

Hybrid thiacalix[4]arene/SiO₂ nanoparticles: synthesis and selective adsorption of aniline and phenol nitro derivatives*

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Hybrid thiacalix[4]arene/SiO₂ nanoparticles based on a thiacalixarene derivative containing simultaneously three benzyl and one triethoxysilyl groups at the lower rim and silicon dioxide nanopowder were obtained for the first time. The adsorbing properties of the synthesized hybrid organo-inorganic nanoparticles in relation to aromatic guest molecules (2,4,6-trinitrophenol, 2,4-dinitrophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline) were studied in comparison with unmodified silicon dioxide particles.

Key words: thiacalix[4]arene, silicon dioxide, surface modification, adsorption.

One of the pressing problems of modern organic and supramolecular chemistry is the development of new non-toxic materials, which are potentially capable of selective substrate recognition.^{1–10} An active search for components for the preparation of new hybrid materials is being carried out, with the goal of developing highly selective systems for catalysis and separation of substrates.

Chemical modification of the surface of mineral oxides is used to obtain a wide range of hybrid materials, the chemical properties of which are determined by the nature of the compound fixed to the surface with a covalent bond. This type of functionalization makes it possible to vary over a wide range and optimize composition, structure, and properties of the obtained materials.

Special attention is given to hybrid organo-inorganic materials based on organosilicon compounds.^{11–14} Silicon dioxide (SiO₂) is interesting as an inorganic component of hybrid materials due to low toxicity, high mechanical and thermal stability.

Among the many macrocyclic objects of supramolecular chemistry, thiacalixarenes take a special place due to their ability to selective complexation, transfer, catalysis,

and the possibility of acting as building blocks for the synthesis of supramolecular architecture.^{14–16} Thiacalix[4]arenes are unique due to the opportunity of obtaining the starting macrocycles by one-step synthesis; the possibility of modifying the upper and lower rims and forming systems with several binding centers; the existence of several configurations capable of fixing a required spatial orientation of binding centers; and the ability to incorporate small molecules in their molecular cavities through hydrophobic interactions, leading to the formation of host–guest type complexes.

However, the applications of thiacalixarenes for the modification of mineral oxide surfaces virtually is not studied. The combination of the properties of nanosized SiO₂ particles and the complexation ability of thiacalixarenes can lead to the development of new materials based on supramolecular systems, which possess specific functions. Thus, silicon dioxide containing hydroxy groups on the surface on its own will adsorb predominantly substrates in which the dominant influence is caused by hydrophilic groups. The introduction of hydrophobic endoreceptors onto the surface of a SiO₂ particle should cardinaly change the adsorbing properties.

The goal of the present work is to develop exoreceptor hybrid materials based on thiacalix[4]arene monoorganosilicon derivative and SiO₂ nanoparticles as the inorganic component, as well as to study the adsorbing properties of

* Based on the Materials of the XIII Andrianov Conference "Organosilicon Compounds: Synthesis, Properties, and Application" (June 28–July 1, 2015, Moscow, Russia).

the obtained materials to the series of aniline and phenol nitro derivatives.

Results and Discussion

Due to the development of the chemistry of macrocyclic compounds, at present, a variety of supramolecular endoreceptors for identification of a wide range of guest molecules has been developed. The possibility of obtaining exoreceptor colloidal structures on their basis, which would combine the advantages of macrocyclic compounds with practically useful properties of inorganic materials, has been attracting more attention of researchers in the last decade. The synthesis of hybrid nanoparticles functionalized with macrocyclic fragments makes it possible to create highly selective fillers for chromatographic, pervaporation, catalytic systems, as well as microfiltration systems. The preparation of such hybrid materials is performed in two subsequent steps:

