Self-assembly of nanosized aggregates based on the photoswitchable *p-tert*-butyl thiacalix[4]arene derivative and Fe^{III}, Cu^{II}, and Ag^I cations*

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New *p-tert*-butyl thiacalix[4]arene tetrasubstituted at the lower rim and containing the azobenzene fragments in the *1,3-alternate* configuration was synthesized. Its receptor properties with respect to d-metal cations (Fe³⁺, Cu²⁺, Ag⁺) were studied using UV spectroscopy and dynamic light scattering (DLS). The ability of *p-tert*-butyl thiacalix[4]arene to molecular recognition of silver cations was estimated by UV spectroscopy. The aggregation of these systems was studied by the dynamic light scattering method.

Key words: self-assembly, thiacalix[4]arenes, molecular recognition, dynamic light scattering (DLS), silver cations, photoswitchers.

The study of conformationally controllable molecules is highlighted in foldamer research, which aims at creating synthetic analogues of biopolymers that can change the size, shape, and spatial arrangement of functional groups under external effects (light, pH).¹ Similar synthetic receptors, which exist in at least two different forms and are reversibly transformed by external effects from one state into another, can be used for storage and processing of information and for the development of molecular switchers, *viz.*, "intellectual" materials, on the basis of these receptors.

Presently, calix[4]arene is widely used as a molecular platform for design of similar molecular structures.^{2,3} Advantages of this compound are in a possibility of its modification by the introduction of various functional groups at both the lower (hydroxy groups) and upper rims of the macrocycle (replacement of the *tert*-butyl group by other fragments) and a possibility to vary the cavity size (for example, due to the introduction of sulfur atoms into the macrocycle).

In this work, we studied routes of the synthesis of *p-tert*butyl calix[4]arene tetrasubstituted at the lower rim and containing azobenzene fragments in the *1,3-alternate* configuration and examined the ability of the synthesized compound to interact with d-metal cations (Fe³⁺, Cu²⁺, Ag⁺) by the dynamic light scattering method.

Experimental

¹H NMR spectra were recorded on a Varian XL-300 spectrometer at a working frequency of 300.0 MHz at 25 °C. Chemical shifts were determined relative to the signals of residual protons

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of the deuterated solvent (CDCl₃, $\delta_{\rm H}$ (CHCl₃) 7.26). IR spectra were measured on a Vector 22 FT-IR spectrometer (Bruker) in the interval of the wave numbers from 400 to 4000 cm⁻¹; resolution 1 cm⁻¹, accumulation 64 scans, detection time 16 s, suspensions in Nujol. Mass spectra (ESI) were obtained on a Bruker Esquire MS mass spectrometer. Elemental analysis of crystalline samples was carried out on a Perkin–Elmer 2400 Series II instrument. Melting points of substances were determined on a Boetius heating stage. Purity of compounds was monitored by boiling and melting points and ¹H NMR spectra. The purity of substances and the reaction course were monitored by thin layer chromatography on Silica G plates, 200 µm, UV 254. The TLC plates were visualized using UV-irradiation with $\lambda = 254$ nm. Electronic spectra were recorded on a Perkin–Elmer Lambda-35 spectrometer, the transmission layer thickness being 1 cm.

N-[(*E*)-4'-(Phenyldiazenyl)phenyl]-2-bromoacetamide. Bromoacetyl bromide (3.98 mL, 45.63 mmol) was added dropwise with stirring for 30 min to 4-aminoazobenzene (10.00 g, 50.70 mmol, pure grade, ZAO Vekton) in benzene (500 mL). The reaction mixture was stirred on reflux for 24 h. After the mixture was cooled, the precipitate was filtered off and recrystallized from EtOH. The yield of the product (orange powder) was 10.46 g (72%), m.p. 168–169 °C. Found (%): C, 52.72; H, 3.69; N, 13.25. $C_{14}H_{12}BrN_3O$. Calculated (%): C, 52.85; H, 3.80; N, 13.21. ¹H NMR, δ : 3.78 (s, 2 H, OCH₂CO); 7.23–7.34 (m, 3 H, Ar(2)H); 7.59 (d, 2 H, Ar(1)H, *J* = 8.8 Hz); 7.62–7.74 (m, 2 H, Ar(2)H); 7.69 (d, 2 H, Ar(1)H, *J* = 8.8 Hz); 9.97 (s, 1 H, NH). IR, v/cm⁻¹: 3260 (NH); 1660 (C=O).

