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O-Alkylated p-nitrocalix[4]arenes, synthesis, LB-monolayers and NLO-properties

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Four tetraalkylethers (1a–d, C_{10}, C_{14}, C_{16}, C_{18}) of *p*-tert-butylcalix[4]-arene were prepared in the cone conformation. Ipso-nitration led to the corresponding ethers of *p*-nitrocalix[4]arene (2a–d). The octadecylether 2d formed Langmuir monolayers with solid state packing at the air-water interface and multilayers could be obtained with the Blodgett technique. Determination of the second order polarizability of 2b with the EFISH method gave a value of $\beta_z = 1.4 \cdot 10^{-50}$ Cm^3 V^{-2}.

INTRODUCTION

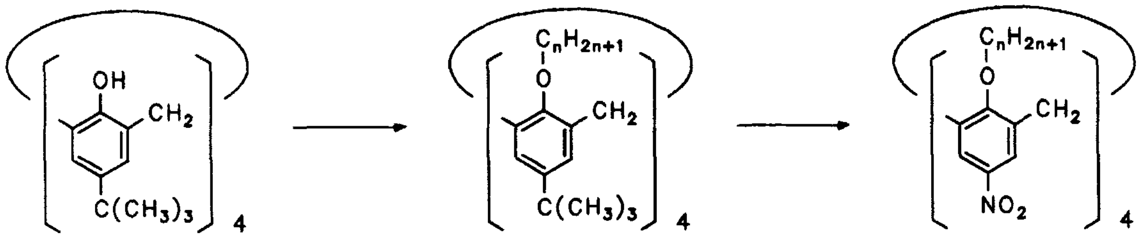
There is a continuously increasing interest in materials showing non-linear optical properties, e.g. for the frequency doubling of laser light. To exhibit second-order NLO properties a material must contain hyperpolarizable moieties (e.g. donor acceptor substituted extended π-electron systems) which are arranged in a non-centrosymmetric fashion. Recently it was reported, that the tetrapropylether of *p*-nitrocalix[4]-arene fixed in the cone-conformation showed a remarkable second oder polarizability ($\beta_z = 1.1 \cdot 10^{-49}$ Cm^3 V^{-2}) and could be oriented in a polymer matrix by strong electric fields, leading to materials for second harmonic generation.[1] The necessary orientation of the molecules can be obtained also by the Langmuir-Blodgett technique.[2] We therefore synthesized tetraether derivatives of *p*-nitrocalix[4]arene with longer O-alkyl chains and studied their spreading behaviour at the air-water interface.

SYNTHESIS

Two pathways may be envisaged for the preparation of compounds **2**, namely O-alkylation of *p*-nitrocalix[4]-arene (which is amenable via the corresponding tetrasulfonated calixarene or by direct nitration of the unsubstituted calix[4]arene) or O-alkylation ot *t*-butylcalix[4]arene followed by ipso-nitration. We have chosen the latter way (Scheme 1), in analogy to the synthesis of the above mentioned O-propyl derivatives.

Alkylation of *t*-butylcalix[4]arene was done at 85 °C in DMF, using sodium hydride as base and the required alkyl bromide, both applied in excess to ensure complete reaction. The pure tetraethers **1** were obtained in 64–70% yield. All compounds were found to be exclusively in the cone-conformation, a necessary prerequisite for the formation of ordered LB-layers as well as for high dipole moments and high β-values. This can be unambiguously deduced from the ^{1}H NMR spectrum showing one singlet each for the aromatic (6.76 ppm) and the *t*-butyl protons (1.06 ppm) and a pair of doublets (4.39 and 3.09 ppm, $^2J = 12.4$ Hz) for the methylene groups (Ar-CH$_2$-Ar) and also one set of signals for the alkyl chains. The chemical shifts of these signals are virtually identical for all four compounds **1a–d**. All these tetraethers show low melting points, increasing slightly from **1a** (70–71 °C) to **1d** (93–94 °C), that is with increasing length of the alkyl residue.