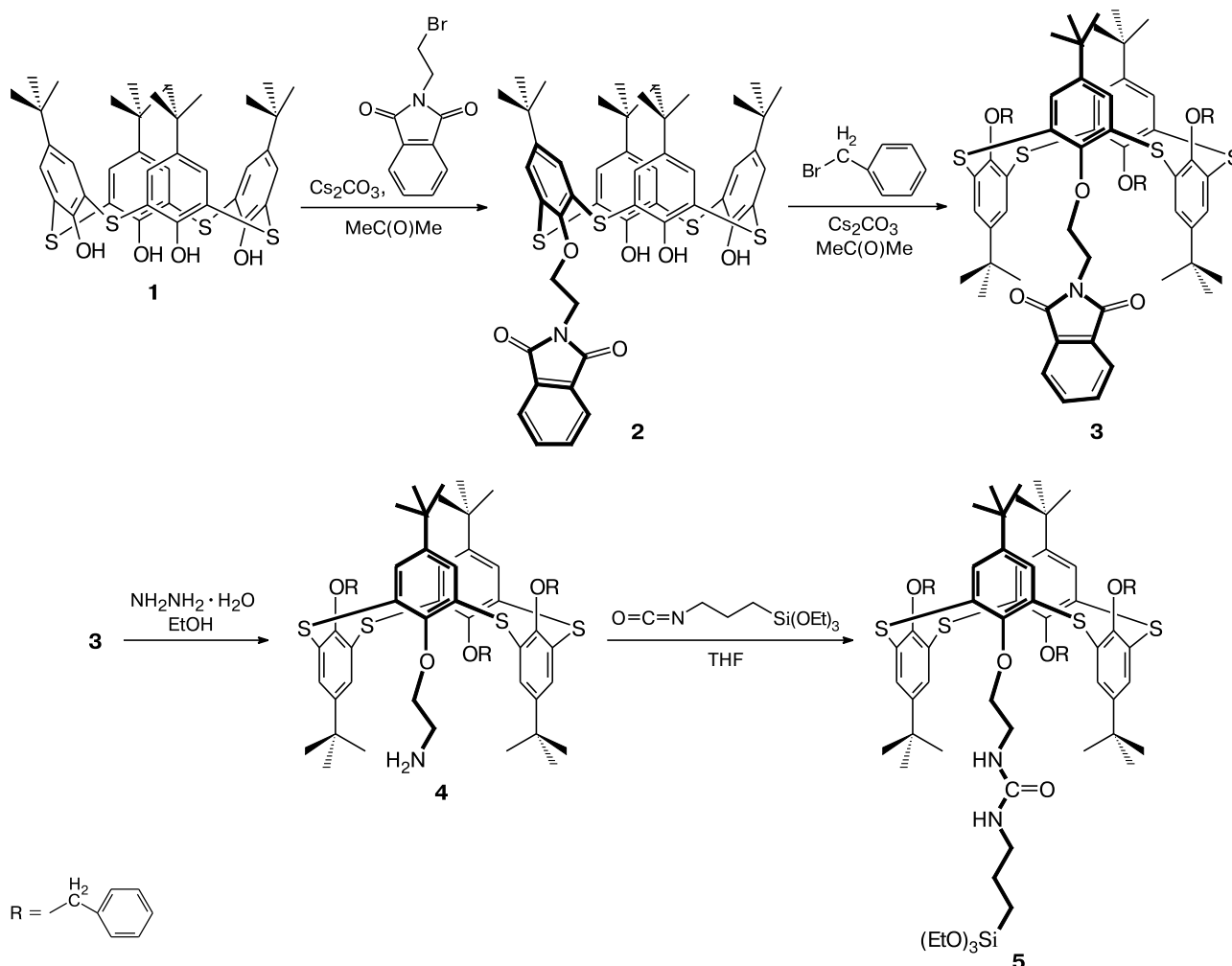
1) the synthesis of differently substituted *p-tert*-butylthiacalix[4]arene containing a structural fragment at the

lower rim, which acts as an anchor (a γ -ureidopropyltriethoxysilyl fragment) and allows to "sew" this macrocycle to the substrate;

2) the chemical modification of silica nanoparticles with differently substituted *p-tert*-butylthiacalix[4]arene containing a γ -ureidopropyltriethoxysilyl fragment at the lower rim.

The synthesis of a differently substituted *p-tert*-butylthiacalix[4]arene derivative containing a γ -ureidopropyltriethoxysilyl fragment at the lower rim, was carried out in four steps (Scheme 1). In the first step, by alkylation of *p-tert*-butylthiacalix[4]arene (**1**) with bromoethylphthalimide in the presence of cesium carbonate monophthalimide **2** was obtained (see Ref. 17). In the second and third steps the alkylation of compound **2** with benzyl bromide¹⁸ in the presence of cesium carbonate and the subsequent hydrazinolysis lead to the formation of monoamine **4**. For the preparation of differently substituted thiacalixarene **5**, during the last step the reaction of monoamine **4** and 3-(triethoxysilyl)propyl isocyanate in dry THF was carried out. The structure of the new deriva-

Scheme 1



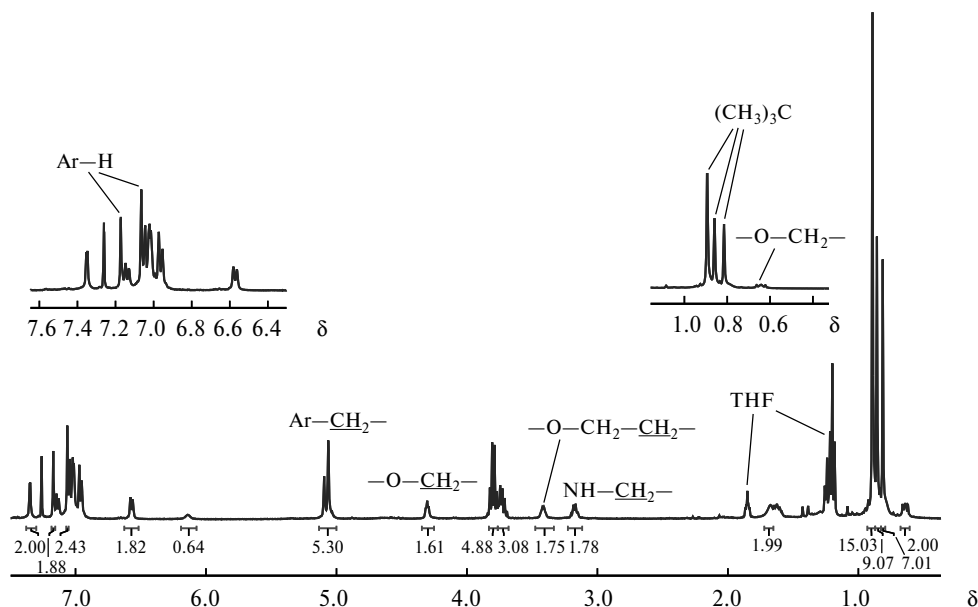


Fig. 1. ^1H NMR spectrum of compound **5**.