5,11,17,23-Tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]arene-25,26,27,28-tetraol (1), 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-2,8,14,20-tetrathiacalix[4]arene (2), and 5,11,17,23-tetra-*tert*-butyl-25,26, 27,28-tetrakis(carboxymethoxy)-2,8,14,20-tetrathiacalix[4]arene (3) were synthesized according to earlier described procedures.⁴⁻⁶

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5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[2-oxo-2-{4-[(E)-2-phenyl-1-diazenyl]anilino}ethoxy]-2,8,14,20-tetrathiacalix[4]arene 1,3-alternate (4). A mixture of p-tert-butyl thiacalix[4]arene 1 (1.00 g, 1.39 mmol), N-[(E)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide (3.54 g, 11.12 mmol), cesium carbonate (3.62 g, 11.12 mmol), and acetone (60 mL) was refluxed for 12 h. The solvent was distilled off in vacuo. The residue was dissolved in CHCl₃ (40 mL) and washed with a 2 M HCl solution (40 mL). The organic phase was dried with Na_2SO_4 , and the solvent was removed in vacuo. The product was isolated by recrystallization from an acetonitrile-chloroform mixture. An orange powder was obtained in a yield of 1.05 g (45%), m.p. 300-301 °C. Found (%): C, 69.40; H, 5.53; N, 9.57. C₉₆H₉₂N₁₂O₈S₄. Calculated (%): C, 69.04; H, 5.55; N, 10.06. ¹H NMR, δ: 0.73 (s, 36 H, Bu^t); 4.94 (s, 8 H, OCH₂CO); 7.45-7.58 (m, 12 H, Ar(2)H); 7.54 (s, 8 H, ArH); 7.76 (d, 8 H, Ar(1)H, J = 8.8 Hz; 7.91–8.00 (m, 8 H, Ar(2)H); 7.99 (d, 8 H, Ar(1)H, J = 8.8 Hz); 8.72 (s, 4 H, NH). IR, v/cm⁻¹: 3389 (NH nonassociated); 3289 (NH associated); 1706 (C=O). MS, m/z $(I_{\rm rel} (\%))$: 1691.6 $[M + Na]^+$ (100).

Determination of the stability constant and stoichiometry of the complex by UV titration.⁷ A $5 \cdot 10^{-6}$ M solution of silver nitrate (0.03, 0.05, 0.08, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1.10, and 1.20 mL) was added to a solution of receptor 4. The volume was brought to 5 mL with dichloromethane, while the concentration of *p*-tert-butyl thiacalix[4]arene tetrasubstituted with the azobenzene fragments $(3 \cdot 10^{-6} \text{ mol } \text{L}^{-1})$ remained constant. Then the UV spectra of the obtained solutions were recorded. Three independent experiments were carried out for each series. The *t*-Student criterion was used in statistical data processing.

Determination of the stoichiometry by the isomolar series method. To determine the composition of the complex by the isomolar series method, we prepared several solutions in which the ratio of concentrations of silver nitrate and *p-tert*-butyl thiacalix[4]arene **4** tetrasubstituted with the azobenzene fragments ranged from 13 : 2 to 2 : 13. The initial concentration of both the substrate and receptor was $5 \cdot 10^{-6}$ mol L⁻¹. The absorbance of the complex (A_c) at the wavelength 347.6 nm was determined as the difference between the absorbance of the measured solutions (A_0) and solutions of pure *p-tert*-butyl thiacalix[4]arene with a specified concentration (A_H). The maximum in the plot of ($A_0 - A_H$) vs G/(H + G) (G is silver nitrate) indicates the composition of the complex.