Ipso-nitration of **1a** was readily done under the conditions described by Reinhoudt[3] *et al.*, namely by addition of an excess of 100% HNO$_3$ to a solution of **1a** in CH$_2$Cl$_2$/acetic acid at 0 °C. The tetranitro compound **2a** was obtained in an excellent yield of 89%, and was analytically pure (t.l.c., elemental analysis, ^{1}H NMR) without complicated purifications. Due to the lower solubility of the compounds with longer alkyl chains these conditions could not be applied to **2b–c**. Reactions in suspension or with larger amounts of solvent and reagent (thus keeping its concentration constant) did not give the desired



1 a b c d **2 a–d**

n = 10 14 16 18

product. The best result to date was obtained with 100% HNO_3/conc. H_2SO_4 in $CHCl_3$ at 0 °C. However, the crude product had to be separated and purified by flash-column chromatography, yielding pure **2b** and **2c** in 49% and 36%, respectively. The same reaction conditions led to only 14% yield in the case of **2d**, while a slightly better yield (18%) was obtained with HNO_3 in $CHCl_3$/acetic acid/acetic acid anhydride, conditions which were less successful for **2b, c**. It should be noted that ipso-nitration of compounds **1** is strongly dependent on the appropriate reaction conditions, which have to be evaluated for each individual compound. In principal excellent yields may be possible, if these conditions are found.

Melting points of **2** are similarly low as those of **1**, but they decrease continuously with increasing chain length from **2a** (123–124 °C) to **2d** (90–91 °C). The constitution and purity of compounds **2** were confirmed by t.l.c., elemental analysis,[4] mass and ^1H NMR spectra. Here the main differences in comparison to **1** are the complete disappearance of the *t*-butyl signal and the downfield shift of the singlet for the aromatic protons (7.55 ppm) due to the adjacent nitro group. Smaller downfield shifts (0.1 and 0.3 ppm) are observed for the A- and B-part of the Ar-CH_2-Ar protons, while all other signals remain virtually unchanged.

LANGMUIR-BLODGETT STUDIES

Compounds **2** were studied at various temperatures at the air-water interface with the Langmuir technique. Typical surface pressure-area diagrams (isotherms) are shown in Fig 1. At room temperature only **2d** forms a monolayer with solid state packing. Collapse pressure (49 mN/m) and limiting area per molecule (107 Å^2, extrapolated to zero pressure) correspond favourably to values found for *p*-octadecylcalix[4]arene (50 mN/m, 103 Å^2) on aqueous sodium hydroxide,[5] indicating that in both cases the arrangement of the molecules is mainly determined by a close packing of the alkyl residues. Figure 1b shows that the limiting area per molecule decreases with decreasing temperature whereas the collapse pressure remains nearly constant. The π/A isotherm at 5 °C may be interpreted in terms of further condensed phases in addition to the solid analogous phase formed at higher pressures (limiting area per molecule 93 Å^2 extrapolated to zero pressure). A similar behaviour with virtually the same limiting area and collapse pressure is found for **2c** at 5 °C (Fig. 1*a*). In this case a drastic decrease of the collapse pressure is observed for increasing temperature and the behaviour at 20 °C may be described as the formation of a liquid analogous phase. Further decrease in the length of the alkyl ether chain in compounds **2b** and **2a** leads to the complete disappearance of the solid analogous phase at all temperatures.

Thus, deposition of multilayers by the Blodgett technique seems suitable only for **2d**. In a first preliminary experiment 16 LB-layers were transferred to a silicium carrier (at room temperature with a surface pressure held at 25 mN/m). This was sufficient to study the deposition by small angle X-ray diffraction. A Bragg-peak at $2\theta = 2°$ leads to a thickness of 43 Å of the repeating layers, which is more than the estimated length (29 Å) of the stretched calixarene molecule. As expected, deposition of double layers occurs (Y-type), but the alkyl chains (or the whole molecules) in the doublelayers are somewhat declined, thus leading to a thickness lower than 2×29 Å. A partial interpenetration of the alkyl residues in the double layers would be another explanation.

