

Preparation and Properties of Organic Dispersions of Monodisperse Silica Receptor Colloids Grafted with Calixarene Derivatives or Alkyl Chains

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We introduce cation-selective receptor colloids consisting of a monodisperse inorganic silica core grafted with an organic layer containing calixarene receptor molecules. The surface layer is designed to provide chemical selectivity (toward Cs⁺) as well as colloidal stability in organic solvents of interest in which silica spheres otherwise may flocculate. Grafting procedures for commercial- and laboratory-made silica dispersions are investigated for 25,27-bis[1-(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (designed and synthesized for this purpose), octadecyl alcohol, and mixtures ("cografting") of both compounds. Special attention is given to the nature of the solvent, which markedly influences grafting densities and colloidal stability during and after grafting procedures. NMR, elemental analysis, and light scattering are used to characterize a variety of carefully purified, grafted silica dispersions and to demonstrate, among other things, the presence of calixarene groups on the silica spheres. Preliminary complexation experiments with cesium chloride are reported. NMR and electrophoresis indicate that calixarene–silica colloids indeed are receptors for cesium cations.

1. Introduction

Organic surface coatings are of interest for separation processes¹ as well as for fundamental studies on colloidal model dispersions.² In studies on model colloids the coating is chemically "passive". Its purpose is mainly to stabilize particles against aggregation in some solvent or to influence physical interactions between the colloids.^{3–6} In separation techniques, the surface coating of a material may be "active" in the sense that it very selectively binds certain species such as enzymes and other biomolecules (ref 1 discusses many examples of carrier surface groups and their applications in affinity separation).

Also in the field of supramolecular chemistry and liquid membranes, selective binding is a well-documented phenomenon.^{7–14} A versatile class of molecules which can recognize cations or anions are the *calixarenes*: cyclic

oligomers produced by condensation of para-substituted phenols with formaldehyde.⁷ These receptors can form self-assembled monolayers on a surface.^{8–10} Suppose calixarenes are *covalently* bonded to an (inorganic) surface with the "host cavity" protruding into the solution, such that it can pick up the guest molecule. If this surface belongs to a colloidal particle, then one would have a *receptor colloid*, which may very specifically collect certain ions from the environment in which it is diffusing.

The aim of the present work is to investigate the synthesis of such a receptor colloid in a stable (nonaggregated) dispersion. The colloid was designed to have a well-defined inorganic core and a grafted organic surface layer containing receptor molecules. (A sketch of this type of colloid is given in Figure 1). This layer endows the colloid with chemical selectivity but at the same time renders the colloid dispersible in an organic solvent of interest.

For the uncoated starting colloids we selected small, fairly monodisperse silica particles (radius < 100 nm), and for the active group of the surface coating we choose a calix[4]arene-crown-6 which specifically binds cesium.^{11–14} From a colloid chemical point of view such calixarene–silica receptor colloids are interesting because of the possibility to attain and control surface charge (i.e. Cs⁺) on silica in an *organic* solvent. Bare silica flocculates in many organic solvents. Even if sufficient surface charge is present to sustain a stabilizing double-layer repulsion, the origin (and amount) of surface charge is often difficult to assess. With respect to separation processes, the small,

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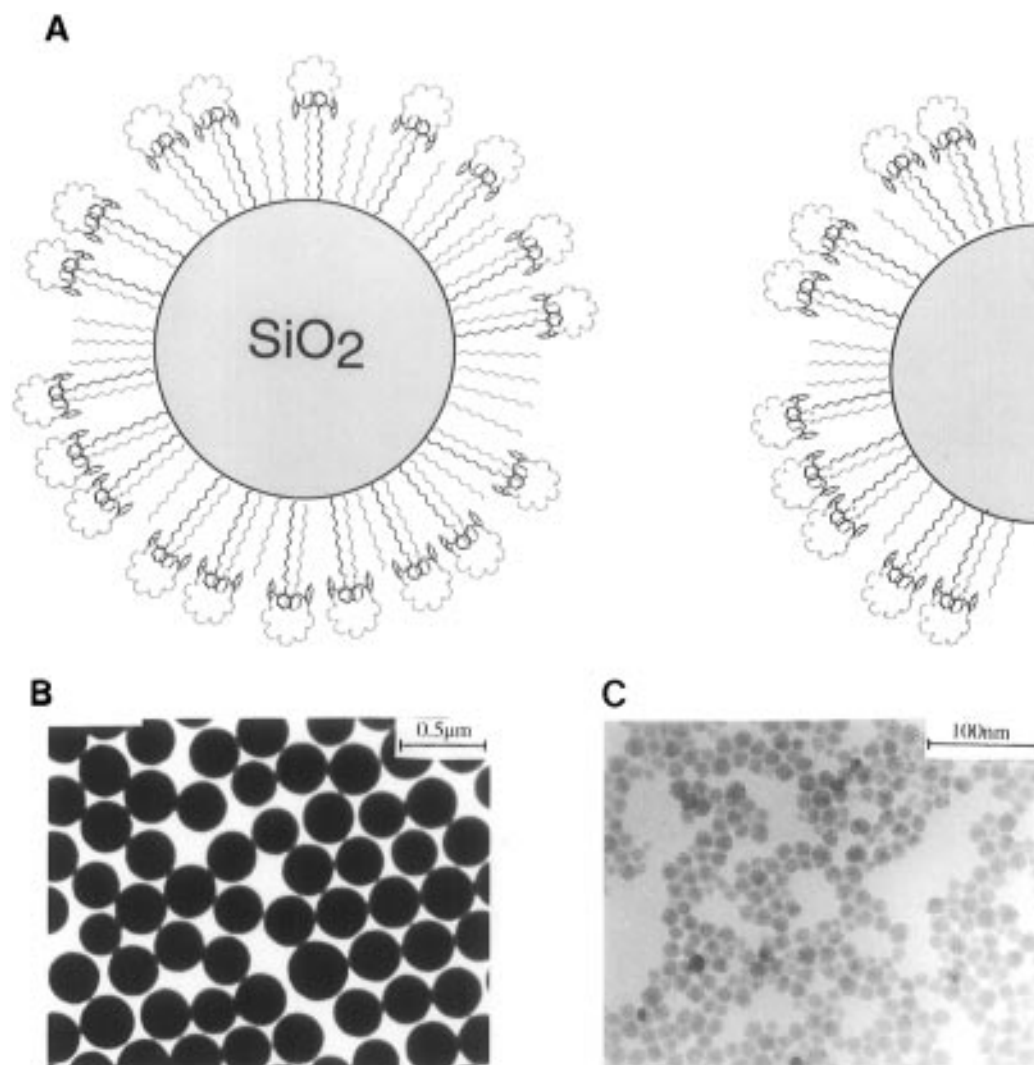


Figure 1. (A) Sketch of silica spheres grafted with alkyl chains. Some chains are functionalized with a macrocyclic receptor (calix[4]arene-crown-6). The sketch is not on scale: the calix[4]arene derivative occupies an area of about 1 nm^2 , and the radius of Stöber silica spheres on transmission electron micrographs such as in part B is about 85 nm. Part C depicts Ludox particles.

modified colloids combine a high surface area and diffusivity (in comparison with the micron size particles in silica gel^{15,16}). Nevertheless the colloids are in principle still large enough to allow recovery by sedimentation or filtration. Furthermore the modified colloids may be useful for transport experiments as carriers.

The uncoated silica colloids in this study are either commercial Ludox particles (radius $\sim 15 \text{ nm}$) in water or laboratory-made silica spheres (radius $\sim 90 \text{ nm}$) in ethanol–ammonia, following Stöber.¹⁷ The small Ludox particles are convenient for NMR because of their high specific surface area. The Stöber spheres were in addition selected to check the influence of the type of silica on the properties of the final coated dispersions. Moreover, our coating procedures can be compared with well-established ones for these Stöber spheres.^{2,18,19}

The first step in our experiments was the design and synthesis of an appropriate calixarene derivative. It is well-known that surface silanol groups from silica particles can be esterified with octadecyl alcohol to yield colloids

with a dense alkane brush grafted on their surface.^{2,18,19} Stable dispersions of small grafted particles in a variety of organic solvents can be obtained. This motivated us to synthesize a calix[4]arene-crown-6-ether with two pendant undecyl chains with terminal OH groups, which can react with the silica surface. A terminal triethoxysilane group is also an option for grafting purposes,^{3,6} but we preferred a monofunctional group which promotes monolayer formation. (It also allows a better comparison of occupied area per molecule with results from Langmuir–Blodgett films and with grafting densities of alkyl chains on silica.) Moreover, a “cografting” procedure is conceivable in which a mixture of the calixarene derivative and octadecyl alcohol is used. Such a variable coating composition may be useful to optimize colloidal stability in a certain solvent.

