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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–SiO_2 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–SiO_2 hybrid particles showed affinity to nitrophenols.

Keywords: thiacalix[4]arene, silica, surface modification, adsorption, nitrophenol, nitroaniline

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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 nitrophenols 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 consumption, 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-