Dynamic light scattering method.⁷ Particle sizes were determined on a Zetasizer Nano ZS instrument. The results were processed using the DTS (Dispersion Technology Software 4.20) program. The experimental conditions are as follows: solvent CH₂Cl₂ (HPLC), temperature 2–30 °C, wavelength of a He-Ne laser 633 nm, and power 4 MW. Solutions of the systems under study were prepared by the dissolution of weighed samples of d-metal nitrates $(2.32 \cdot 10^{-4} \text{ mol } \text{L}^{-1})$ in a $5 \cdot 10^{-6} M$ solutions (10 mL) of *p-tert*-butyl thiacalix[4]arene 4 containing the azobenzene groups in CH₂Cl₂ (HPLC), then the solutions were stirred for 3 h, and the measurement was carried out. When determining the particle size in the system containing p-tert-butyl thiacalix[4]arene 4 and AgNO₃ (chemical pure), $Cu(NO_3)_2 \cdot 3H_2O$ (chemical pure), or $Fe(NO_3)_3 \cdot 9H_2O$ (chemical pure), the configuration of this macrocycle was transformed from the trans- into cis-form due to the irradiation of the samples with the UV lamp (UVGL-25; Compact UV Lamp; D/N 95-0021-10) at the wavelengths 365 and 254 nm. The error of the dynamic light scattering method for particle size determination is less than 2%. More than three independent experiments were carried out for each system during the determination of the hydrodynamic particle size. The *t*-Student criterion was used in statistical processing.

Results and Discussion

Two possible approaches to the synthesis of *p*-tertbutyl thiacalix[4]arenes tetrasubstituted at the lower rim in different configurations are described in literature (Scheme 1). The first approach is the primary preparation according to published procedures⁸ of tetraethers based on *p*-tert-butyl thiacalix[4]arene **1** in the configurations cone, partial cone, and 1,3-alternate followed by the functionalization of the substituents at the lower rim of the macrocycle by various fragments.

In the second approach, the one-step synthesis of the tetrasubstituted products in various configurations is carried out by the direct alkylation of the hydroxy groups at the lower rim of thiacalix[4]arene with alkyl halides bearing the carbonyl groups in the presence of alkaline metal carbonates.^{9–11} This case, as the formation of tetraethers based on *p-tert*-butyl thiacalix[4]arene **1**, is characterized by the template effect of the cation.¹²

The study of aggregation of the stereoisomers of *p-tert*butyl thiacalix[4]arenes tetrasubstituted at the lower rim and containing the secondary amide group showed that for the *cone* configuration aggregates are formed upon complex formation predominantly as dimers.¹³ However, *1,3-alternate* turned out to be more interesting conformer for the formation of nanosized structure for the creation of photoswitchable aggregates. In the case of creation of extended photoswitchable aggregates based on the stereoisomer, their size can change upon irradiation. Therefore, we chose the azobenzene moiety as a photoswitchable fragment.

Primarily to study the first synthetic approach, we synthesized tetraester based on *p-tert*-butyl thiacalix[4]arene **2** in the *1,3-alternate* configuration.⁵ Hydrolysis of compound **2** in the presence of LiOH in a THF— H_2O system afforded tetraacid **3** based on *p-tert*-butyl thiacalix[4]arene (Scheme 2).⁶ Then we studied the reaction of acid chloride, which was obtained by the interaction of acid **3** with thionyl chloride, with 4-aminoazobenzene in dichloromethane in the presence of triethylamine.¹³ It turned out that a poorly separable mixture of the partial acylation products is formed.

To accomplish the second approach, we studied the reaction of *p*-tert-butyl thiacalix[4]arene **1** with N-[(*E*)-4'-(phenyldiazenyl)phenyl]-2-bromoacetamide in the presence of cesium carbonate in acetone. Tetrasubstituted product **4** in the *1,3-alternate* conformation was isolated in a yield of 45%.

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Scheme 1



The ability of *p*-tert-butyl thiacalix[4]arene **4** containing the azobenzene fragments in the *1,3-alternate* configuration to change its conformation under UV irradiation at 365 nm due to the *trans*—*cis*-isomerization of the photoswitchable fragments was studied by electronic spectroscopy. It was found that the spectrum of the *trans*-form of the compound exhibited several absorption band near 230 nm, which is characteristic of the macrocyclic ring of *p*-tert-butyl thiacalix[4]arene,¹⁴ and at $\lambda = 350$ and 450 nm corresponding to the $\pi - \pi^*$ and $n - \pi^*$ electron transitions of the azobenzene fragments (Fig. 1). *p*-tert-Butyl thiacalix[4]arene **4** is transformed from



Scheme 2



the *trans*- into *cis*-form under UV irradiation at 365 nm for 20 min. In this case, the charge-transfer band at 350 nm disappears and the absorption intensity at



Fig. 1. UV spectra $(5 \cdot 10^{-6} \text{ mol } L^{-1}, 1 \text{ cm cell})$ of *p*-tert-butyl thiacalix[4]arene **4** in the *trans*- (1) and *cis*-forms (2) in dichloromethane.