tive of thiacalixarene **5** was characterized by NMR and IR spectroscopy, mass spectrometry, and its composition was confirmed by elemental analysis.

In the ^1H NMR spectrum of compound **5** (Fig. 1) the signals of the *tert*-butyl and oxymethylene protons of benzyl fragments are as three (δ 0.89, 0.85, 0.81) and two singlets (δ 5.06 and 5.09), respectively. The signals of the ethoxysilyl fragment protons appear as a multiplet at δ 0.64. The signals of aromatic protons of macrocycle **5** are presented as two singlets (δ 7.06 and 7.09) and two doublets (δ 6.57 and 7.35). The signals of amide protons are presented as a multiplet at δ 6.14. The chemical shifts, the integrated intensity, and splitting patterns of proton signals in the ^1H NMR spectrum of compound **5** are in good agreement with the suggested structure and conformation (*1,3*-alternate) of *p-tert*-butylthiacalix[4]arene **5**. As an example, Fig. 2 shows a MALDI mass spectrum of differently substituted at the lower rim *p-tert*-butylthiacalix[4]arene **5** ($M(\text{C}_{73}\text{H}_{92}\text{N}_2\text{O}_8\text{S}_4\text{Si}) = 1280.3$), where peaks of molecular ions (m/z 1281.3 [$\text{M} + \text{H}$] $^+$, m/z 1303.5 [$\text{M} + \text{Na}$] $^+$, and m/z 1319.5 [$\text{M} + \text{K}$] $^+$) can be observed.

The obtained macrocycle **5** is in the *1,3*-alternate conformation, which was confirmed by 2D NOESY ^1H – ^1H NMR spectroscopy data: cross-peaks between protons of *tert*-butyl and phenyl, aryl and oxymethylene groups are present.

For the preparation of hybrid organo-inorganic particles, commercially available SiO_2 nanopowder with particle diameter 12 nm was chosen as the substrate for chemical modification. Due to the presence of one anchor function in the structure of synthesized thiacalixarene **5**, it can be expected that modification of silica will occur according to Scheme 2 with the formation of a monolayer of thiacalixarene on the surface of the particle.

The functionalization of the surface was carried out in an anhydrous acetic acid,¹⁹ which activates the ethoxysilyl group of thiacalixarene **5**. In agreement with work published earlier,²⁰ it is recommended that thiacalixarene **5** is introduced into the reaction mixture in excess in relation to the SiO_2 nanopowder. This is necessary because of the side process of polycondensation of ethoxysilyl groups with the formation of oligo/polyfused products. An excess of macrocycle **5** allows to form the maximum number of Si–O–Si bonds between the macrocycle and the substrate. After the completion of the modifying process, the hybrid particles **6** were separated from the acetic acid, low-molecular-weight compounds, and macrocyclic products of oligo/polycondensation by repeating the cycle centrifugation-dispersion in acetone three times. The use of acetone provides a high

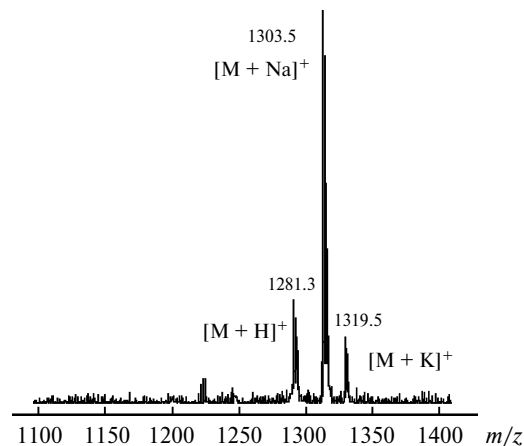
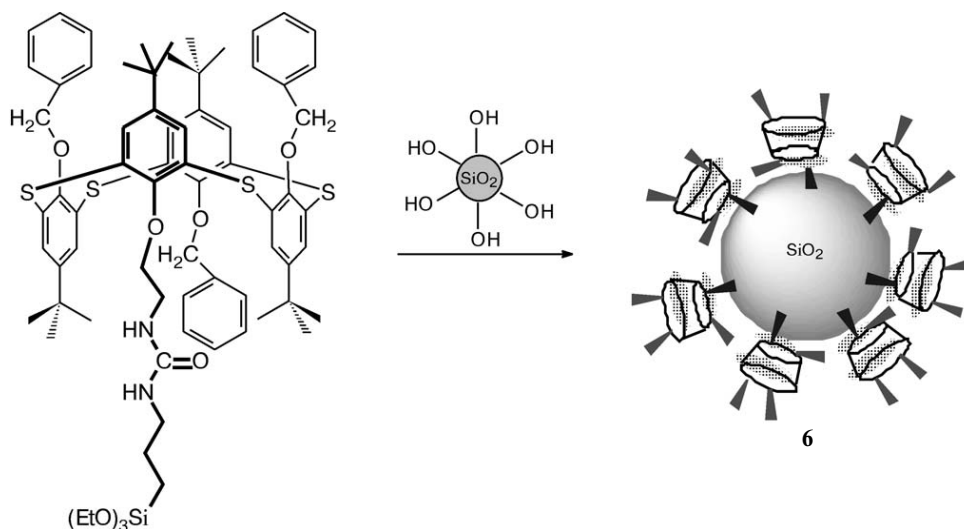