The second major issue in our study was the control of the colloidal stability of the silica dispersions during the various processing steps. It is not sufficient to master the chemistry needed to synthesize and graft the calix[4]arene derivative. One also has to avoid aggregation of the small colloids to large (visible) flocs; otherwise one loses the advantages over silica gel mentioned earlier. For example the accessible surface area decreases, and particle diffusion vanishes. Moreover, *in situ* characterization of dispersed particles with light scattering is not possible if extensive aggregation takes place.

Colloidal stability of grafted particles requires sufficient affinity between the grafted surface layers and the solvent.

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If the layers experience a "poor solvent", they will stick together and induce aggregation. The interplay between surface layers and solvents is very subtle, and even marginal changes in solvent composition may produce colloidal instability. The fundamental reason for this sensitivity is the large surface (interaction energy) of colloids in comparison with molecules, whereas the thermal translational energy is the same.²

What is required is a common good solvent for the charged "bare" silica particles, the less polar organic molecules, and the final grafted particles. In addition the boiling point of the solvent must be high enough to allow removal of water and lower alcohols (in which the initial silica is dispersed) by distillation. We selected 2-nitrophenyl octyl ether (NPOE) and triethyl phosphate (TEP) and performed in both solvents (co)grafting with 25,27-bis[1-(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 and octadecyl alcohol.

NPOE was chosen because it is a good solvent for calixarenes. Moreover, with respect to possible applications, it is also being used in supported liquid membranes as the carrier solvent for calixarenes in the porous polymer membrane, separating the aqueous source and the receiving phases.¹¹ TEP was selected because of its ability (in exploratory experiments) to disperse both charged and hydrophobic silica particles.

After grafting of silica in TEP or NPOE, the dispersions were purified by removing unreacted grafting agents by extensive centrifugation procedures. ¹³C CP MAS, ¹H NMR MAS, and TOCSY NMR experiments were performed to investigate the presence of 25,27-bis[1-(11-undecyl)oxy]calix[4]arene-crown-6 and octadecyl chains on the silica particles.^{20,21} In addition, elemental analysis was carried out for supporting evidence and to estimate grafting densities on the silica.

Any rapid flocculation of particles during or after grafting procedures is easy to observe visually. Light-scattering measurements on dispersions were performed to detect any small aggregates in the dispersions. Both light scattering and transmission electron microscopy were used to determine the size of (grafted) silica particles.

Finally, dispersions of 25,27-bis[1-(11-undecyl)oxy]calix[4]arene-crown-6 silica colloids in chloroform were brought in contact with an aqueous cesium chloride solution. ¹H MAS NMR spectroscopy was used to establish whether the modified silica in these preliminary complexation experiments indeed behaves as a receptor colloid toward cesium. Electrophoresis experiments were conducted to find additional evidence for Cs⁺ on silica particles.

2. Experimental Section

2.1. Synthesis of Calix[4]arene Derivative. All compounds were of reagent purity and used as supplied unless stated otherwise. Commercial dichloromethane was freshly distilled. Acetonitrile was stored over molecular sieves (3 Å). Column chromatography separation was carried out using silica gel (0.040–0.063 nm, Kieselgel 60, Merck). Melting points were measured on a Reichert melting point apparatus and are uncorrected. Refractive indices were determined with a Carl Zeiss 37865 (Germany) apparatus. ¹H NMR spectra, recorded in CDCl₃ at 250 MHz on a Bruker AC 250 spectrometer at room temperature (21 °C), were referenced to tetramethylsilane (TMS) at 0.00 as an internal standard. ¹³C NMR spectra were recorded on a Bruker AC 250 spectrometer. Fast atom bombardment (FAB) spectra were obtained with a Finnigan MAT 90 mass spectrometer, using 3-nitrobenzyl alcohol as a matrix. Microanalytical samples were dried for at least 48 h at 15 mmHg.

Differential scanning calorimetry (DSC) results were recorded with a Mettler DSC12E only for the final product. When reactions were performed under a dry argon atmosphere, all glassware was flame dried. Langmuir–Blodgett films were studied for compounds **4** and **5** (See Figure 2).

The starting calix[4]arene (**1**) was synthesized as described elsewhere.²²

11-Bromoundecyl 2-tetrahydropyranyl ether (**2**) was obtained from 11-bromoundecan-1-ol and dihydropyran according to a literature procedure²³ in 85% yield.

25,27-Bis[1-(11-(2-tetrahydropyranyl)oxy)undecyl]oxy]calix[4]arene Ether (**3**). A mixture of calix[4]arene (**1**) (7.46 g, 17.6 mmol), K₂CO₃ (2.49 g, 18 mmol), and 11-bromoundecyl 2-tetrahydropyranyl ether (11.8 g, 35 mmol) in CH₃CN (300 mL) was refluxed for 48 h under a dry argon atmosphere. The solvent was removed under reduced pressure on a rotary evaporator, and the residue was taken up into CH₂Cl₂ (100 mL). The organic phase was washed with HCl (1 N, 50 mL), demineralized water (300 mL), and brine (100 mL). Column chromatography (SiO₂, CH₂Cl₂) afforded **3** (10.18 g, 62%) as a white solid: mp 98–100 °C; FAB (M + Na⁺ 956, calc 932.6); ¹H NMR δ 8.22 (s, 2H, ArOH), 7.04 (d, 4H, *J* = 7.5 Hz, *m*-ArH), 6.91 (d, 4H, *J* = 7.5 Hz, *m*-ArH), 6.73 (t, 2H, *J* = 7.5 Hz, *p*-ArH), 6.63 (t, 2H, *J* = 7.5 Hz, *p*-ArH), 4.57 (t, 2H, *J* = 3.5 Hz, OCHO), 4.31 and 3.37 (ABq, 8H, *J* = 12.9 Hz, ArCH₂Ar), 3.99 (t, 4H, *J* = 6.9 Hz, ArOCH₂), 3.9–3.3 (m, 8H, CH₂OCH, ArCH₂Ar), 2.1–2.0 (m, 4H, CH₂CHO), 1.9–1.3 (m, 30H, CH₂); ¹³C NMR δ 153.4 and 152.0 (s, Ar-25,27,26,28), 133.5 and 128.2 (s, Ar-1,3,7,9,13,15,19,21), 128.9 and 128.4 (d, Ar-4,6,10,12,16,18,22,24), 125.2 and 118.9 (d, Ar-5,11,17,23), 98.8 (d, OCHO), 76.78 (t, ArOCH₂), 67.7 and 62.3 (t, CH₂OCH), 31.5 (t, ArCH₂Ar), 30.8, 30.0, 29.8, 29.7, 29.6, 29.5, 26.3, 26.0, 25.5, 19.7 (t, CH₂). Anal. Calc for C₆₀H₈₄O₈: C, 77.21; H, 9.07. Found: C, 77.24; H, 9.43.

25,27-Bis[1-(11-(2-tetrahydropyranyl)oxy)undecyl]oxy]calix[4]arene-crown-6 (**4**). A mixture of 25,27-bis[1-(11-(2-tetrahydropyranyl)oxy)undecyl]oxy]calix[4]arene ether (**3**) (2.35 g, 2 mmol) and Cs₂CO₃ (2.61 g, 8 mmol) in CH₃CN (600 mL) was gently refluxed for 30 min, after which a solution of pentaethylene glycol ditosylate (1.32 g, 2.4 mmol) dissolved in CH₃CN (200 mL) was added dropwise. The mixture was refluxed gently for 72 h under a dry argon atmosphere. The solvent was removed under reduced pressure, and the residue was taken up into CH₂Cl₂ (100 mL). The organic phase was washed with HCl (1 N, 250 mL), demineralized water (500 mL), and brine (100 mL). Column chromatography (SiO₂, ethyl acetate–hexane 75:25) afforded **4** (1.4 g, 48%) as a liquid with refractive index [α]_D²⁰ 1.5349: FAB (M + Na⁺ 1157.4, calc 1134.7); ¹H NMR δ 7.07 (d, 4H, *J* = 7.5 Hz, *m*-ArH), 7.01 (d, 4H, *J* = 7.5 Hz, *m*-ArH), 6.82 (t, 2H, *J* = 7.4 Hz, *p*-ArH), 6.76 (t, *J* = 7.5 Hz, 2H, *p*-ArH), 4.59 (t, 2H, *J* = 3.5 Hz, OCHO), 3.9–3.4 (m, 40H, OCH₂), 1.8–1.2 [34H, CH₂(chain)]; ¹³C NMR δ 156.9 and 156.4 (s, Ar-25,26,27,28), 134.1 and 133.7 (s, Ar-1,3,7,9,13,15,19,21), 129.8 and 129.6 (d, Ar-4,6,10,12,16,18,22,24), 122.1 (d, Ar-5,11,17,23), 96.8 (d, OCHO), 71.2, 71.1, 71.0, 70.6, 69.9, 67.7, 62.3, 60.4 (t, CH₂), 37.9 (t, ArCH₂-Ar), 30.6, 29.8, 29.75, 29.7, 29.6, 29.3, 26.8, 25.8, 25.5, 19.7, 14.2 (t, CH₂CH₂CH₂).