450 nm noticeably increases. In addition, substantial changes occur at 200—300 nm, for example, an additional charge-transfer band appears at 257 nm (see Fig. 1). This process is reversible, because already 3 h after macrocycle **4** returns completely to the initial state with the *trans*-configuration.

It was shown by spectrophotometry that the hyperchromic effect was observed upon the interaction of macrocycle **4** in the *trans*-form with silver nitrate in dichloromethane (Fig. 2). For the quantitative estimation of complex formation, we determined the stability constant log $K_{st} = 4.73$ and the 1 : 1 stoichiometry of the formed complexes cation—*p-tert*-butyl thiacalix[4]arene **4** by UV titration with the variation of the substrate concentration (Fig. 3). The changes in the absorbance *A* were detected at the wavelength corresponding to the maximum absorption in the charge-transfer region ($\lambda_{max} = 235.9$ nm), because no substantial changes were observed in the spectra at the wavelengths 350 and 450 nm. The 1 : 1 substrate

Table 1. Dependence of the aggregate size (hydrodynamic diameters of peak 2, 3 mean intensity $-d_2$, d_3 , nm), peak 2, 3 area intensity $(S_2, S_3, \%)^*$, and the polydispersity index (PDI) on the ratio of the reactants: *p-tert*-butyl thiacalix[4]arene 4 (H) and silver nitrate (G)

Ratio G/H	Isomer	d_2/S_2	d_3/S_3	PDI
$5 \cdot 10^{-7} / 5 \cdot 10^{-6}$	trans	_	152.3±112.6/100	0.90±0.32
	cis		257.3±67.6/100	$0.89 {\pm} 0.07$
$5 \cdot 10^{-6} / 5 \cdot 10^{-6}$	trans	63.2±11.9/92.9±13.1	3015.0±1334.2/7.1±13.1	$0.28 {\pm} 0.11$
	cis	63.6±6.9/100	_	$0.34 {\pm} 0.24$
$5 \cdot 10^{-5} / 5 \cdot 10^{-6}$	trans	41.4±3.7/75.2±16.9	289.3±205.3/24.8±16.9	$0.34 {\pm} 0.17$
	cis	42.6±8.5/61.8±42.9	185.3±126.2/38.2±42.9	$0.70 {\pm} 0.32$
$5 \cdot 10^{-4} / 5 \cdot 10^{-6}$	trans	$41.7 \pm 2.8 / 100$	_	$0.20 {\pm} 0.06$
	cis	60.6±2.7/100	_	$0.15 {\pm} 0.03$

* The d_1 and S_1 values were not determined.

to receptor ratio was also confirmed by the isomolar series method (Fig. 4).

It was found by the dynamic light scattering studies of the systems containing p-tert-butyl thiacalix[4]arene **4**



Fig. 2. UV spectra $(3 \cdot 10^{-6} \text{ mol } \text{L}^{-1}, 1\text{-cm cell})$ of *p*-tertbutyl thiacalix[4]arene **4** in the *trans*-form and its 1 : 1 complexes with silver nitrate at different substrate concentrations $(3 \cdot 10^{-7} - 1.2 \cdot 10^{-5} \text{ mol } \text{L}^{-1})$ in dichloromethane.