EFISH MEASUREMENTS

The second order polarizability β of molecule **2b** was determined by electric field induced second harmonic generation (EFISH). A static external electric field E_0 induces an effective second order nonlinearity $d = \Gamma E_0$ in a liquid solution leading to frequency-doubling

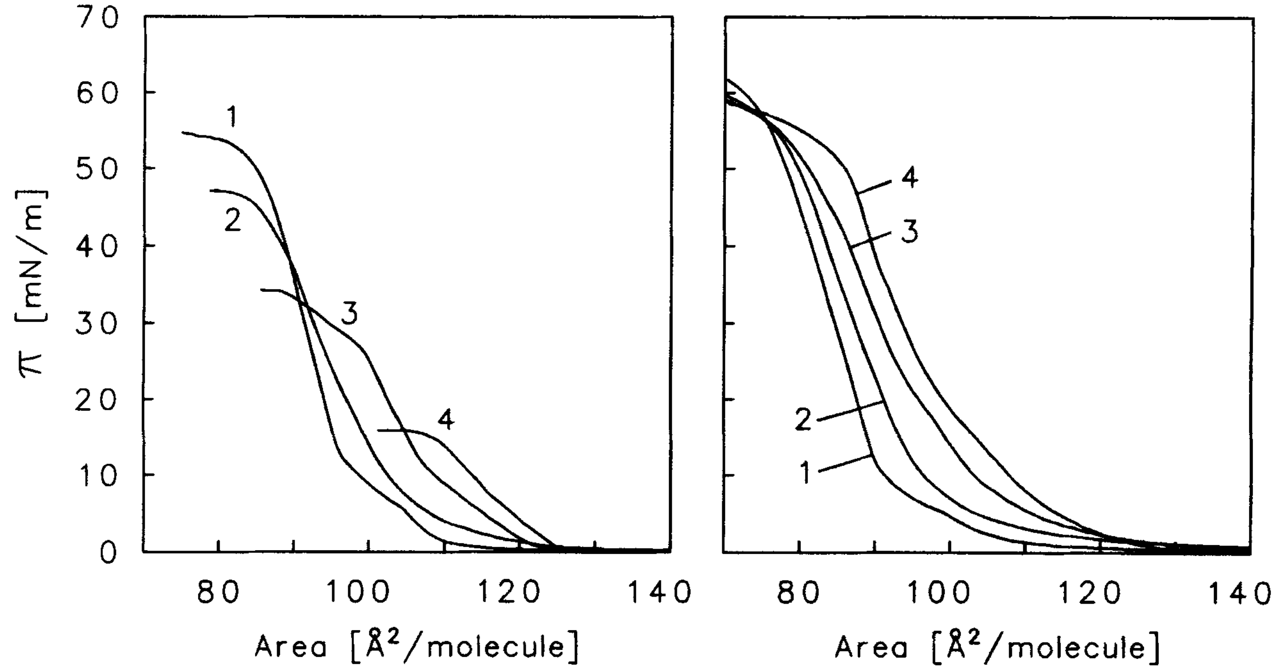


Figure 1 Surface pressure—Area (π/A) isotherms on a water subphase at four different temperatures: **a** (left): compound **2c**, 5 °C (1), 8 °C (2), 12 °C (3), 20 °C (4). **b** (right): compound **2d**, 5 °C (1), 10 °C (2), 15 °C (3), 20 °C (4).

of the pulses of a Nd:YAG laser (1064 nm, TEM_{00}, 63 mJ). A detailed description of the device used in this work was given recently.[6] The nonlinearity of the solution was determined relative to quartz (d_{11} = 0.5 pm/V)[7] for various mass fractions ($w_2 = 0..10^{-2}$) of the solute. From these measurements one obtains the partial molar quantity (PMQ)

$$Z_2^\Gamma = \lim_{w_2 \to 0} \left(\frac{\partial[\varepsilon_0 \Gamma V]}{\partial n_2} \right)_{p,T,n_1} \qquad (1)$$

T is the temperature, p the pressure and V the volume of the phase; n_1 and n_2 are the amounts of solvent (1) and solute (2) and ε_0 the permittivity of free space.