25,27-Bis[1-(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (**5**) was obtained in analogy with ref 23 in 87% yield. Column chromatography (SiO₂, ethyl acetate–dichloromethane 75:25) afforded **5** (1.4 g, 85%) as a white solid: mp 116–118 °C; FAB (M + Na⁺ 989.8, calc 966.6); ¹H NMR δ 7.08 (d, 4H, *J* = 7.5 Hz, *m*-ArH), 7.01 (d, 4H, *J* = 7.5 Hz, *m*-ArH), 6.8–6.7 (m, 4H, *p*-ArH), 3.8–3.33 (m, 36H, OCH₂), 1.6–1.2 (m, 38H, CH₂); ¹³C NMR δ 156.9 and 153 (s, Ar-25,26,27,28), 134.1 and 133.8 (s, Ar-1,3,7,9-13,15,19,21), 129.8 and 129.6 (d, Ar-4,6,10,12,16,18,22,24), 122.1 (d, Ar-5,11,17,23), 71.1, 70.9, 70.6, 69.9, 63.0 (t, ArOCH₂CH₂), 37.9 (t, ArCH₂Ar), 32.8, 29.7, 29.5, 29.3, 25.8 (t, CH₂CH₂). Anal. Calc for C₆₀H₈₆O₁₀: C, 74.55; H, 8.97. Found: C, 74.38; H, 8.99.

2-Nitrophenyl octyl ether (NPOE) was synthesized as described elsewhere.²⁴ The purity of the compound was checked by gas chromatography.

2.2. Preparation and Purification of Silica Particles Grafted with Calixarene and/or Octadecyl Groups. All

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Table 1. Experimental Details for (Co)grafting Reaction in 2-Nitrophenyl Octyl Ether (NPOE)

code	compound 5 (g)	octadecyl alcohol (g)	NPOE (mL)	silica (g)
SA11NPOE			20	1
SLNPOE			50	2
SA11C ₁₈		7	25	9
SLC ₁₈ NPOE		10	25	1.48
SLCALIXNPOE	0.143		50	2.1
SA11CALIX	0.3		25	9
SA11CALIXC ₁₈	0.3	7	25	9
SLCALIXC ₁₈ NPOE	0.4	10	25	1.48

glassware was cleaned with aqueous HF (8%) solution, hot tap water, and doubly distilled water. The chemicals were used as supplied without further purification unless stated otherwise. Dowex 50W × 4 acid ion exchange and Dowex 1 × 4 anion exchange resins were regenerated by subsequent rinsing with hot water, methanol, HCl (3 N), or NaOH (3 N), respectively, and cold demineralized water until pH = 6.²⁵ The starting dispersions of bare, uncoated silica spheres were prepared by the Stöber synthesis¹⁷ or supplied by DuPont (Ludox AS-40). Universal indicator pH 0–14 (Merck) was used to check the pH of the Ludox dispersion. Coating procedures were carried out under a slow flow of nitrogen dried by passing it over CaCl₂. Dispersions of coated particles were purified from free organic compounds by centrifugation either for 20 h in an ultracentrifuge (Beckman L-60) in the case of Ludox particles or for 6 h in a table centrifuge (Beckman GS-6) in the case of larger Stöber silica spheres. Centrifugation procedures were in most cases repeated four times.

The particles were characterized with transmission electron microscopy (Phillips CM 10). ¹³C CP-MAS NMR spectra were measured on a Varian Unity 400 WB NMR spectrometer. Elemental analysis was performed by Mikroanalytisches Labor Pascher (Remagen, Germany) on silica particles dried for 48 h at 70 °C under a nitrogen atmosphere. The colloidal stability of the dispersions in various solvents, that is, the absence of large particle aggregates, was checked visually.

It is important to note that NMR and elemental analysis only detect organic groups on the silica surface, because free molecules are removed by sedimentation. Suppose, for example, the n_0 moles of free molecules and a silica volume fraction ϕ_{disp} are present in a volume V of dispersion after the grafting procedure. Centrifugation produces a sediment with silica volume fraction ϕ_{sed} and a fraction of the n_0 moles. This sediment is redispersed in a volume V of pure solvent. After x centrifugation steps the number of free molecules in the sediment is about

$$n(x) = (1 - \phi_{\text{sed}})^x (\phi_{\text{disp}} / \phi_{\text{sed}})^x n_0 \quad (1)$$

For random close-packed spheres the sediment density will be close to $\phi_{\text{sed}} = 0.64$. The silica concentrations in the grafting procedures are of the order $\phi_{\text{disp}} \sim 0.01$. One can easily verify that, for $x \geq 3$ sedimentation steps, the amount of unreacted compounds will be negligible.

Particle codes. The following codes are used. **SA11** refers to ungrafted Stöber silica spheres, and **SL** to ungrafted Ludox particles. The solvent in which particles have been refluxed or grafted appears at the end of the code, after the grafting agent(s). For example, **SLTEP** denotes bare Ludox silica after refluxing in pure triethyl phosphate (TEP), and **SA11C₁₈-CALIXNPOE** is the code for **SA11** particles grafted with octadecyl alcohol and compound **5** in NPOE. These particle codes also appear in Tables 1 and 2, which contain the amounts of reagents used in the grafting procedures.

Silica dispersion in ethanol–ammonia (SA11) was prepared as follows. Freshly distilled tetraethoxysilane (100 mL, TES, Fluka) was added to a mixture of absolute ethanol (2 L, Nedalco technical grade) and ammonium hydroxide (140 mL, 25%, Merck). The mixture was stirred for 18 h at 15.5 °C in a thermostatic bath. The obtained particles, coded **SA11**, have a radius of about 90 nm, as determined by light scattering and particle dimensions on transmission electron micrographs, such as in Figure 1. The silica weight concentration of the final **SA11** dispersion was $c = 10$ g/L.

Table 2. Experimental Details for (Co)grafting Reaction in Triethyl Phosphate (TEP)

code	compound 5 (g)	octadecyl alcohol (g)	TEP (mL)	silica (g)
SLTEP			50	1.6
SLCALIXTEP	0.2			
	0.15		70	2.1
			50	2
SLC ₁₈ TEP		7	70	2.1
SLCALIXC ₁₈ TEP	0.055	14	50	2
SA11C ₁₈ TEP		3	25	2
SA11TEP			25	2
SA11CALIXTEP	0.06		20	2

Silica Ludox particles in water (SL) were obtained from aqueous Ludox dispersion, purified by removal of Na⁺. Sodium ions may cause particle flocculation when particles are transferred to organic solvents.²¹ A Ludox dispersion (100 mL, $c = 40\%$ w/w) was diluted with demineralized water (100 mL). The dilute dispersion was passed subsequently through an anion exchange column to remove any Cl[−] from the system and through an acid cation exchange column to remove Na⁺. During the latter exchange the pH of the dispersion drops from 10 to 3, which is close to the isoelectric point of silica. To prevent flocculation of particles, the pH of the dispersion is raised to pH = 10 with a few drops of ammonia.²⁶ The final dispersion, coded **SL**, has a silica concentration of about $c = 160$ g/L.

Bare Silica in High Boiling Point Solvents (SA11NPOE, SLNPOE, SA11TEP, and SLTEP). Previous to the grafting reactions, the colloidal stability of dispersions (**SA11** and **SL**) in NPOE or triethyl phosphate (TEP) was checked. This was done by performing blank experiments by treating the particles in NPOE or TEP without any organic grafting agents. (This also gives reference particles for comparison with grafted colloids, for example, in solid state NMR; see section 2.4.) Ludox silica particles have been transferred from water to ethanol and then gradually to other polar solvents by distillation.²⁶ Using the same procedure, Stöber silica spheres were transferred from ethanol to NPOE. The procedure was typically as follows: A silica dispersion (10 mL, **SA11** or **SL**) was transferred to pure ethanol by distilling water and ammonia. During the distillation, propanol (10 mL) and ethanol (100 mL) were added to remove all water from the system. When the distillate had the refractive index of pure ethanol, distillation was stopped. The particles in pure ethanol were added gradually to pure NPOE (without coating agent, see Tables 1 and 2), removing gently the ethanol by distillation. After all ethanol was distilled, the temperature was raised to 140–160 °C and kept at this value for 4 days under dry nitrogen. The dispersions coded **SA11NPOE**, **SLNPOE**, **SA11TEP**, and **SLTEP** were sedimented and redispersed five times to transfer particles again to pure ethanol.