Fig. 3. Plot of $\log[Ag_nL^+] - \log[L]$ vs $\log[Ag^+]$; y = kx + b, y = 1.06602x + 4.73495.

tetrasubstituted by the azobenzene fragments that this macrocycle existing in both the *trans*- and *cis*-configurations was incapable of self-association to form nanoscaled aggregates. Similar experiments for silver, copper, and iron nitrates also showed the absence of any particles in the range from 0.6 to 6000 nm. However, the introduction of silver nitrate into the system containing *p-tert*butyl thiacalix[4]arene **4** resulted in the formation of supramolecular associates under the conditions analogous to UV titration (Table 1). The change in the cation to *p-tert*-butyl thiacalix[4]arene ratio exerts an effect on both the shape of the UV spectra and the size of formed particles (see Table 1). It should be mentioned that the transition from the *trans*- to *cis*-isomer of compound **4** in the presence of inorganic salts occurs irreversibly.

It was shown by dynamic light scattering that supramolecular aggregates, whose size changed with an increase in the silver nitrate concentration, were formed during UV titration. In these nanoscaled particles the cation to



Fig. 4. Job plot for the complex formation of *p*-tert-butyl thiacalix[4]arene (H) **4** and silver nitrate (G); A_0 is the observed optical absorption; A_H is the absorbance of solutions of pure *p*-tert-butyl thiacalix[4]arene **4** with the specified concentration.

<i>T</i> /°C	Isomer	d_1/S_1	d_2/S_2	PDI
2*	trans	_	65.8±4.1/99.6±0.7	0.24 ± 0.02
	cis	9.7±1.5/6.1±1.6	66.5±1.5/93.9±1.6	$0.24{\pm}0.02$
5	trans	11.1±3.2/2.3±3.9	64.8±7.5/97.7±3.9	$0.24{\pm}0.01$
	cis	$10.2\pm 2.1/6.1\pm 1.9$	68.1±0.9/93.9±1.9	0.24 ± 0.003
10	trans	$10.3 \pm 4.5 / 3.0 \pm 3.5$	65.9±4.4/97.0±3.5	$0.24{\pm}0.02$
	cis	—	68.9±1.6/100	$0.20 {\pm} 0.01$
15	trans	_	$71.9 \pm 1.9 / 100$	$0.24{\pm}0.01$
	cis	_	65.8±16.6/100	0.19 ± 0.18
20	trans	—	64.7±6.8/100	0.21 ± 0.07
	cis	_	64.6±7.5/100	$0.20 {\pm} 0.05$
25	trans	_	54.7±2.1/100	$0.08 {\pm} 0.01$
	cis	_	52.9±1.4/100	$0.10 {\pm} 0.03$
30	trans	_	53.7±3.3/100	$0.09 {\pm} 0.02$
	cis	_	50.1±1.9/100	$0.17 {\pm} 0.02$

Table 2. Temperature dependence of the aggregate size (hydrodynamic diameters of peak 1, 2 mean intensity $-d_1$, d_2 , nm), peak 1, 2 area intensity $(S_1, S_2, \%)^*$ and the polydispersity index (PDI) of the *p-tert*-butyl thiacalix[4]arene 4 (H)-silver nitrate (G) (1:1) system

* The d_3/S_3 values are 5360.0±127.1/0.4±0.7, and they were not determined at other temperatures.

p-tert-butyl thiacalix[4]arene ratio determined by the methods of UV titration and isomolar series is 1:1. The linear dependence (see Fig. 3) demonstrates that the cation to *p-tert*-butyl thiacalix[4]arene ratio remains constant for the aggregates with different sizes. The values of mean hydrodynamic diameters, *i.e.*, sizes of solvated particles that exist in the Brownian motion state, polydispersity indices (estimation of the distribution width for the system), and surface areas of the maxima (estimation of the distribution width in intensity units for one type of particles) are given in Table 1. The obtained data indicate that the substantial difference in the hydrodynamic diameters between the aggregates formed by the *cis*- and *trans*-isomers of *p*-*tert*-butyl thiacalix[4]arene **4** and silver cations is observed when the substrate concentration is $5 \cdot 10^{-7}$ and $5 \cdot 10^{-4}$ mol L⁻¹, respectively. However, for the system with the cation to *p*-tert-butyl thiacalix[4]arene 4 ratio equal to 1:10 the polydispersity index is 0.9, which indicates that the associates are unstable under these conditions. Raising the concentration the silver cations, one can control the size of the supramolecular aggregates formed by two photoswitchable cis- and trans-isomers of *p*-tert-butyl calix[4]arene. It was also shown that, on going from the *trans*- to *cis*-isomer, the temperature change from 2 to 30 °C exerts no effect on the size of aggregates consisting of *p*-tert-butyl thiacalix[4]arene **4** molecules and silver cations (Table 2). However, it turned out that the aggregates formed by *p-tert*-butyl thiacalix-[4] arene tetrasubstituted by the azobenzene fragments with the silver cations exhibit the general dependence of decreasing the hydrodynamic particle size from 65 to 50 nm with the temperature increase from 20 to 30 °C (see Table 2).