According to the general formalism given by Liptay[8-10] the PMQ Z_2^Γ can be converted into a model molar quantity (MMQ) ζ_2^Γ. The MMQ ζ_2^Γ of the EFISH measurement is related to the scalar product of the dipole μ and the vector part of the second order polarizability tensor $\beta(-2\omega;\omega,\omega)$ of the solute molecules by

$$\zeta_2^\Gamma = N_A L_{2\omega} L_\omega^2 L_0 \left(\frac{\mu \cdot \beta}{5kT} \right). \qquad (2)$$

The components of β are given by $\beta_i = \Sigma_k \beta_{ikk}$. N_A and k are Avogadro's constant and Boltzmann's constant, respectively. $L_\Omega = (\varepsilon_\Omega + 2)/3$ with $\Omega = 0$, ω, 2ω are Lorentz local field factors at the indicated frequencies. In eqn. (2) the dependence of β on the static field $\gamma(-2\omega;\omega,\omega,0)$ is neglected. Furthermore Kleinman symmetry of the tensor β is assumed.

Table 1 Results of EFISH,[a] refractive[b] and dielectric measurements on **2b** in tetrachloromethane. $T = 298$ K

Z_2^Γ	$/10-^{36}$ Cm^4 V$-^3$ mol$-^1$	121 ± 14
ζ_2^Γ	$/10^{-36}$ Cm^4 V^{-3} mol^{-1}	70 ± 15
μ_z	$/10^{-30}$ Cm [D]	47 ± 3 [14 ± 1]
1/3 tr(α)	$/10^{-40}$ CV^{-1} m^2 [Å^3]	164 ± 8 [147 ± 7]
β_z	$/10^{-50}$ CV^{-2} m^3 [10^{-30} esu]	1.4 ± 0.3 [3.8 ± 0.8]

[a] at $\lambda = 1064$ nm.
[b] at $\lambda = 1080$ nm.
Experimental errors correspond to 95% confidence.

The dipole μ and the trace of the first order polarizability α were determined from dielectric, refractive and density measurements applying a similar formalism as described above.[8] Local field corrections were made within the Lorentz model. The results are given in Table 1.

The vector part of the second order polarizability of **2b** is surprisingly low when compared to results for *p*-nitroanisole. β was determined by Cheng *et al.*[11] to be $1.9 \cdot 10^{-50}$ C V^{-2} m^3 [$5.1 \cdot 10^{-30}$ esu] at $\lambda = 1910$ nm. This value can be extrapolated to $2.7 \cdot 10^{-50}$ C V^{-2} m^3 [$7.3 \cdot 10^{-30}$ esu] at $\lambda = 1064$ nm using the two level dispersion expression.[12] Thus β(1064 nm) of **2b** which contains four *p*-nitrophenyl ether subunits appears to be smaller than β(1064 nm) of a single *p*-nitroanisole molecule.

This discrepancy is not completely understood at present. We are aware of at least two factors that lead to a reduction of the effective second order polarizability of **2b**. First it must be taken into account that for calix[4]arenes in the cone conformation the molecular axis of the aromatic subunits is not parallel to the C_4 axis. The angle δ between both axes can be estimated from the dipoles of **2b** and *p*-nitroanisole, $47 \cdot 10^{-30}$ Cm [14 D] and $15 \cdot 10^{-30}$ Cm [4.6 D][11] to be $\delta = 40° \pm 6°$. This reduces the contribution of a *p*-nitrophenyl ether subunit to β of **2b** along the C_4 axis by a factor of about $\cos\delta = 0.77$.