Octadecyl Grafting of Silica (SA11C₁₈NPOE, SLC₁₈NPOE, SA11C₁₈TEP, and SLC₁₈TEP). Procedures for coating silica particles with alkyl chains are well documented.^{18,19} The esterification reaction between SiOH groups on the silica surface and the hydroxyl group of octadecyl alcohol takes place at high temperature (~180 °C) in molten octadecyl alcohol. In our work, grafting of the alcohol on the silica surface is performed in a solvent with a high boiling point (NPOE or TEP). The procedure was typically as follows. A dispersion of Ludox particles or Stöber silica spheres in ethanol (prepared as described above) was added to a solution of an excess of octadecyl alcohol in NPOE or TEP. From the mixture, the ethanol was gradually removed by distillation. After all the ethanol was distilled, the mixture was stirred at 140–160 °C for 4 days under dry nitrogen. The particles coded **SA11C₁₈NPOE**, **SLC₁₈NPOE**, **SA11C₁₈TEP**, and **SLC₁₈TEP** were sedimented and redispersed five times to transfer them to cyclohexane.

Calix[4]arene Grafting of Silica (SA11CALIXNPOE, SL-CALIXNPOE, SA11CALIXTEP, and SLCALIXTEP). A dispersion of particles in pure ethanol was added to a solution of 25,27-bis[(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (**5**) (see Tables 1 and 2) in NPOE or TEP, removing gently the ethanol by distillation. After all ethanol was distilled, the mixture was

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Table 3. Elemental Analysis Results^a

A. Grafted Ludox Silica								
	SL	SLNPOE	SLC ₁₈ - NPOE	SLCALIX- NPOE	SLCALIXC ₁₈ - NPOE	SLTEP	SLC ₁₈ - TEP	SLCALIX- TEP
C (%)	0.22	1.70	14.96	13.38	7.76	1.94	9.06	2.67
H (%)	0.28	0.52	2.68	1.82	1.47	0.66	1.75	0.82
P (%)						0.80		
molar ratio								
H/C	15.27	3.67	2.15	1.63	2.27	4.08	2.32	3.69
C/P						6.22		
estimated ^b number of groups per nm ² silica		ethoxy	C ₁₈	calix		TEP	C ₁₈	calix
		3.8	3.8	1.0		1.4	1.8	0.06
		±0.7	±0.7	±0.2		±0.2	±0.3	±0.01
B. Grafted Stöber Silica								
	SA11	SA11- NPOE	SA11C ₁₈ - NPOE	SA11CALIX- NPOE	SA11CALIXC ₁₈ - NPOE	SA11- TEP	SA11C ₁₈ - TEP	SA11CALIX- TEP
C (%)	3.79		3.80		4.72	4.47	5.75	5.32
H (%)	1.39		1.43		1.46	1.42	1.70	1.50
P (%)						0.09		
molar ratio								
H/C	4.40		4.52		3.71	3.8	3.55	3.38
C/P						127.5		
estimated ^b number of groups per nm ² silica						TEP	C ₁₈	calix
						1.0	1.9	0.02
						±0.1	±0.2	

^a Particles were dried at 70 °C/1 atm under nitrogen with a weight loss in the range 0.5–5%. ^b Uncertainties are mainly due to the choice of the size of the SL particles and/or the amount of TEP which is present on the silica.

stirred at 145–160 °C for 4 days under dry nitrogen. Centrifugation was carried out three times to transfer the particles to chloroform. We note that a grafting time of 4 days is required to render the particles dispersible in chloroform. When a sample of the reaction mixture is added to chloroform after 2–3 days, flocculation occurs, indicating that the surface coverage is still too low.

Calix[4]arene Octadecyl Cografting of Silica (SA11CALIXC₁₈-NPOE, SLCALIXC₁₈NPOE, and SLCALIXC₁₈TEP). Performing the coating procedure in NPOE and TEP allows the possibility of coating the silica particles successively with 25,27-bis[(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (**5**) and octadecyl alcohol. The quantities used in these reactions are presented in Tables 1 and 2. The procedure was typically as follows: A dispersion of SL (1.48 g) in pure ethanol (10 mL) was added to a solution of **5** (0.4 g) in NPOE or TEP (50 mL). The ethanol was distilled, and the resulting dispersion in NPOE or TEP was heated at 145–160 °C under dry nitrogen. After 2 days octadecyl alcohol was added, keeping the dispersion at 145–160 °C for 2 more days. The final dispersion was sedimented five times and redispersed in chloroform.

2.3. Complexation Experiments. Complexation experiments of free 25,27-bis[(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 ether or SLCALIXNPOE in deuterated chloroform were performed as follows. A solution of compound **5** in CDCl₃ or silica dispersion SLCALIXNPOE in chloroform (2 mL) and a saturated aqueous solution of CsCl (2 mL) were gently shaken for 1 week. The organic layer was separated and investigated with ¹H NMR.^{11,13}

2.4. MAS NMR. ¹³C CP-MAS spectra²⁸ were obtained with a Varian Unity 400WB NMR spectrometer equipped with a broadband CP-MAS probe head. The 90° pulse lengths for ¹³C and ¹H were 3.5 μs. The samples were spun at 6000 Hz (5 mm ZrO₂ rotors), and the cross-polarization times were 1 ms. Typically 8000 transients were acquired with a relaxation delay time of 5 s. Hexamethylbenzene was used to optimize experimental parameters and as an external chemical shift reference. Solid state ³¹P MAS NMR spectra were obtained at a spinning rate of 3000 Hz. H₃PO₄ (85%) was used as a chemical shift reference. High-resolution ¹H NMR spectra of silica dispersions were obtained by spinning the liquid sample at the magic angle at ca. 800–2000 Hz (in the same probe head which was used for the solid state CP experiments). To facilitate quantitative evaluation of the ¹H MAS NMR spectra, a relaxation delay of 5 s was used. TOCSY (MLEV17) experiments²⁷ under magic angle spinning

conditions were performed with mixing times of 35 ms, and TPPI²⁹ was used for signal accumulation in the *t*₁ dimension. The 1D and 2D ¹H MAS spectra were recorded via the ¹H decoupler channel; the broad-band (“observe”) channel was tuned to the ²H frequency and employed for ²H field locking.

2.5. Light Scattering. Light scattering was used to determine the size of particles or particle aggregates in the dispersion. Dynamic light scattering (laser wavelength λ = 488 nm) on dilute (*c* < 1 g/L), dust-free silica dispersions was performed as described elsewhere.^{30,31} Measurements were done at various scattering angles θ, i.e. at various scattering vectors *K* = (4π*n*/λ) sin(θ/2), with *n* the refractive index of the solvent. A diffusion coefficient *D*₀ was obtained from the initial slope of the intensity autocorrelation function using a cumulant analysis.^{30,31} A hydrodynamic particle radius *R*_h was obtained from the Stokes–Einstein equation *D*₀ = *k*_B*T*/6πη*R*_h, with η the solvent viscosity and *k*_B*T* the thermal energy. Static light scattering measurements were performed with a Fica-50 photometer, and scattering intensity profiles were analyzed using the Guinier approximation.³

2.6. Electrophoresis. To determine the sign of any (net) surface charge on grafted particles, before and after complexation, the following simple, qualitative experiment was performed. Two electrodes, connected to a 4.5 V battery, were immersed in a stagnant silica dispersion in a closed vessel. Any migration of colloids to an electrode leads to silica deposition on the electrode surface. The method was checked for aqueous dispersion of negatively charged, bare silica particles and positively charged boehmite (AlOOH) colloids which produced clearly visible deposits on a time scale of minutes to hours.

