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Nitrothiacalixarenes with alkyl groups at the lower rim: design, synthesis and aggregation behaviour at the air–water interface and in solution

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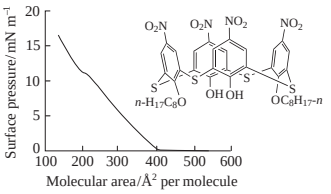
Di-*n*-octylated tetranitrothiacalix[4]arene, a new multidipolar D-π-A chromophore has been synthesized and the dependence of its aggregation in solution and at the air–water interface on the concentration of solution and spreading solvent has been evaluated.



A relevant field of modern materials science is the investigation of nonlinear optical properties of noncentrosymmetric structures, which can be used for the storage of holographic memory, signal amplification, as well as the protection of materials against powerful irradiation. The materials based on organic chromophores, which exhibit these properties, are superior to inorganic materials in higher hyperpolarizability and facile modification. However, their remarkable drawback is relatively low photochemical stability, as well as the ability to form centrosymmetric associates, which reduce the magnitude of the dipole moment.[1] One of the possible routes towards the increase in the stability of chromophores and amplification of nonlinear optical effect is the employment of macrocycles such as calixarenes, whose structures allow one to introduce a diverse number of chromophoric fragments at appropriate orientation.[2,3] As exemplified by calixarenes containing nitro and azo fragments, an increase in the hyperpolarizability coefficient as compared to analogous phenol derivatives was predicted by theoretical calculations and experimentally demonstrated.[4–6]

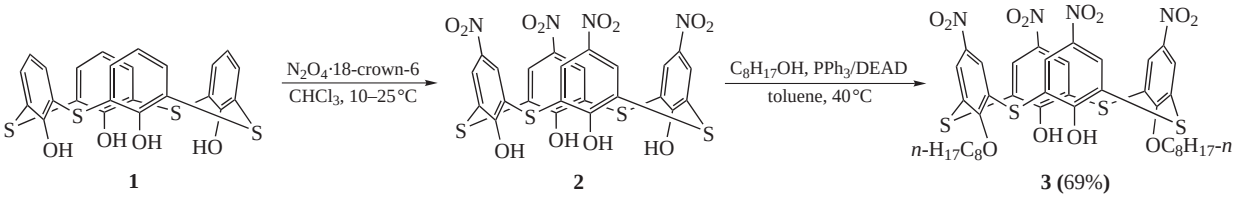
In spite of evident advantages of calixarene scaffold (relatively rigid framework of the molecule, broad opportunities towards regio-, stereo-, and iteroselective functionalization),[7–11] the retention of stereoisomeric form of the macrocycle and the design of ordered films on their basis with a uniaxial orientation of dipoles of molecules is still topical. It is known that one of the factors affecting the stability of stereoisomeric form of macrocycle is the competition between polar groups for the formation of hydrogen bonds.[12] For this reason, the controlled formation of highly organized ultrathin Langmuir films of thiacalixarenes with the given orientation of chromophoric fragments relative to the solid substrate may provide both an increase in thermal stability of multidipolar systems and elimination of the demand to apply an additional electric field (in contrast with corona poled films of chromophore-containing oligomers and polymers)[13,14] during the study of nonlinear optical activity of macrocyclic chromophores.[15,16]

We have recently shown that thiacalix[4]arenes bearing hydroneutral nitrile and hydrophilic crown-ether fragments[17,18] can form organized Langmuir monolayers. In addition, there are examples of the formation of Langmuir monolayers of tetranitrocalix[4]arenes with various alkyl fragments on the lower rim.[19] The aim of this work was to synthesize new macrocyclic chromophore based on nitrothiacalix[4]arene in cone configuration and to optimize the conditions of ultrathin film formation with preorganized macrocycles *via* Langmuir monolayer method.