Second, the average conformation of the alkoxy groups in **2b** and *p*-nitroanisole may be different. We made AM1 calculations (MOPAC 6.00)[13,14] for *p*-nitroanisole varying the dihedral angle δ of the methoxy group with respect to the aromatic plane. It was found that β is strongly δ dependent, $\beta(\delta = 0°)$ being almost three times as large as $\beta(\delta = 90°)$. Due to steric hindrance of the long alkoxy chains in **2b** it can be expected that the average dihedral angle δ of the *p*-nitrophenyl ether subunits in **2b** deviates more strongly from 0° as compared to the single *p*-nitroanisole molecule leading to a further reduction of β.

It is well known[15] that second order polarizabilities can be strongly solvent dependent. Therefore the high β value reported by Reinhoudt *et al.*[1] for O-propyl-*p*-nitrocalix[4]arene cannot be compared to our results because neither the solvent nor local field corrections are specified in that work. We will investigate the solvent dependence of β of O-alkyl-*p*-nitrocalix[4]arenes in a subsequent study.

EXPERIMENTAL

General procedure for the synthesis of tetraalkylethers 1

A suspension of 3.0 g (4.05 mmol) *p*-tert-butyl calix[4]-arene and 2.05 g (81 mmol) NaH (95%) in 140 mL DMF was stirred at room temperature for 30 min. The alkylbromide (49 mmol) was added and stirring continued for 4 hours at 85 °C. the formation of a white precipitate started after 1–3 h depending on the alkylbromide. After cooling to 0 °C excess NaH was destroyed by water/methanol, the tetraether filtered by suction and thoroughly washed with water and methanol. The crude product was dissolved in 100–250 mL boiling $CHCl_3$, and the hot solution filtered three to four times through a fresh filter to remove excess alkylbromide, which remains as an oil on the filter. The filtrate was finally concentrated and analytically pure **1** was obtained by precipitation with methanol.

1a White powder, 70%, m.p. 70–71 °C, Rf = 0.35 (petroleum ether/ethyl acetate 4:1); ^{1}H-NMR (200 MHz, $CDCl_3$): δ/ppm: 6.76 (s, 8H, Ar**H**); 4.40 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 3.83 (t, 8H, $^3J = 7.6$ Hz, O**CH$_2$**); 3.10 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 1.9–2.15 (br m, 8H, OCH$_2$**CH$_2$**); 1.1–1.5 (br m, 56H, OCH$_2$CH$_2$(**CH$_2$**)$_7$CH$_3$); 1.07 (s, 36H, C(**CH$_3$**)$_3$); 0.88 (t, 12H, O(CH$_2$)$_9$**CH$_3$**). *Anal.* Calcd. for $C_{84}H_{136}O_4$: C, 83.38; H 11.33. Found: C, 83.35; H, 11.34.

1b White powder, 68%, m.p. 83–84 °C, Rf = 0.43 (petroleum ether/ethyl acetate 4:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ/ppm: 6.76 (s, 8H, Ar**H**); 4.40 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 3.83 (t, 8H, $^3J = 7.6$ Hz, O**CH$_2$**); 3.09 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 1.9–2.15 (br m, 8H, OCH$_2$**CH$_2$**); 1.1–1.5 (br m, 88H, OCH$_2$CH$_2$(**CH$_2$**)$_{11}$CH$_3$); 1.06 (s, 36H, C(**CH$_3$**)$_3$); 0.87 (t, 12H, O(CH$_2$)$_{13}$**CH$_3$**). *Anal.* Calcd. for $C_{100}H_{168}O_4$: C, 83.73; H, 11.81. Found: C, 83.70; H, 12.14.