Fig. 2. MALDI-TOF mass spectrum of compound **5**.

Scheme 2



stability of the colloid system to sedimentation and aggregation for 24 h.

A successful carrying out of SiO₂ nanoparticle modification with thiacalixarene **5** of organic substituents is confirmed using the combined thermogravimetry and differential scanning calorimetry (TG/DSC/MS) method (Fig. 3). It was found that the first step on the thermogravimetric curve corresponds to the removal of the water molecules (*m/z* 18) formed in the process of dehydroxylation of the silanol groups on the silicon dioxide surface, which did not react with the triethoxysilyl group of thiacalixarene due to steric factors.²¹ At higher temperatures, a decomposition of the chemically grafted to the surface organic part occurs (5.93%), which is confirmed by CO₂

formation (*m/z* 44), with the multi-step nature of this process visible from the TG curve. At the thermal decomposition of organic compounds, the disintegration occurs at the least strong bond, and the temperature necessary for the thermolysis is inversely proportional to the thermodynamic stability of newly formed free radicals, normally this is the cleavage of the C–O, C–S, C–N bonds. The breaking of the considerably stronger C–C bonds (345.5 kJ mol⁻¹) and C=C bonds (615.5 kJ mol⁻¹) occurs at temperature higher than 400 °C.

The information about the percent content of the organic component allows to calculate the maximum amount of adsorbate, which can be absorbed with this adsorbent: 59.3 mg of calixarene is contained in 1 g of

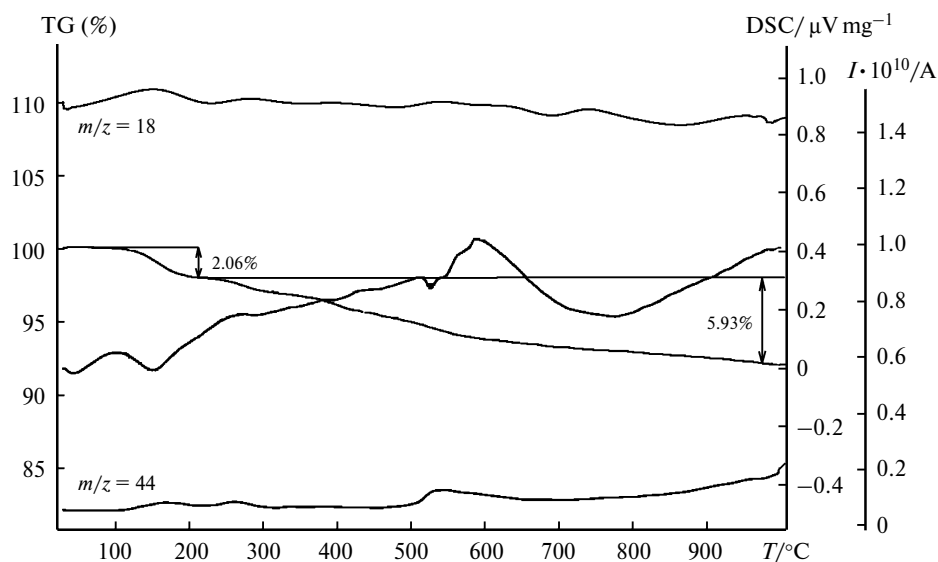


Fig. 3. The results of TG/DSC/MS analysis of particles **6**.

hybrid particles **6**. Apart from that, knowing the mass loss of the organic component, it is possible to calculate the number of thiacalixarene molecules on the surface of the modified particles **6**. According to the characteristics of a commercial SiO_2 sample, the surface area is $175\text{--}225\text{ m}^2\text{ g}^{-1}$ (BET) or $175\text{--}225 \cdot 10^{18}\text{ nm}^2\text{ g}^{-1}$. The amount of calixarene **5** used for modifying SiO_2 particles is 0.033 g ($2.58 \cdot 10^{-5}\text{ mol}$). This amount of calixarenes contains $15.5 \cdot 10^{18}$ molecules ($2.58 \cdot 10^{-5}\text{ mol} \times 6.023 \cdot 10^{23}$). Knowing the surface area of the particles with a 12 nm diameter and the number of molecules, we find that the number of calixarene molecules for 1 nm^2 is $21\text{--}27$ molecules for 100 nm^2 or that the surface of one SiO_2 particle contains $95\text{--}122$ molecules of calixarene.