3. Results and Discussions

3.1. Synthesis and Properties of 25,27-Bis[(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (5**).** Compound **5** was specifically designed for coupling a calix[4]arene-crown-6 group to a silica surface via its hydroxyl groups. The (elemental) analysis results in section 2.1 show that the reaction scheme as depicted in Figure 2 indeed yields compound **5**. We note that **5** has the 1,3 alternate conformation, as in the other alkylated calix-

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Synthesis

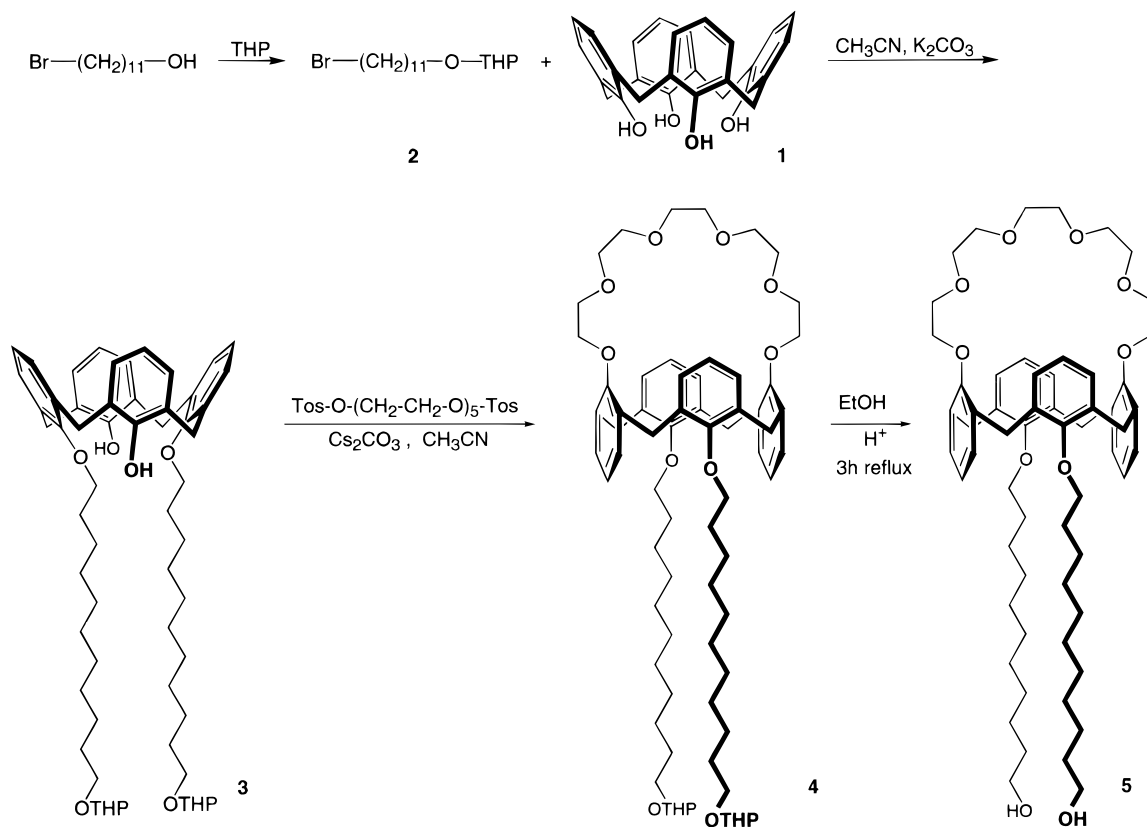


Figure 2. Synthesis scheme for the calixarene derivative **5**, having two pendant alkyl chains with terminal OH groups by which it can be attached to a silica particle.

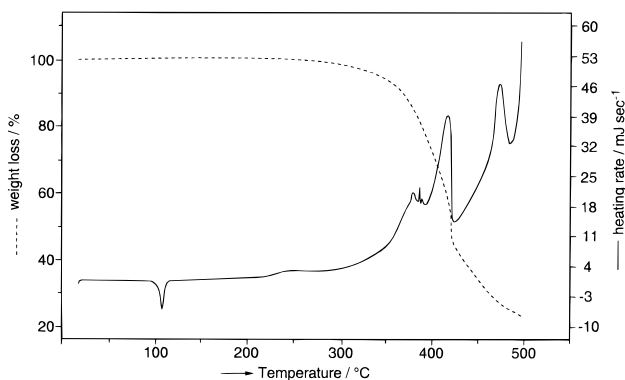


Figure 3. Differential scanning calorimetry results for compound **5**, showing that it is stable at the grafting temperature of 160 °C.

[4]arene-crown-6 compounds synthesized by alkylation in the presence of salt.^{12,14}

The grafting of **5** onto silica particles takes place at a temperature in the range 140–160 °C. No decomposition of **5** will take place at this temperature. The differential scanning calorimetry results in Figure 3 show that **5** decomposes only above 250 °C.

The Langmuir-Blodgett (LB) isotherms of compound **4** reveal a monolayer on water corresponding to an area of about 1 nm² per molecule. This area gives an indication of the silica surface per calix group, in the case the calix molecules would form a dense (mono)layer on silica particles. This point is further discussed in section 3.7.

In compound **4** the hydroxyl groups are blocked by tetrahydropyranyl groups. In compound **5** unprotected, free OH groups are present. Their presence is also manifested by their interaction with the water surface directly after spreading.³²

3.2. Bare Silica Particles in High Boiling Point Solvents.

Silica particles were generally stable (i.e. no visible flocs) in mixtures of NPOE or TEP and ethanol and also at elevated temperatures. Removal of ethanol by distillation generally resulted in a stable dispersion of silica particles. The concentration of the dispersion, nevertheless, is a critical factor for the stability of Ludox particles in pure NPOE. The bare Ludox particles seem to be stable in NPOE only at very low concentrations. At the concentration used in the coating procedure, sometimes space-filling gels were formed. By diluting these gels with NPOE or ethanol, a stable dispersion was regenerated, as judged by visual inspection. However, small aggregates may still be present (see section 3.6).

No flocculation was observed after stirring the dispersions in NPOE or TEP at 145–160 °C for 4 days. The resulting **SA11NPOE** and **SLNPOE** particles show the same colloidal stability (Table 4) in various solvents as the initial **SA11** and **SL** dispersions.

This result, together with the fact that in solid state NMR (Figures 4B and 5B) no aromatic signals are present, indicates that NPOE does not adsorb onto the silica surface. (In contrast, ³¹P MAS NMR spectra clearly reveal the presence of TEP on particles grafted in TEP.) The weak aliphatic resonances which appear in the ¹³C CP-MAS spectrum (Figure 4B) of **SLNPOE** dispersions are also intriguing. These resonances can be assigned to ethoxy moieties attached to the silica surface. Possibly, during the thermal treatment the adsorbed ethanol and propanol reacted with SiOH from the silica surface. These findings are confirmed by elemental analysis (section 3.7).

3.3. Octadecyl-Grafted Silica Particles. NPOE is a polar organic solvent with a high boiling point in which bare particles are fairly stable (see section 3.2). This

Table 4. Colloidal Stability of Silica Dispersions in Various Solvents^a

silica	stability in given solvent							
	H ₂ O	ETOH	THF	DMF	NPOE	CHCl ₃	C ₇ H ₈	CHX
SA11SL	S	S	S		FS	IS	IS	IS
SA11NPOE	S	S	S		FS	IS	IS	IS
SLNPOE	S	S	S		FS	IS	IS	IS
SA11CALIX	IS	IS	IS	FS	FS	S	IS	IS
SLCALIXNPOE	IS	IS	IS	FS	FS	S	IS	IS
SA11CALIXC ₁₈	IS	IS	IS	FS	FS	S	IS	IS
SLCALIXC ₁₈ NPOE	IS	IS	IS	FS	FS	S	IS	IS
SA11C ₁₈	IS	IS	IS	S	S	S	S	S
SLC ₁₈ NPOE	IS	IS	IS	S	S	S	S	S

^a S = stable; FS = stable for a short period of time; IS = instable.