1c White powder, 67%, m.p. 89–90 °C, Rf = 0.47 (petroleum ether/ethyl acetate 4:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ/ppm: 6.76 (s, 8H, Ar**H**); 4.39 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 3.82 (t, 8H, $^3J = 7.4$ Hz, O**CH$_2$**); 3.08 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 1.9–2.15 (br m, 8H, OCH$_2$**CH$_2$**); 1.1–1.5 (br m, 104H, OCH$_2$CH$_2$(**CH$_2$**)$_{13}$CH$_3$); 1.06 (s, 36H, C(**CH$_3$**)$_3$), 0.87 (t, 12H, O(CH$_2$)$_{15}$**CH$_3$**). *Anal.* Calcd. for $C_{108}H_{184}O_4$: C, 83.87; H, 11.99. Found: C, 83.78; H, 12.42.

1d White powder, 64%, m.p. 93–94 °C; Rf = 0.95 (petroleum ether/ethyl acetate 4:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ/ppm: 6.75 (s, 8H, Ar**H**); 4.38 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 3.82 (t, 8H, $^3J = 7.5$ Hz, O**CH$_2$**); 3.08 (d, 4H, $^2J = 12.4$ Hz, Ar**CH$_2$**Ar); 1.9–2.15 (br m, 8H, OCH$_2$**CH$_2$**); 1.1–1.5 (br m, 120H, OCH$_2$CH$_2$(**CH$_2$**)$_{15}$CH$_3$); 1.05 (s, 36H, C(**CH$_3$**)$_3$); 0.86 (t, 12H, O(CH$_2$)$_{17}$**CH$_3$**). *Anal.* Calcd. for $C_{116}H_{200}O_4$: C, 83.99; H, 12.15. Found: C, 83.72; H, 12.23.

Ipso-nitration of compounds 1

2a The decylether **1a** (0.7 g, 0.58 mmol) was dissolved in a mixture of 45 mL CH_2Cl_2 and 5.9 g acetic acid, the solution cooled to 0 °C and 1.93 mL HNO_3 (100%) were added with vigorous stirring over a period of 90 min. The reaction mixture became black immediately after the first drops had been added. After complete addition the mixture was stirred for a further 30 min with ice cooling, and then at room temperature until the colour had turned to pale-yellow (about 2 h). Water (40 mL) was added, the organic phase was separated, washed twice with 30 mL water and evaporated. The crude residue was washed twice with 30 mL methanol, three times with 40 mL water and dried to give 0.62 g (89%) of **2a** as a white-yellow powder, m.p. 123–124 °C; Rf = 0.25 (petroleum ether/ethyl acetate 6:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm: 7.55 (s, 8H, Ar**H**); 4.48 (d, 4H, $^2J = 14.0$ Hz, Ar**CH$_2$**Ar); 3.95 (t, 8H, $^3J = 7.4$ Hz, O**CH$_2$**); 3.38 (d, 4H, $^2J = 14.0$ Hz, Ar**CH$_2$**Ar); 1.7–1.95 (br m, 8H, OCH$_2$**CH$_2$**); 1.45-1.15 (br m, 56H, (**CH$_2$**)$_7$CH$_3$); 0.86 (t, 12H, $^3J = 6.8$ Hz, O(CH$_2$)$_9$**CH$_3$**).

Anal. Calcd. for $C_{68}H_{100}N_4O_{12}$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.84; H, 8.58; N, 4.54.

