 146.5, 146.8, 147.6, 155.6, 158.4, 159.7, 168.0, 168.4, 168.7. Mass spectrum (ESI), *m/z*: 1788.8 [*M* + Na]$^+$. Found, %: C 56.92; H 7.73; N 3.17; S 7.26. C$_{84}$H$_{140}$N$_4$O$_{20}$S$_4$Si$_4$. Calculated, %: C 57.11; H 7.99; N 3.17; S 7.26. *M* 1765.3.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis{2-oxo-2-[3-(triethoxysilyl)propylamino]ethoxy}-2,8,14,20-tetrathiacalix[4]arene (**6, *1,3-alternate***). Yield 0.24 g (63.5%), light brown powder, mp 125°C. IR spectrum, ν, cm^{-1}: 3210, 2962 (N–H), 1673 (C=O), 1244 (C–O–C), 799 (Si–O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.60–0.66 m (8H, H$_2$Si), 1.21 s [36H, (CH$_3$)$_3$C], 1.21 t (36H, CH$_2$CH$_3$, $^3J_{HH}$ = 7.0), 1.66–1.77 m (8H, CH$_2$CH$_2$CH$_2$), 3.35 d.t (8H, NHCH$_2$, $^3J_{HH}$ = 14.5, 6.5), 3.81 q (24H, CH$_2$CH$_3$, $^3J_{HH}$ = 7.0), 4.04 s (8H, OCH$_2$CO), 7.54 s (8H$_{Ar}$), 7.90 t (4H, NH, $^3J_{HH}$ = 5.6). ^{13}C NMR spectrum, δ$_C$, ppm: 8.4, 18.5, 23.3, 31.3, 34.4, 42.4, 58.6, 71.6, 127.3, 133.8, 147.5, 157.2, 168.2. Mass spectrum (ESI), *m/z*: 1788.8 [*M* + Na]$^+$. Found, %: C 56.87; H 7.52; N 3.58; S 7.61. C$_{84}$H$_{140}$N$_4$O$_{20}$S$_4$Si$_4$. Calculated, %: C 57.11; H 7.99; N 3.17; S 7.26. *M* 1765.3.

Surface modification of silica particles with compounds 4–6 (general procedure). Thiacalixarene **4–6**, 0.04 g, was dispersed by ultrasonication in 5 mL of glacial acetic acid, after which 0.4 g of silica nanopowder [Sigma-Aldrich, 12 nm, specific surface area 175–225 m^2/g (BET)] suspended in 15 mL of glacial acetic acid. The colloid suspension was dispersed in an ultrasonic bath for 1 h, washed with methanol (3×30 mL), and methanol was separated by centrifugation. The resulting wet powder was dispersed by ultrasonication in 5 mL of methanol.

Silica particles modified with compound 4 (7). IR spectrum, ν, cm^{-1}: 3726 (N–H), 1738 (amide I), 1087, 808, 466 (Si–O–Si). Found, %: C 3.44; H 0.48; N 1.40; S 0.57; Si 44.38 (for particles containing 3.74% of thiacalixarene **4** by TG–DSC–MS data). $C_{72}H_{116}N_4O_{20}S_4Si_4$. Calculated, %: C 52.15; H 7.05; N 3.38; O 21.22; S 7.73; Si 8.47.

Silica particles modified with compound 5 (8). IR spectrum, ν, cm^{-1}: 3745 (N–H), 1625 (amide I), 1085, 810 (Si–O–Si). Found, %: C 3.88; H 2.13; N 1.90; S 0.57; Si 57.38 (for particles containing 5.46% of thiacalixarene **5** by TG–DSC–MS data). $C_{72}H_{116}N_4O_{20}S_4Si_4$. Calculated, %: C 52.15; H 7.05; N 3.38; O 21.22; S 7.73; Si 8.47.

Silica particles modified with compound 6 (9). IR spectrum, ν, cm^{-1}: 3521 (N–H), 1651 (amide I), 1087, 808, 466 (Si–O–Si). Found, %: C 4.44; H 1.48; N 2.40; S 1.57; Si 45.38 (for particles containing 6.04% of thiacalixarene **6** by TG–DSC–MS data). $C_{72}H_{116}N_4O_{20}S_4Si_4$. Calculated, %: C 52.15; H 7.05; N 3.38; O 21.22; S 7.73; Si 8.47.

Adsorption of nitroanilines and nitrophenols. Adsorbent: adsorbate weight ratio 1 : 1. Adsorbent sample (*cone* 0.0095 g, *partial cone* 0.0065 g, *1,3-alternate* 0.007 g) was stirred with 5 mL of adsorbate (c 5×10^{-5} M in water) for 24 h at room temperature, and the aqueous solution over the sorbent layer was filtered through a nylon filter (pore size 0.45 μm). The residual concentration of the solute in the filtrate was determined by spectrophotometry measuring absorbance at the characteristic wavelength of the solute (see table).

The saturation time of the tested adsorbents was determined by kinetic measurements in the course of stirring of adsorbate–adsorbent systems at 25±2°C. Samples were taken in 30 min and 1, 2, 3, 4, and 24 h, filtered though a through a nylon filter (pore size 0.45 μm), and electronic absorption spectra of the filtrates were measured. After 24 h, the optical density of the solutions no longer changed, which indicated complete saturation.

The recoveries of adsorbates (R, %) were calculated by Eq. (1). Taking into account that, according to the Bouguer–Lambert–Beer law, $A \sim c$, we can write Eq. (2).

$$R = \frac{(c_0 - c_a)}{c_0} \times 100\%, \qquad (1)$$

$$R = \frac{(A_0 - A_a)}{A_0} \times 100\%. \qquad (2)$$

Here c_0 and c_r (mg/L) are the initial and residual concentration of the adsorbate and A_0 and A_a, optical densities of the solution before and after sorption. Each experiment was performed in triplicate, and the experimental results were averaged.

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