To synthesize the target product, the sequence of transformations was accomplished, which involves the functionalization of upper and lower rims of thiacalix[4]arene **1** under the conditions of electrophilic aromatic substitution and the Mitsunobu reaction, respectively (Scheme 1).† Due to hydrolytic instability of

† ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Mass spectra were recorded on Bruker Ultraflex III TOF/TOF (MALDI, *p*-nitroaniline matrix) and Amazon X (ESI, DMF solvent) mass spectrometers. IR spectra were acquired on a Bruker Vector-22 IR Fourier spectrometer in KBr pellet. Thiacalixarenes **1** and **2** were synthesized as reported.[20,21]

25,27-Dihydroxy-26,28-dioctyloxy-5,11,17,23-tetranitro-2,8,14,20-tetrathiacalix[4]arene **3**. Triphenylphosphine (0.427 g, 1.630 mmol) and octan-1-ol (1.20 ml, 7.400 mmol) were added in one portion to the solution of compound **2** (0.500 g, 0.740 mmol) in toluene (120 ml), and then diethyl azodicarboxylate (0.250 ml, 1.630 mmol) was added dropwise at room temperature; the mixture was stirred at 40 °C for 40 h. After removal of solvent, the residue was washed with ethanol and the target product was isolated as a yellow powder, yield 0.460 g (69%), mp 199 °C (decomp.).



Scheme 1

distally disubstituted thiacalixarenes[18] in alkaline medium and weak reactivity of the produced phenolate anion of thiacalixarene bearing acceptor substituents on the upper rim upon nucleophilic substitution, alkylation of nitrocalixarene **2** was carried out under Mitsunobu conditions. As a result, disubstituted product **3** was obtained in 69% yield.

The final step of this work was the investigation of aggregation behaviour of chromophoric thiacalixarene **3**. Preliminary evaluation of the sizes of molecules of compound **3** by MM+ molecular modelling reveals that the orientation of molecules at the interface is not clear according to the monolayer compression isotherms, because the limiting molecular area at horizontal orientation differs little from that at the vertical orientation (86.2 and 89.9 Å^2, respectively) (see Online Supplementary Materials).

To form monolayer, compound **3** (150 μl of 0.1 mM solution) was spread onto the water surface with the area of nearly 240 cm^2. The formation and compression of monolayers were studied by UV-VIS reflection–absorption spectroscopy.[22] In the case of calixarene in monolayer at the air–water interface, bathochromic shift of the absorption band was observed (λ_{max} = 292 nm) (Figure S1) with respect to the chloroform solution (λ_{max} = 274 nm). It indicates the tilted orientation of macrocycle and J-aggregate formation[23] and may also be related to solvatochromism, since the replacement of the solvate shell of calixarene upon addition of 15 vol% methanol resulted in bathochromic shift (3 nm) of the main absorption band in the solution spectrum (Figure S1, inset). Strong tendency of compound **3** towards aggregation is also confirmed by AFM data [Figure 1(*a*)], which were recorded for the films formed by the deposition of the calixarene **3** solution (0.01 mM) in $CHCl_3$–MeOH (85 : 15) onto the gold substrate. In AFM images, a variety of aggregates with the sizes of ~50 nm is observed.

Irreproducibility of compression isotherms (dependence of the surface pressure in monolayer on the area per one molecule of compound **3** on the water subphase) was observed in the case of monolayers formed under the described conditions. Limiting molecular areas were less than 80 Å^2, which proves the impossibility of the formation of a true monolayer in the system and is presumably related to the aggregation of the molecules of **3** in solution, as recorded by dynamic light scattering. With the aim to break the aggregate structure, a 5-fold dilution of calixarene solutions in chloroform (from 0.1 to 0.02 mM) was attempted; however, this resulted in the gradual increase in the aggregate size (from 10 to 100 nm according to the particle size distribution by number) (Table 1).