2b A solution of the tetradecylether **1b** (0.7 g, 0.49 mmol) in 80 mL $CHCl_3$ was cooled to 0 °C. A cooled mixture of 1.55 mL HNO_3 (100%) and 1.80 mL conc. H_2SO_4 was added with vigorous stirring over a period of 90 min. Again the reaction mixture became black immediately after the first drops had been added. After complete addition the mixture was stirred for a further 30 min with ice cooling, and then at room temperature until the colour had turned to pale-yellow (about 2 h). Water (60 mL) was added, the organic phase was separated, washed three times with 50 mL water, and concentrated to 20 mL. The crude product was precipitated by the addition of methanol (200 mL), dissolved in a small amount of $CHCl_3$ and purified by flash column chromatography (silica gel, 70–230 mesh ASTM, E. Merck, petroleum ether/ethyl acetate 10:1). Finally 333 mg (49%) of a white powder was obtained, m.p. 114–115 °C, Rf = 0.30 (petroleum ether/ethyl acetate 6:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ/ppm: 7.55 (s, 8H, ArH); 4.49 (d, 4H, $^2J = 14.0$ Hz, $ArCH_2Ar$); 3.96 (t, 8H, $^3J = 7.3$ Hz, OCH_2); 3.38 (d, 4H, $^2J = 14.0$ Hz, $ArCH_2Ar$); 1.75–1.95 (br m, 8H, OCH_2CH_2); 1.1–1.5 (br m, 88H, $(CH_2)_{11}CH_3$); 0.86 (t, 12H, $O(CH_2)_{13}CH_3$). *Anal.* Calcd. for $C_{84}H_{132}N_4O_{12}$: C, 72.58; H, 9.57; N, 4.03. Found: C, 72.47; H, 9.64; N, 4.05.

2c A suspension of the hexadecylether **1c** (0.7 g, 0.45 mmol) in 75 mL $CHCl_3$ was treated with 1.4 mL HNO_3 (100%)/1 mL conc. H_2SO_4 as described for **2b**. Analogous work up finally gave 241 mg (36%) of a white powder, m.p. 110.5–111.5 °C, Rf = 0.33 (petroleum ether/ethyl acetate 6:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm: 7.55 (s, 8H, ArH); 4.46 (d, 4H, $^2J = 14.0$ Hz, $ArCH_2Ar$); 3.95 (t, 8H, $^3J = 7.4$ Hz, OCH_2); 3.38 (d, 4H, $^2J = 14.0$ Hz, $ArCH_2Ar$); 1.8–1.95 (br m, 8H, OCH_2CH_2); 1.15–1.45 (br m, 104H, $(CH_2)_{13}CH_3$); 0.86 (t, 12H, $^3J = 6.8$ Hz, $O(CH_2)_{15}CH_3$). FD-MS m/z = 1502.1 (M^+, 100%); *Anal.* Calcd. for $C_{92}H_{148}N_4O_{12}$: C, 73.56; H, 9.93; N, 3.73. Found: C, 73.63; H, 9.93; N, 3.75.

2d A suspension of octadecylether **1d** (0.7 g, 0.42 mmol) in 32 mL $CHCl_3$, 11 mL acetic acid, and 6 mL acetic acid anhydride was cooled to 0 °C. With vigorous stirring 1.3 mL HNO_3 (100%) was added over 90 min. After 30–45 min the suspension slowly became dark. After complete addition the mixture was stirred with ice cooling for further 30 min, then at room temperature until the colour turned to yellow (about 2 h). Water (40 mL) and $CHCl_3$ (60 mL) were added, the organic phase separated, washed three times with 60 mL water and concentrated to 40 mL. A yellow crude product was precipitated by the addition of 150 mL methanol. Further purification by flash chromatography (petroleum ether/ethyl acetate 12:1) was as described above. Finally 188 mg (18%) of **2d** was obtained as a white powder, m.p. 90–91 °C, Rf = 0.34 (petroleum ether/ethyl acetate 6:1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm: 7.55 (s, 8H, ArH); 4.46 (d, 4H, $^2J = 14.4$ Hz, $ArCH_2Ar$); 3.95 (t, 8H, $^3J = 7.4$ Hz, OCH_2); 3.37 (d, 4H, $^2J = 14.4$ Hz, $ArCH_2Ar$); 1.7–1.95 (br m, 8H, OCH_2CH_2); 1.15–1.45 (br m, 120H, $(CH_2)_{15}CH_3$); 0.86 (t, 12H, $^3J = 6.8$ Hz, $O(CH_2)_{17}CH_3$). ^{13}C-NMR (50.3 MHz, $CDCl_3$), δ/ppm: 123.96 (CH); 135.40 ($C\text{-}CH_2$); 142.83 ($C\text{-}NO_2$); 161.65 (C-O); 14.08 ($O(CH_2)_{17}CH_3$). *Anal.* Calcd. for $C_{100}H_{164}N_4O_{12}$: C, 74.53; H, 10.26; N, 3.47. Found: C, 74.21; H, 10.31; N, 3.35.