Analysis of surface topography. The presence of hydroxy groups on the silicon dioxide surface results in an aggregation of particles in polar solvents, which leads to an increase of their size. Surface functionalization of silicon dioxide is one of the ways of preventing this process.²²

The modification of nanoparticles with a 12 nm diameter with thiacalixarene **5** containing hydrophobic benzyl fragments, leads to the formation of a monodispersed colloidal system with hybrid particles of 13 nm in hydrodynamic diameter and a polydispersion index $\text{PDI} = 0.12$ according to the dynamic light scattering data. The latter indicates a monomolecular coating of the functionalized nanoparticles with a layer of thiacalixarene **5**. Analogous size characteristics were obtained using a STEM detector on SEM (Fig. 4). The sample under study was prepared by diluting the colloidal suspension with CHCl_3 to the 10^{-4} g mL^{-1} concentration with subsequent deposition of the obtained solution on the polymer substrate surface. After the removal of the solvent, the morphology of the structures formed on the substrate was studied using the STEM method. It was found that the evaporation of the solvent leads to the formation of 13-nm spherical colloidal structures from the particles.

Adsorption of phenol and aniline nitro derivatives on hybrid particles **6.** One of the most important ecological problems is the purification of water from phenol and aniline nitro derivatives, which are either used as reactants, or are side products of chemical processes, petrochemical production, oil processing, rubber, on paper plants, as well as in the production of pesticides, paints, and plastics.^{23,24} The adsorption of phenol and aniline nitro derivatives on different adsorbents is one of the common approaches for water purification from these contaminants.^{14,15,25,26} Silica unmodified and modified with organic substituents is a widely used adsorbent for binding various organic contaminants. The change of the chemical nature of the silicon dioxide surface by surface chemical reactions leads to a change of the adsorption activity of both polar and non-polar molecules. The hydrophobic properties of the modified surface are explained by either a decrease of the number of structural OH groups, or a considerable weakening

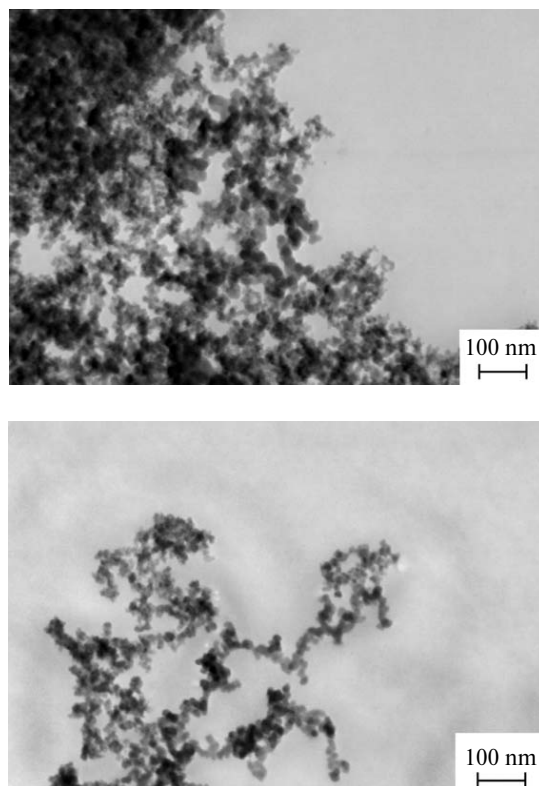


Fig. 4. STEM images of the particles formed during the SiO_2 surface modification with macrocycle **5**.

of the dispersal attractive forces potential.²⁷ In connection with the above, we studied the sorptional ability of the starting silica powder (12 nm) and of that modified with macrocycle **5** containing three benzyl fragments at the lower rim, in relation to a series of aromatic nitro derivatives (2,4,6-trinitrophenol, 2,4-dinitrophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline). In order to do this, a weighed amount of the particles was mixed with a solution of the adsorbate over 24 h at $\sim 20\text{ }^\circ\text{C}$. This time was sufficient for the full saturation of the particles with the sorbate, which was controlled by spectrophotometry ($A_a = \text{const}$). The extraction efficiencies of each aromatic guest are given in Table 1. It can be seen that there is a binding selectivity to phenol and aniline derivatives for the two types of sorbents. The unmodified SiO_2 adsorbs nitrophenols exclusively. Clearly, this is caused by the nature of the silicon dioxide surface. The unmodified SiO_2 powder contains on the surface a large amount of hydroxy groups of different types, which can exhibit either acidic or basic properties.²⁸ From the fact of this selectivity to nitrophenols, which are stronger acids than phenols due to an electron-withdrawing influence of the nitro groups, it can be supposed that the hydroxy groups of SiO_2 in an aqueous solution exhibit mostly a basic character, rather than the acidic one. The binding of the adsorbate with the SiO_2 surface occurs due to the inter-

Table 1. Adsorption ability of SiO₂ and hybrid particles **6** toward a number of aromatic nitro compounds

Adsorbate	Adsorption ability (%)	
	Particles 6	SiO ₂
2,4,6-triNP	—*	28±4
2,4-diNP	35±4	62±4
2-NA	17±3	—*
3-NA	—*	—*
4-NA	—*	—*
2,4-diNA	30±3	—*

Designations: 2,4,6-triNP is the 2,4,6-trinitrophenol, 2,4-diNP is the 2,4-dinitrophenol, 2-NA is the 2-nitroaniline, 3-NA is the 3-nitroaniline, 4-NA is the 4-nitroaniline, 2,4-diNA is the 2,4-dinitroaniline.