¹³C Solid State NMR SL

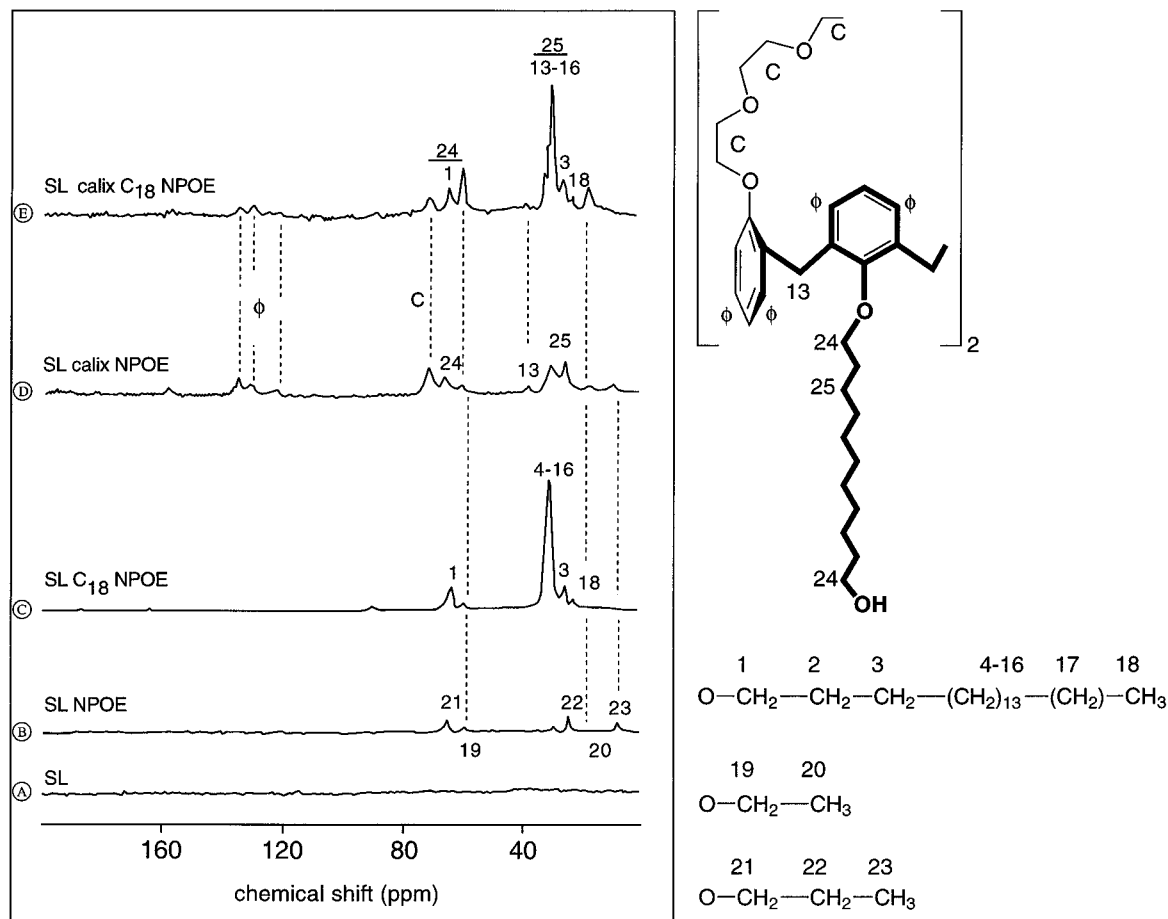


Figure 4. ¹³C CP-MAS spectra and shift assignments for silica ludox (SL) particles grafted in 2-nitrophenyl octyl ether (NPOE): (A) starting SL particles, dried from water; (B) SL particles transferred via ethanol to NPOE and kept in pure NPOE under grafting conditions (4 days of stirring at 160 °C); (C) SL particles grafted with octadecyl chains in NPOE; (D) calix-grafted silica particles in NPOE; (E) SL particles cografed with calixarenes and octadecyl chains in NPOE. Samples were, before drying, purified from unreacted grafting agents by extensive sedimentation procedures, so signals are due to organic moieties on the silica surface.

suggests that NPOE and also TEP are suitable media for grafting alcohols onto silica, especially when one has to use small quantities of expensive compounds. (The conventional grafting procedure for octadecyl alcohol requires a large amount of alcohol to form a melt in which silica is dispersed.¹⁸) First, we verified whether the esterification reaction between silica and an alcohol indeed occurs in these solvents (reaction conditions as described in section 2.2).

In the ¹³C CP-MAS spectrum of octadecyl-grafted particles (SLC₁₈NPOE) the signals of long-chain alkoxy moieties can be clearly discerned (Figure 4C). The position and intensity ratios of these resonances are in accordance with data obtained for alkoxy silane-based silica particles

coated with octadecyl alcohol.³³ Besides the presence of the octadecyl chains, the ¹³C CP-MAS spectra of SA11C₁₈-NPOE (Figure 5C) also show the presence of propoxy and ethoxy moieties. The latter can also be detected before grafting (Figure 5A) and have been trapped in the particles during the Stober synthesis of SA11.³³ The propoxy moieties are most likely trapped in small pores inside the interior of the SA11 particles during the grafting procedure (*vide supra*). (It is possible that during the procedure some extra ethoxy moieties are absorbed in the pores of SA11, but these cannot be distinguished from the ethoxy already present in the bare particles). The absence of

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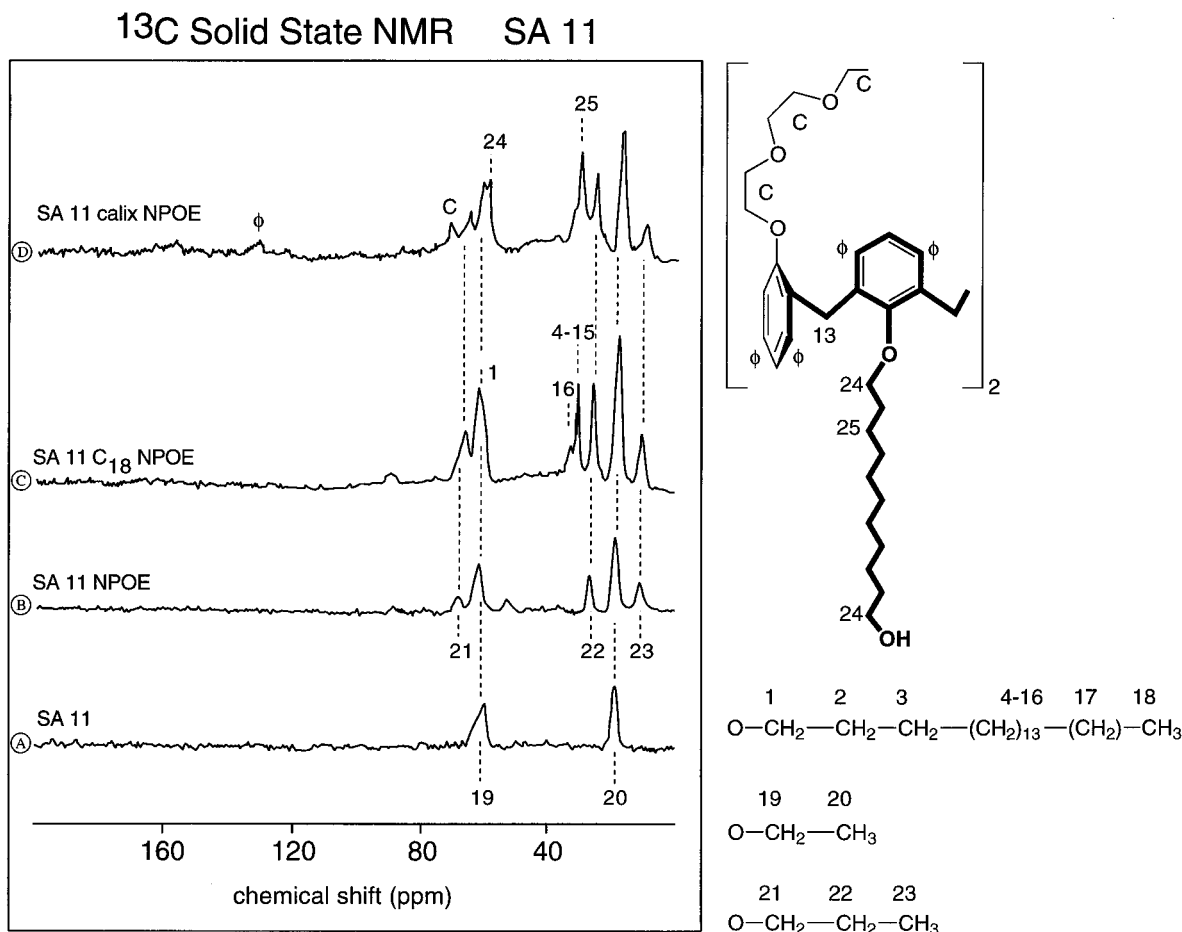


Figure 5. ^{13}C CP-MAS spectra and shift assignments of Stober silica (SA) spheres grafted in 2-nitrophenyl octyl ether (NPOE): (A) starting spheres dried from ethanol-ammonia; (B) spheres transferred to NPOE and kept in pure NPOE under grafting conditions (4 days of stirring at 160°C); (C) silica spheres grafted with octadecyl alcohol and (D) calixarene groups. Signals are only due to organic molecules on the silica surface.

any aromatic signals in ^{13}C CPMAS spectra excludes the presence of NPOE adsorbed to the silica surface of SA11. In the ^{13}C CP-MAS spectra of SL C_{18} NPOE also signals from ethoxy and propoxy are present, but these are small compared to the signals of the octadecyl chains. A similar picture is obtained when the octadecyl grafting is performed in triethyl phosphate (TEP).

The presence of alkyl chains on silica particles is also demonstrated by the carbon content from elemental analysis (see Table 3) and the colloidal stability of the dispersions in various solvents (see Table 4).

3.4. Calix-Grafted Silica. The esterification reaction between the silica surface and the calix[4]arene-crown-6 with HO-terminated alkyl chains is similar to the reaction of octadecyl alcohol with silica particles. The presence of 5 on the SL CALIXNPOE , SA11 CALIXNPOE , and SL CALIXTEP particle surfaces is evident from the presence of several resonances in the aromatic regions (Figure 4D and 5D) of the ^{13}C CP MAS spectra. Further support is found in the resonance at 71 ppm, which can be ascribed to the crown methylene carbons. Also in these ^{13}C CP MAS spectra significant (SA11 CALIXNPOE) or trace (SL CALIXNPOE) amounts of ethoxy and propoxy moieties can be observed (whose origin was described in the previous section). The ^{31}P MAS NMR spectrum of SL CALIXTEP reveals the presence of TEP.