LANGMUIR BLODGETT EXPERIMENTS

Surface pressure—Area (π/A) isotherms were measured on a Langmuir-type film balance "Lauda FW 1" equipped with a MS-DOS computer. Ultra pure water (electrical conductivity: 10^{-18} S/cm) was obtained with Milli-Q system (Millipore Co.). Compounds were spread from solutions in chloroform (0.2–0.4 mg/ml). To ascertain the reproducibility, all isotherms were measured at least 3 times (compression speed: 1.2 cm/min). Transfers to a Si-carrier were carrried out with a "Lauda Filmlift FL-1" (speed: 5 mm/min), while the surface pressure was maintained at 25 mN/m.

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REFERENCES

1 Kelderman, E., Derhaeg, L., Heesink, G.J.T., Verboom, W., Engbersen, J.F.J., van Hulst, N.F., Persoons, A., Reinhoudt, D.N.; *Angew. Chem.* **1992**, *104*, 1107.

2 See for instance: Cnossen, G., Drabe, K.E., Wiersma, D.A.; *J. Chem. Phys.* **1992**, *97*, 4512. Bjornholm, T., Geisler, T., Larsen, J., Jorgensen, M.; *J. Chem. Soc., Chem. Commun.* **1992**, 815. Li, D., Ratner, M.A., Marks, T.J., Zhang, C., Yang, J., Wong, G.K.; *J. Am. Chem. Soc.* **1990**, *112*, 7389 (and references cited there).

3 Verboom, W., Durie, A., Egberink, R., Asfari, Z., Reinhoudt, D.N.; *J. Org. Chem.* **1992**, *57*, 1313.

4 The difficulties frequently encountered with elemental analysis of calixarenes were not found with these low melting compounds.

In addition to inclusion phenomena these difficulties could be caused therefore by incomplete combustion of the usually high melting calixarene (derivative)s under standardized conditions.

5 Nakamoto, Y., Kallinowski, G., Böhmer, V., Vogt, W.; *Langmuir* **1989**, *5*, 1116.

6 Wortmann, R., Krämer, P., Glania, C., Lebus, S., Detzer, N.; submitted to *Chemical Physics*.

7 Landolt-Börnstein; Vol III/11, Springer, Berlin, **1979**, p. 671.

8 Liptay, W., Wehning, D., Becker, J., Rehm, T.; *Z. Naturforsch.* **1982**, *37a*, 1369.

9 Liptay, W., Becker, J., Wehning, D., Lang, W.; *Z. Naturforsch.* **1982**, *37a*, 1396.

10 Wortmann, R., Krämer, P.; in preparation.

11 Cheng, L.-T., Tam, W., Stevenson, S.H., Meredith, G.R., Rikken, G., Marder, S.R.; *J. Phys. Chem.* **1991**, *95*, 10631.

12 Würther, F., Effenberger, F., Wortmann, R., Krämer, P.; submitted to *Chemical Physics*.

13 Stewart, J.J.P.; MOPAC 6.00, A general purpose molecular orbital package (QCPE 1990).

14 Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., Stewart, J.J.P.; *J. Am. Chem. Soc.* **1985**, *107*, 3902.

15 Stähelin, M., Burland, D.M., Rice, J.E.; *Chem. Phys. Lett.* **1992**, *191*, 245.