* Adsorption on the particles is absent.

molecular hydrogen bonds between the hydroxy groups of the adsorbent and the guest. However, the adsorption ability of unmodified SiO₂ turned out to be considerably lower in relation to 2,4,6-trinitrophenol, which exhibits more acidic properties in comparison with 2,4-dinitrophenol due to the presence of three nitro groups. Clearly, in this case a considerable role is played by the steric blockage of the hydroxy group and, respectively, its accessibility for binding with the particle surface, which is more favorable specifically in the case of 2,4-dinitrophenol.

Chemical modification of SiO₂ with thiacalixarene containing three benzyl fragments at the lower rim imposes a different character on the synthesized particles: hydrophobic rather than hydrophilic, as is the case for the starting silicon dioxide nanopowder. Taking into account only this factor, one can assume that particles **6** should adsorb all the studied guest molecules without exception. However, particles **6** adsorb predominantly aniline nitro derivatives (2-nitroaniline and 2,4-dinitroaniline) and 2,4-dinitrophenol. The adsorption of the latter is possible if free hydroxy groups remain on the surface of modified particle **6**, which did not react with thiacalixarene **5** as a result of steric effects, and 2,4-dinitrophenol is adsorbed (on account of hydrogen bonds) by particles **6** with an efficiency about twice less than in the case of the starting SiO₂, whereas the adsorption of 2,4,6-trinitrophenol on the modified particles is altogether equal to zero. The presence of free silanol groups was confirmed by thermogravimetric analysis: water loss as a result of dehydroxylation of the silanol groups during heating of the sample of particles **6** was equal to 20.6 mg of water per 1 g of modified sorbent. Knowing the surface area of SiO₂ ($175\text{--}225 \cdot 10^{18} \text{ nm}^2 \text{ g}^{-1}$) and the mass of the lost water, it is not difficult to calculate that the number of hydroxy groups per 1 nm² of sorbent surface is about 3–4 groups. The previous calculations on the number of calixarene molecules on the surface of SiO₂ nanoparticles showed that the area corre-

sponding to one thiacalixarene molecule is equal to about 3.7–4.6 nm². Given that the external size of calixarene is about ~1 nm, it is clear that the packing of thiacalixarene on the surface of nanoparticles **6** is not dense. This fact confirms the accessibility of hydroxy groups on the surface for adsorbent sorption.

Of all the aniline nitro derivatives, the efficiency of extraction (*R*, %) of 2,4-dinitroaniline turned out to be almost twice as high as in the case of 2-nitroaniline (30% versus 17%), with 3- and 4-nitroanilines not becoming bound with synthesized hybrid particles. Clearly, apart from the hydrophobic effect, a considerable role is played by the steric factor, which favors the binding of precisely 2-nitroaniline in contrast to other isomers.

The presence of an additional (the second) acceptor nitro group at position 4 of the aniline structure leads to a shift of the electron density from the aromatic system, and the dinitroaniline molecule becomes an acceptor with respect to the donor benzyl fragments of particles **6**, which leads to the formation of a charge-transfer complex and correspondingly causes the extraction of 2,4-dinitroaniline by particles **6**.

Summing up the above, the extraction of nitro derivatives for unmodified SiO₂ particles is possible due to the formation of hydrogen bonds between the sorbate and sorbent molecules. Surface modification with aromatic compounds opens up the possibility of binding hydrophobic molecules using $\pi\text{--}\pi$ stacking and the formation of charge-transfer complexes, with the steric factor playing a considerable role.

In conclusion, we obtained and characterized thiacalix[4]arene/SiO₂ hybrid nanoparticles based on the derivative of thiacalixarene synthesized for the first time and containing at the lower rim simultaneously three benzyl and one triethoxysilyl groups. Using dynamic light scattering and transmission microscopy methods, the formation of nanoparticles with a diameter of 13 nm was confirmed, which indicates a monomolecular coating of the SiO₂ surface. The study of silicon dioxide and hybrid particles based on it as adsorbents of aromatic nitro derivatives (2,4,6-trinitrophenol, 2,4-dinitrophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline) revealed a dependence of adsorption selectivity on the nature of the particles: hydrophilic unmodified particles adsorb on the surface a substrate with pronounced acidic properties due to the hydrogen bonding, whereas silicon dioxide modified by hydrophobic macrocyclic compounds binds the closely related in the nature guest molecules predominantly due to the $\pi\text{--}\pi$ stacking.