NMR characterization of silica particles grafted with organic species has been limited to the observation of the ^{13}C nucleus. The small natural abundance and low gyromagnetic ratio of this nucleus seriously hamper the observation of surface species. Though the ^1H nucleus has almost 100% natural abundance and a high gyro-

magnetic ratio, its observation in the solid state is impeded by strong homonuclear dipolar couplings (due to immobilization of the spin system) which lead to very broad signals. When calixarene-grafted SL particles (SL CALIXNPOE) are dispersed in CDCl_3 , however, some broad signals can be discerned in the aliphatic region of the ^1H NMR spectrum. Apparently, the motion of the grafted particles in the dispersion is fast enough to quench the dipolar couplings significantly. A further reduction of the ^1H line widths can be attained by spinning the dispersion at the magic angle at a rate of 800–1000 Hz. The ^1H NMR lines can now unambiguously be assigned to grafted species. The main effect of magic-angle spinning is the removal of line-broadening effects due to slow motion of surface species and/or field discontinuities near the silica surface.^{20,21} Compared to the ^{13}C CP-MAS spectra of the solid particles the ^1H NMR MAS spectrum (Figure 6A) of the dispersion shows much better resolution and sensitivity. One other advantage which should be mentioned is that the ^1H MAS spectra are acquired by direct excitation (Bloch decay) whereas ^{13}C solid state spectra require cross-polarization (CP) in order to yield sufficient sensitivity. Cross-polarized spectra do not lend themselves for quantitative analysis, however, in contrast with Bloch decay spectra (as long as caution is exerted with the choice of proper relaxation delays). No traces of other surface-adsorbed species can be observed in the ^1H MAS spectrum.

The sensitivity and resolution of the ^1H MAS NMR experiment are sufficient to facilitate a so-called homonuclear TOCSY experiment. In the two-dimensional homonuclear TOCSY (or HOHAHA) experiment, connectivities can be observed between J -coupled spins. These

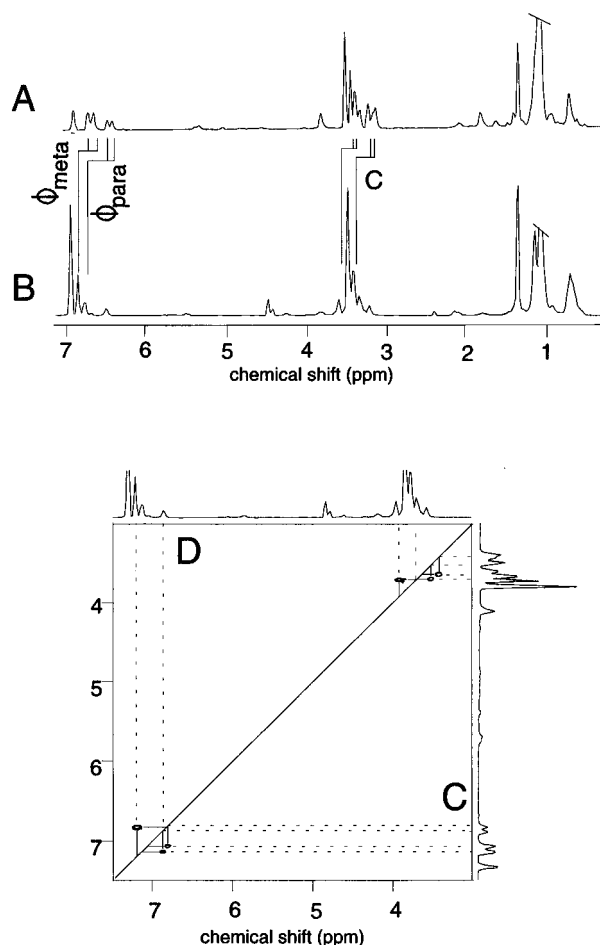


Figure 6. (A) ^1H MAS spectrum of SLCALIXNPOE dispersed in CDCl_3 . Assignments of aromatic and crown protons have been indicated. (B) ^1H MAS spectrum of a dispersion of SLCALIXNPOE upon complexation with Cs^+ . Complexation-induced shifts have been indicated by straight lines. In parts C and D two TOCSY spectra are combined. Below the diagonal (C) the TOCSY spectrum is presented which is recorded under the same conditions as for the ^1H MAS spectrum in part A (uncomplexed dispersed SLCALIXNPOE). Above the diagonal (D) the TOCSY spectrum is presented of dispersed SLCALIXNPOE complexed with Cs^+ . The J -correlated connectivities indicated in the TOCSY spectra confirm the unambiguous assignments made in parts A and B.

through-bond connectivities help in making (or supporting) assignments in complicated spin systems. In Figure 6B the ^1H MAS TOCSY spectrum is shown of a dispersion of SLCALIXNPOE in CDCl_3 . The observed through-bond connectivities are in accordance with the spectral positions presented for the free species; see section 2.1. The connectivity pattern observed between minor resonances reveals the presence of traces of NPOE in the samples (approximately 10%).

3.5. Calix-Octadecyl-Cografted Silica Particles.

Cografting of silica particles with calix and octadecyl was expected to influence the properties of the dispersions. Surprisingly SLCALIX $_{18}$ NPOE and SA11CALIX $_{18}$ NPOE are acting in various solvents similar to silica particles coated only with calixarene. This could imply that octadecyl chains are not grafted on the silica surface for steric hindrance reasons. However, the presence of both octadecyl and **5** on the cografted Ludox particles (SLCALIX $_{18}$ NPOE) is demonstrated by the ^{13}C CP-MAS spectrum in Figure 4E. The unfavorable surface-to-volume ratio for the SA11 particles impedes the observation of ^{13}C nuclei by the CP-MAS experiment, but the ^1H MAS NMR experiment clearly shows the presence of **5** and octadecyl species on their surface.

3.6. Colloid Stability and Light Scattering.

The stability behavior of the various colloids is summarized in Table 4. Some noteworthy results are the following. The Stöber silica (SA11) spheres modified with calixarene in NPOE have a much better colloidal stability than the Ludox (SL) particles. No gelation takes place when SA11 spheres are transferred by distillation from ethanol to pure NPOE, in contrast to SL particles. Sediments of SA11CALIXNPOE particles redisperse easily in chloroform and dimethylformamide. They flocculate in cyclohexane and ethanol. Remarkably the flocs in ethanol, and also stable suspensions in chloroform, can be dried and redispersed in chloroform to nonaggregated particles. The silica spheres (SA11CALIXNPOE) grafted with **5** have a long-term stability in chloroform: no aggregates were visible even after 8 months. Because of their size, the spheres settle eventually under the influence of gravity. In that case the dispersion can be easily homogenized by a few minutes of ultrasonication.

The Stöber silica (SA11) spheres grafted with octadecyl alcohol in NPOE show the same behavior as silica spheres grafted in an octadecyl alcohol melt:^{18,19} they form stable dispersions, in apolar solvents such as cyclohexane, and can also be redispersed after drying. The dynamic light scattering results for all modified Stöber silica spheres confirm that aggregation of particles is absent: diffusion coefficients of coated particles yield hydrodynamic radii which are the same as for the initial silica spheres (radius 90 nm) in ethanol–ammonia, as prepared by the Stöber synthesis.

The Ludox particles modified in NPOE show no visible signs of flocculation. The dispersity of grafted Ludox in various solvents follows the same trend as for grafted Stöber spheres mentioned above (see Table 4). Light-scattering results, however, indicate that all Ludox systems contain small particle aggregates when a coating reaction has been performed. We observed that uncoated Ludox particles tend to form a gel when transferred to NPOE. The gel disappears upon dilution and (or) mechanical stirring. Very likely small aggregates remain present which are subsequently coated.

Light-scattering measurements on Ludox particles in TEP (before, during, and after a coating procedure) yield reproducibly the same radius of about 15 nm expected for nonaggregated, freely diffusing colloids, in contrast to the results for Ludox particles in NPOE. So neither TEP nor the coating procedure destroys the colloidal stability of the Ludox particles. The sedimentation procedure to remove unreacted compounds, however, can induce aggregation in the case of SLCALIXTEP. Upon redispersion of calixarene–Ludox sediments in chloroform, aggregates remain present and no reliable light-scattering measurements are possible. The compressed sediments of SLC $_{18}$ TEP Ludox particles redisperse easily to free particles in cyclohexane and chloroform.