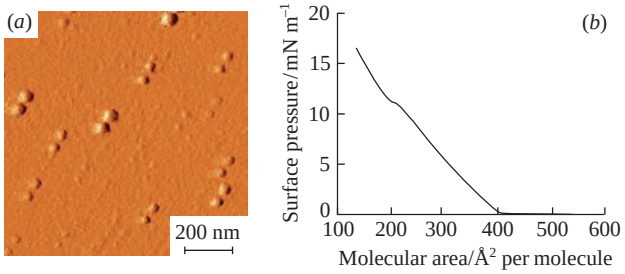


Figure 1 (*a*) AFM image of nitrothiacalix[4]arene **3** aggregates on the gold substrate; (*b*) compression isotherm of compound **3** at the air–water interface [*C* = 0.02 mM in $CHCl_3$–MeOH (85 : 15) solvent].

Table 1 Dependence of the compound **3** particle sizes on solvent, concentration, and time after the preparation of solution.

Solvent	Concentration of **3** / mmol dm^{-3}	Particle size distribution by number / nm (polydispersity index)	
		Initial	After 1 h
$CHCl_3$	0.1	~0.6, 10, 100 (0.191)	~10, 100 (0.307)
	0.02	~50 (0.221)	~100 (0.253)
$CHCl_3$–MeOH (85 : 15)	0.1	~1 (0.290)	~1 (0.311)
	0.02	~1 (0.660)	~1 (0.230)

Assuming that, in nonpolar chloroform, inverse micelles of compound **3** with the orientation of nitro groups inwards of the micelle could be formed, methanol was added to chloroform solution to increase the polarity of the solution and decrease the thermodynamic stability of mentioned aggregates. It was discovered that aggregates disappear already at 15% content of methanol in the mixture (see Table 1). The absence of aggregates in the solution provided true Langmuir monolayer formation in the case of calixarene **3** [Figure 1(*b*)] with the mean molecular area of A_0 ~ 400 Å^2 per molecule and compressibility modulus of C_s^{-1} = 26 mN m^{-1} at the first linear section of the isotherm, which corresponds to the liquid-expanded state of the monolayer.[24] The form of the obtained isotherm and compressibility value, as well as possibility to achieve relatively high surface pressure values (*ca.* 15 mN m^{-1}), give basis to believe that such monolayer may further be transferred onto the solid substrate.[16]

In conclusion, we have synthesized chromophore **3** in *cone* configuration with nitro and alkyl groups using the Mitsunobu reaction and nitration. Thiacalixarene **3** forms aggregates in chloroform, as well as at the air–solid substrate interface. In addition, the possibility of J-aggregate formation upon monolayer compression on the water subphase cannot be excluded (bathochromic shift of the adsorption band). High aggregation ability makes it impossible to prepare reproducible Langmuir monolayers from the chloroform solution of chromophore **3**. However, with the dilution of this solution by methanol (up to 15 vol%), aggregates are not formed in the solution and compression isotherms prove the formation of true monolayers.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2017.07.033.

^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.51 (s, 4H, *m*-H_{Ar}), 8.49 (s, 4H, *m*-H_{Ar}), 4.05 (t, 4H, OCH_2, $^3J_{HH}$ 6.8 Hz), 1.60 (m, 4H, CH_2), 1.43 (m, 4H, CH_2), 1.33–1.20 (m, 12H, CH_2), 1.04 (m, 4H, CH_2), 0.86 (t, 6H, Me, $^3J_{HH}$ 6.8 Hz). ^{13}C NMR (100.57 MHz, $CDCl_3$) δ: 163.8, 161.9, 144.1, 140.4, 132.2, 131.0, 129.4, 129.1, 77.0, 31.7, 29.3, 29.2, 29.2, 25.3, 22.7, 14.2. IR (KBr, ν/cm^{-1}) 3327 (OH), 2926 (C_{Ar}–H), 1521 (NO_2), 1338 (NO_2). MS (ESI), *m*/*z*: 899.4 $[M–H]^-$. Found (%): C, 52.56; H, 4.80; N, 6.47. Calc. for $C_{40}H_{44}N_4O_{12}S_4 \cdot H_2O$ (%): C, 52.27; H, 5.04; N, 6.10.

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