Experimental

The ¹H and ¹³C NMR spectra were obtained on a Bruker Avance-400 spectrometer at a working frequency of 400 and 100 MHz, the solvent was CDCl₃. The elemental analysis of the

crystal samples was performed on a Perkin Elmer 2400 Series II instrument. IR spectra were recorded on a Spectrum 400 Fourier-transform spectrometer (Perkin Elmer). Mass spectra were obtained on a Bruker Ultraflex III MALDI-TOF mass spectrometer (in a 4-nitroaniline matrix). Melting points of the compounds were determined on a Boetius heating stage. Additional control of compound purity and reaction progress was carried out using thin-layer chromatography on Silica G plates, 200 μm , UV 254. First degree deionized water with a resistance of $>18.0\ \text{M}\Omega$ at 25 $^{\circ}\text{C}$ was obtained from distilled water on a Millipore-Q system. Particle size in a solution was determined by the dynamic light scattering method on a Zetasizer Nano ZS (Malvern) analyzer of nanoparticle size, equipped with a He-Ne laser (4 mV) with a wavelength of 633 nm, the angle of detection of scattered light was equal to 173 $^{\circ}$ (with an automatic determination of position of measurement inside a cell). The standard error of the measurements of particle hydrodynamic diameter was less than 1% of the average value of six measurements. Electron absorption spectra were recorded on a Shimadzu UV-3600 spectrometer, with a pathway of 1 cm. The dispersion of the samples with ultrasound was carried out on a Sonics Vibracell VCX 500 instrument using an electrode of the stepwise microtype ($d = 3\ \text{mm}$), submerged in a mixture of the solvent and the undissolved compound. Analysis using the method of combined thermogravimetry and differential scanning calorimetry (TG/DSC) was carried out on a STA 449 C Jupiter thermoanalyzer (Netzsch). The analysis was carried out in a 40- μL platinum crucibles with a cover which had one opening 0.5 mm in diameter, at the constant heating rates (10 K min^{-1} and 4 K min^{-1}) in a dynamic argon environment (flow rate 20 mL min^{-1}) at normal atmospheric pressure. Samples with a mass of 10–20 mg were used for analysis. The heating range was 303–1173 K. Transmission electron microscopy (TEM) experiments were carried out on a Merlin analytic scanning autoemission electron microscopy complex (Carl Zeiss) in the STEM regime after evaporation of the solutions in chloroform with a concentration of $10^{-4}\ \text{g mL}^{-1}$ on a nickel grid (150 mesh, covered with formvar) over 1 h. Specialization sheet resolution of the microscope in the STEM regime is 0.6 nm, which allows to measure particle size with an accuracy of 1 nm. Measurements of the particle size was done using the microscope software.

Standard error for the measurements of particle hydrodynamic diameter was $<1\%$ from of the average value of six measurements.

Compounds **1–4** were synthesized according to the procedure described earlier.¹⁷

5,11,17,23-Tetra-tert-butyl-25,26,27-tribenzoxy-28-[2'- γ -ureidopropyltriethoxysilyl]-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate) (5). A mixture of thiacalix[4]arene **4** (0.50 g, 0.48 mmol) and 3-isocyanatopropyltriethoxysilane (0.12 mL, 0.48 mmol) in anhydrous THF (20 mL) was refluxed for 168 h in a round-bottom flask with a reflux condenser. The solvent was evaporated at reduced pressure. The residue was washed with anhydrous *n*-hexane (3 \times 10 mL) and dried *in vacuo* over P_2O_5 . The yield was 0.51 g (76 %). M.p. 125–131. $^1\text{H NMR}$, δ : 0.64 (m, 2 H, CH_2Si); 0.81 (s, 7 H, $(\text{CH}_3)_3\text{C}$); 0.85 (s, 9 H, $(\text{CH}_3)_3\text{C}$); 0.89 (s, 15 H, $(\text{CH}_3)_3\text{C}$); 1.64 (m, 2 H, NHCH_2CH_2); 3.18 (dd, 2 H, NHCH_2CH_2 , $^3J = 4.5\ \text{Hz}$); 3.42 (t, 2 H, OCH_2CH_2 , $^3J = 4.5\ \text{Hz}$); 3.80 (dd, 3 H, OCH_2CH_3 , $^3J = 7.0\ \text{Hz}$); 4.31 (t, 2 H, OCH_2CH_2 , $^3J = 4.5\ \text{Hz}$); 5.06 (s, 4 H, Ph^1CH_2); 5.09 (s, 2 H, Ph^2CH_2); 6.14 (m, 1 H, NHC(O)NH); 7.06, 7.17 (s, 4 H, Ar^1H);