3.7. Elemental Analysis.

The former sections clearly demonstrate the presence of organic layers of compound **5** and/or octadecyl chains on silica particles. The layers are firmly attached to the silica cores. They also seem to be in general quite dense and fairly resistant to hydrolysis. In an illustrative experiment we stirred grafted silica particles in an aqueous sodium hydroxide solution (pH = 12.6). The idea was to (partly) dissolve the silica particles and/or hydrolyze the Si–O–C bonds by which grafting agents are linked to the silica. Any organic groups were extracted from the aqueous solution with methylene chloride. However, even after several weeks of stirring only minute amounts of extracted organic groups could be detected by NMR. This shows that the grafting layer is indeed quite stable against hydrolysis. We observed, however, that particles coated in TEP are less resistant

to hydrolysis than particles grafted in NPOE. This suggests that hydrolysis of the covalently linked phosphate (esters) preferentially takes place.

To gain more insight in grafted layers, we consider the results of elemental analysis, summarized in Table 3, starting with bare Ludox **SL** particles, going from left to right in Table 3A.

Grafted Ludox Particles. The **SL** particles contain some carbon, which may be due to a contamination with polyelectrolytes²⁵ from the resin used to remove Na⁺ ions. The **SLNPOE** particles contain more carbon, reflecting the presence of ethoxy or propoxy groups, as indicated by the NMR results. (Indeed, if the carbon would only stem from NPOE, for which H/C = 1.5, the measured H/C ratio would have been smaller.) The carbon content is equivalent to 3.8 ± 0.7 ethoxy groups per square nanometer of silica.

The **SLC₁₈NPOE** colloids have a ratio H/C = 2.15, which is close to the value of 2 for octadecyl chains. (The difference is due to protons from alkoxy groups or silanol.) Remarkably, the elemental composition is virtually the same as for Ludox particles grafted with C₁₈ chains in a melt of octadecyl alcohol;²⁶ the H/C ratios are even identical. This demonstrates that the grafting in NPOE is a good alternative and that very little NPOE is present on the final particles (as was also concluded from NMR).

To estimate the chain number density *c* on **SLC₁₈NPOE**, we use a mass density of 1.6 g/mL for grafted Ludox²⁶ and an average particle radius $R = 17 \pm 3$ nm. After evaluating the surface area per gram, assuming smooth spheres, it turns out that $c \approx 3.8 \pm 0.7$ nm⁻². As most bare silicas have about five silanols per square nanometer³⁴ we can conclude that the majority of these silanols (or ethoxy groups) have reacted with octadecyl alcohol to form a fairly dense alkyl layer.

Calix derivate **5** has a lower H/C ratio (H/C = 1.4) than octadecyl alcohol. Indeed we see that **SLCALIXNPOE** has the lowest H/C ratio of all the grafted Ludox systems (see Table 3A). From the carbon content we now find a coverage of $c = 1 \pm 0.18$ (calix) molecules per square nanometer. Remarkably, this area of 1 nm² per molecule is also the value found from Langmuir–Blodgett films.²⁶

The cograftering produces particles of **SLCALIXC₁₈NPOE** which have, according to NMR, indeed both moieties on the surface. The carbon content is about half the value for the “single grafted” systems for reasons which are not clear.

The elemental analysis results for the Ludox coated in TEP indicate that this solvent interferes with the grafting procedure and leads to lower surface coverages. The **SLTEP** particles, kept in refluxing TEP for several days, still contain TEP, despite the extensive washing procedures with ethanol (The presence of TEP on the particles was also detected by ³¹P MAS NMR). There is 0.8 wt % phosphorus present, and a molar ratio of C/P = 6.22, which is close to the value of C/P = 6 for pure TEP. The phosphorus coverage is about $c \approx 1.4 (\pm 0.17)$ nm⁻². So TEP is blocking “anchor sites” for the grafting agents. The affinity of TEP for silica could be explained by a partial transesterification reaction of TEP and the Ludox surface at high temperatures. This would also account for the presence of phosphorus, even after extensive washing with ethanol, as well as the higher instability against basic hydrolysis.

The adherence of TEP to silica also explains the good colloidal stability of (bare) Ludox particles in TEP (section 3.6), because it prevents colloids from touching each other and sticking together as a result of van der Waals attractions. It now also becomes clear why bare silica

tends to aggregate in NPOE, as discussed in section 3.6, because this solvent cannot react with the silica surface.

The **SLC₁₈TEP** and **SLCALIXTEP** colloids have, because of the partial TEP modification, lower surface grafting densities than their NPOE counterparts. These densities (see Table 3A) have been calculated after subtracting the carbon content from **SLTEP**, to correct for the presence of carbon from TEP. But even if all carbon is assigned to C₁₈ or calix, the grafting densities are still significantly lower than those for the particles coated in NPOE.

Grafted Stöber Spheres. The ungrafted **SA11** spheres contain a significant amount of carbon (see Table 3B) because of ethoxy groups which are incorporated in the particles during the Stöber synthesis.^{5,6}

The **SA11TEP** particles, kept in refluxing TEP for several days, still contain TEP, just as do the Ludox particles, despite extensive washing procedures. The mass densities of Stöber spheres are typically 1.8 (± 0.1) g/mL. Assuming smooth spheres with a radius $R = 90$ nm, we find from the phosphorous content a TEP coverage of about $c = 1$ nm⁻² on the silica surface. (The grafting densities for particles grafted in TEP, given in Table 3B, are calculated after subtracting the carbon content of the **SA11TEP** particles.)

3.8. Complexation Reactions. The resolution and sensitivity of the ¹H MAS NMR experiments also facilitate the monitoring of interactions of the organic coating with species in the solvent. Upon complexation of **SLCALIXNPOE** dispersed in CDCl₃ with a saturated Cs⁺ solution, significant changes in the ¹H MAS spectrum can be observed (Figure 6B vs Figure 6A). The observed downfield resonance shifts of the aromatic and OCH₂ protons indicate that the Cs⁺ cation is complexed in the crown moiety and also strongly interacts with the aromatic rings. The complexation-induced chemical shifts can be established unequivocally by means of a ¹H MAS TOCSY experiment (Figure 6D). The structural detail revealed by ¹H MAS NMR for colloidal receptors in the dispersed state is to our knowledge unprecedented and has potential for further studies on the dynamics of colloidal complexation.

3.9. Electrophoresis. The qualitative electrophoresis experiments for particles in NPOE gave the following results. **SA11NPOE** colloids in NPOE accumulated at the positive electrode and, hence, carry negative surface charge. The same observation was made for the grafted particles **SA11CALIXNPOE** and **SA11C₁₈CALIXNPOE**: the surface of the negative electrode remained clean, and a clearly visible deposit was formed after about 12–24 h on the positive electrode. A negative surface charge on grafted silica in (weakly) polar organic solvents is quite common and is possibly due to dissociation of unreacted surface silanol groups.³ The **CALIXC₁₈NPOE** particles, after the complexation experiment from section 2.3 transferred to pure NPOE, accumulated at the negative electrode. The experiment was repeated with several samples, with the same outcome. This shows that the particles are *positively* charged. This unusual behavior for silica particles is consistent with the presence of cesium cations on the surface which apparently outweigh the number of negative surface species. The fact that the complexed particles move at all in an electrical field suggests that the (chloride) counterions are relatively free to join the diffuse electrical double layer around the particles, instead of forming ion pairs with Cs⁺ on the silica surface.

4. Conclusions

We have studied synthesis procedures and properties of stable organic dispersions of silica colloids grafted with

receptor molecules and/or alkyl chains. The receptor is a calix[4]arene-crown-6 with two pendant alkyl chains with terminal OH groups for reaction with surface silanol groups from silica particles. Preliminary complexation experiments indicate that the grafted colloids collect cesium cations from their environment, as confirmed by NMR. Electrophoresis is consistent with a positive silica surface charge due to the complexed cations.

The receptor with alkyl chains and the grafting procedure (both silica colloids and grafting agents in refluxing organic solvent) were designed to mimic the conventional method for esterification of silica with a long-chain alcohol. Our results show that this approach works. A variety of techniques and observations (NMR, light scattering, colloidal stability, elemental analysis) confirm the presence of the expected organic groups (receptors, alkyl chains), firmly attached to the surface of the silica particles. Pertinent results are calix[4]arene-modified silica spheres in chloroform and C₁₈-coated spheres in cyclohexane which disperse easily, even after previous drying.

Another significant finding is that the solvent in which grafting takes place is a key to obtain stable dispersions of particles with a high grafting density. A suitable combination of solvent and type of silica is a first requirement for the synthesis of stable receptor colloids. There seem to be two somewhat conflicting requirements. A solvent such as triethyl phosphate (TEP) partly covers

a silica particle, promoting colloidal stability. The drawback is a lower grafting density of receptor molecules. A solvent such as NPOE, on the other hand, does not react with silica. This promotes a high grafting density because there are no blocked "anchor sites" for the grafting agent. The drawback here is a tendency for small Ludox silica particles to flocculate.

The Stöber silica spheres do not have this tendency to aggregate in NPOE. This suggests that Stöber silica particles in NPOE is an appropriate solvent-silica combination for further study of receptor colloids.

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