It is interesting that the change in the substrate nature substantially affects both the shape of the electronic spec-

tra and the ability of the cis- and trans-isomers of p-tertbutyl thiacalix[4]arene 4 to form nanoscaled aggregates. The addition of copper nitrate to the system, as in the case with the silver cations, induces changes in the UV spectra due to the interaction of this substrate with the macrocycle (Fig. 5). However, no supramolecular selfassociates are formed under these conditions. The absence of nanosized aggregates was established under UV irradiation with the wavelength 365 nm, which is related to the fact that the *trans*-configuration of macrocycle 4 cannot change (see Fig. 5). The transformation of *p-tert*butyl thiacalix[4]arene 4 from the *trans*- into *cis*-form in the presence of copper nitrate can take place upon irradiation with the wavelength 254 nm. Under these conditions, *p-tert*-butyl thiacalix[4]arene **4** only in the *cis*-form can form supramolecular associates with copper nitrate (Table 3). Substantial changes in the sizes of the particles formed by two isomers of macrocycle 4 are observed in the presence of iron nitrate, and the aggregates 62.5 nm in size correspond to the trans-isomer, whereas the cisisomer is characterized by a size of 146.1 nm.

However, unlike the system containing silver nitrate along with *p-tert*-butyl thiacalix[4]arene **4**, the size of supramolecular associates depends on the wavelength of the UV radiation (see Table 3). The UV spectrum of the system consisting of compound **4** and iron nitrate and subjected to the radiation with $\lambda = 254$ nm is similar to that of the *cis*-isomer, whereas in the case of silver nitrate the spectrum is similar to that of the *trans*-form (see Fig. 5).

Thus, both the size of supramolecular aggregates and the ability of photoswitchable thiacalix[4]arene **4** to change its shape on going from the *trans*- to *cis*-isomer can be purposefully controlled by raising the concentration of metal cations, varying their nature, or changing the UV radiation wavelength (254 or 365 nm).

Table 3. Size of aggregates (hydrodynamic diameter of peak 1, 2 mean intensity $-d_1$, d_2 , nm) and peak 1, 2 area intensity $(S_1, S_2, \%)$ for associates of *p-tert*-butyl thiacalix[4]arene **4** (5 · 10⁻⁶ mol L⁻¹) in the *1,3-alternate* configuration with cations of various metals (5 · 10⁻⁴ mol L⁻¹), polydispersity index (PDI)

Cation	Isomer	λ/nm	d_1/S_1	d_2/S_2	PDI
Fe ³⁺	trans	_	65.2±10.8/100	_	0.90±0.11
	cis	365	146.1±48.8/89.7±11.3	4705.0±647.6/12.1±11.3	$0.27 {\pm} 0.06$
		254	125.7±21.0/94.6±4.0	4770.0±578.9/5.4±4.0	$0.19 {\pm} 0.05$
Cu ²⁺	trans	_	_		_
	cis	365	_	_	_
		254	187.9±59.9/85.6±13.5	3730.0±535.8/14.4±13.5	$0.34 {\pm} 0.16$
Ag^+	trans	_	41.7±2.8/100		$0.20 {\pm} 0.06$
	cis	365	60.6±2.7/100	_	$0.15 {\pm} 0.03$
		254	61.1±5.4/100	_	$0.16 {\pm} 0.02$



Fig. 5. UV spectra $(5 \cdot 10^{-6} \text{ mol } \text{L}^{-1}, 1 \text{-cm cell})$ of *p-tert*-butyl thiacalix[4]arene **4** in the *cis*- and *trans*-forms in the presence of silver (*a*), copper (*b*), and iron (*c*) nitrate in dichloromethane (wavelengths of the UV lamp at with the systems were irradiated are given in parentheses).

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