6.57 (d, 2 H, Ar^2H , $^4J = 5.0\ \text{Hz}$); 7.35 (d, 2 H, Ar^2H , $^4J = 5.0\ \text{Hz}$). $^{13}\text{C NMR}$, δ : 7.67, 18.33, 23.53, 30.70, 30.79, 30.81, 33.79, 33.93, 40.47, 43.39, 58.43, 68.41, 71.01, 72.49, 76.72, 77.04, 77.35, 124.89, 126.24, 126.72, 126.94, 127.27, 127.83, 127.92, 128.06, 128.31, 128.52, 129.05, 129.26, 130.19, 137.45, 137.84, 145.49, 146.48, 146.53, 155.98, 156.83, 157.16. $^1\text{H}-^1\text{H NOESY}$: H(33)/H(11a), H(34)/H(11a), H(32)/H(11a), H(29)/H(11h), H(43)/H(3), H(48)/H(5a). MALDI TOF MS, m/z : 1281.3 $[\text{M} + \text{H}]^+$, 1303.5 $[\text{M} + \text{Na}]^+$, 1319.5 $[\text{M} + \text{K}]^+$. IR, ν/cm^{-1} : 1011 (Si—O—C), 1638 (amide I), 1544 (amide II), 3340 (NH). Calculated (%): C, 68.40; H, 7.23; N, 2.19; S, 10.01; Si, 2.19. $\text{C}_{73}\text{H}_{92}\text{N}_2\text{O}_8\text{S}_4\text{Si}$. Found (%): C, 67.21; H, 7.77; N, 3.05; S, 9.98; Si, 2.28.

Thiacalix[4]arene/SiO₂ nanoparticles (6). Silica nanopowder (0.330 g) (Sigma-Aldrich, 12 nm, specific surface area 175–225 $\text{m}^2\ \text{g}^{-1}$ (using the BET method)) in glacial acetic acid (5 mL) was dispersed under ultrasound treatment, then thiacalixarene **5** (0.033 g) was added. After 90 min under ultrasound treatment with a dispersion power of 40% of the maximum, the colloidal suspension was left for 24 h for the condensation of organosilicon thiacalixarene derivative on the surface of the nanoparticles. Then the colloidal suspension was washed with acetone (3 \times 30 mL). Acetone was removed from the particles using centrifugation. The obtained moist powder was dissolved in acetone (5 mL) under ultrasound treatment. The fact of the successful modification of silicon dioxide nanoparticles was confirmed by the presence of characteristic IR bands (see Ref. 13) and NMR spectra. IR, ν/cm^{-1} : 1072, 815, 461 (Si—O—Si); 3422 (NH); 1637 (amide I NH). $^1\text{H NMR}$, δ : 0.87 (m, 2 H, CH_2Si); 1.25 (s, 8 H, $(\text{CH}_3)_3\text{C}$); 3.72 (dd, OCH_2CH_3 , $^3J = 14.0\ \text{Hz}$, $^3J = 7.0\ \text{Hz}$); 5.3 (s, 4 H, Ph^1CH_2); 7.86 (m, Ar^1H); 7.73 (m, Ar^2H). For particles containing 5.93% (according to TG/DSC/MS analysis) of thiacalixarene **5**. Found (%): C, 4.15; H, 0.48; N, 0.17; S, 0.57. $\text{C}_{67}\text{H}_{77}\text{N}_2\text{O}_6\text{S}_4\text{Si}$. Calculated (%): C, 4.05; H, 0.43; N, 0.13; S, 0.57.

Adsorption of aniline and phenol nitro derivatives. The sample **6** (0.005 g) was mixed with adsorbate (5 mL, $5 \cdot 10^{-5}\ \text{mol L}^{-1}$ in water) over 24 h at $\sim 20\ ^{\circ}\text{C}$, then the aqueous solution over the sorbent layer was filtered through a nylon filter (0.45 μm). Residual concentration of the dissolved compound in filtrate was measured using a UV spectrometer (using the absorption maximum at a wavelengths certain for each aromatic compound: 355 (2,4,6-triNP), 282 (2-NA), 280 (3-NA), 271 (4-N), 358 (2,4-diNP) and 413 nm (2,4-diNA).

The time it took for the sorbent to fully saturate was determined by studying the kinetics of sorption during mixing using a magnetic stirrer of the system "sorbate—sorbent" at $25 \pm 2\ ^{\circ}\text{C}$. After different time intervals after the beginning of the sorption process (30, 40 min, 1, 2, 3, 4, 24, 48, 72 h) test samples of the solution were taken, which were then filtered through a filter with a 0.45 μm pore size. Electron absorption spectra were recorded for these aqueous solutions. After 24 h the optical density of the analyte solution remained unchanged, which corresponded to the maximum saturation of the sorbent.

The extraction efficiency of the adsorbate from a solution (R , %) was calculated using the equation

$$R = (c_0 - c_a)/c_0 \cdot 100\%$$

where c_0 and c_a (mg L^{-1}) are the starting and residual concentration of the adsorbate, respectively.

Since according to the Bouguer—Lambert—Beer law $A \sim c$, we can write

$$R = (A_0 - A_a)/A_0 \cdot 100\%,$$

where A_0 and A_a are the optical densities of the solution before and after sorption of the sorbate, respectively. Each adsorption experiment was carried out three times, and the experimental results are the average values.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 13-03-12055 ofi_m).

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Received October 2, 2015;
in revised form January 18, 2016