Self-assembly of tetracationic amphiphiles bearing a calix[4]arene core. Correlation between the core structure and the aggregation properties †

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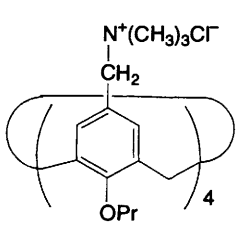
Water-soluble, conformationally-immobilized calix[4]arenes (**1** and **2_n**) with cone and 1,3-alternate conformations have been synthesized: at the *para*-position of each phenyl unit **1** has a $Me_3N^+CH_2$ group and **2_n** has a $Me_3N^+[CH_2]_nOCH_2$ group. Examinations with surface tension, fluorescence and dynamic light-scattering established that in water cone-**1** aggregates into small micellar particles whereas such molecular aggregates are not detected for 1,3-alternate-**1**. In **2_n** both the cone and 1,3-alternate isomers formed aggregates in water but the cone isomers always gave CAC (critical aggregation concentration) values lower than the 1,3-alternate isomers. These results consistently indicate that the cone **2_n** isomers with a cone-shaped hydrophobic surface are more cohesive intermolecularly than the 1,3-alternate **2_n** isomers with a cylindrical hydrophobic surface. From the molecular shape one can expect that the cone isomers favourably form a globular micelle whereas the 1,3-alternate isomers favourably form a two-dimensional lamella. This was evidenced by the fact that 1,3-alternate-**2_n** can form stable vesicular aggregates detectable by an electron microscope whereas cone-**2_n** cannot form such stable aggregates. These results demonstrate that the aggregation properties of calix[4]arene-containing amphiphiles can be controlled by the conformational structure difference in the calix[4]arene core.

In aqueous solution, amphiphilic compounds tend to aggregate so that they can reduce the surface area contacting with the bulk water phase. The energy gain thus obtained is the origin of a hydrophobic force.[1] The concept of the hydrophobic force suggests that if the hydrophobic surface shape of the monomer is different, the resultant aggregate formed in an aqueous medium may have a different three-dimensional architecture. Thus, the desired architecture may be tailor-made by skilfully designing the hydrophobic surface shape of the monomer as a building block. In the formation of synthetic bilayer membranes, for example, Kunitake *et al.*[2] demonstrated that the aggregation morphology can be partly regulated by the shape of the hard segment inserted into the central part of the amphiphile.

For several years, we and others have been accumulating a basic knowledge about the syntheses of various calix[4]arene conformers.[3-13] It has been established that introduction of *O*-substituents bulkier than an ethyl group (*e.g.*, propyl group) can inhibit the conformational isomerism which occurs *via* the oxygen-through-the-annulus rotation.[3,4] We here noticed that the surface shape of each conformer is quite different. If they aggregate in water so that they can reduce the surface area, their aggregation morphology should be also different. The idea has partly been realized by Regen *et al.*[14,15] and others[16,17] in a two-dimensional monolayer system. To the best of our knowledge, however, no precedent exists for the design of three-dimensional architectures from monomeric building blocks. Among calix[4]arene conformers, the surface shape of the cone and 1,3-alternate is particularly different: cone-calix[4]arene has a 'cone'-shaped surface[18] which will aggregate into a globular micelle [as in Fig. 1(*a*)] whereas 1,3-alternate-calix-[4]arene has a cylindrical surface[13,18,19] which will aggregate into a two-dimensional lamella [as in Fig. 1(*b*)]. To test this hypothesis, we synthesized water-soluble, conformationally-immobilized calix[4]arenes **1** and **2_n** (n = 4, 6 and 11) with a cone conformation or with a 1,3-alternate conformation. For synthetic simplicity cone-**1** and 1,3-alternate-**1** carry Cl^- ion whereas cone-**2_n** and 1,3-alternate-**2_n** carry I^- ion. Physical characterizations of these calix[4]arene-based amphiphiles have shown that in aqueous solution the cone isomers tend to aggregate more easily than the corresponding 1,3-alternate isomers and that only 1,3-alternate-**2_{11}** can form stable vesicles detectable by an electron microscope.

Results and discussion

We first examined the aggregate formation of cone-**1** and 1,3-alternate-**1** by three independent methods. Surface tension (Wilhelmy method) of aqueous **1** was measured in 'pure' water. As shown in Fig. 2, the surface tension for cone-**1** abruptly decreased at *ca.* 10^{-5} mol dm^{-3} whereas that for 1,3-alternate-**1** was almost constant up to 10^{-3} mol dm^{-3}. In Fig. 3 we illustrate



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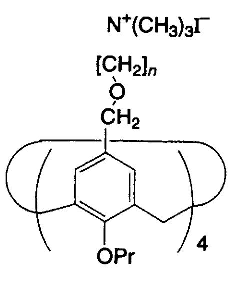
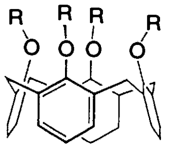
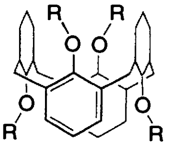


2*n* (*n* = 4, 6, 11)



Cone



1,3-Alternate

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† *Preliminary communication:* S. Arimori, T. Nagasaki and S. Shinkai, *J. Chem. Soc., Perkin Trans. 1*, 1993, 887 (as a *Perkin Communication*).

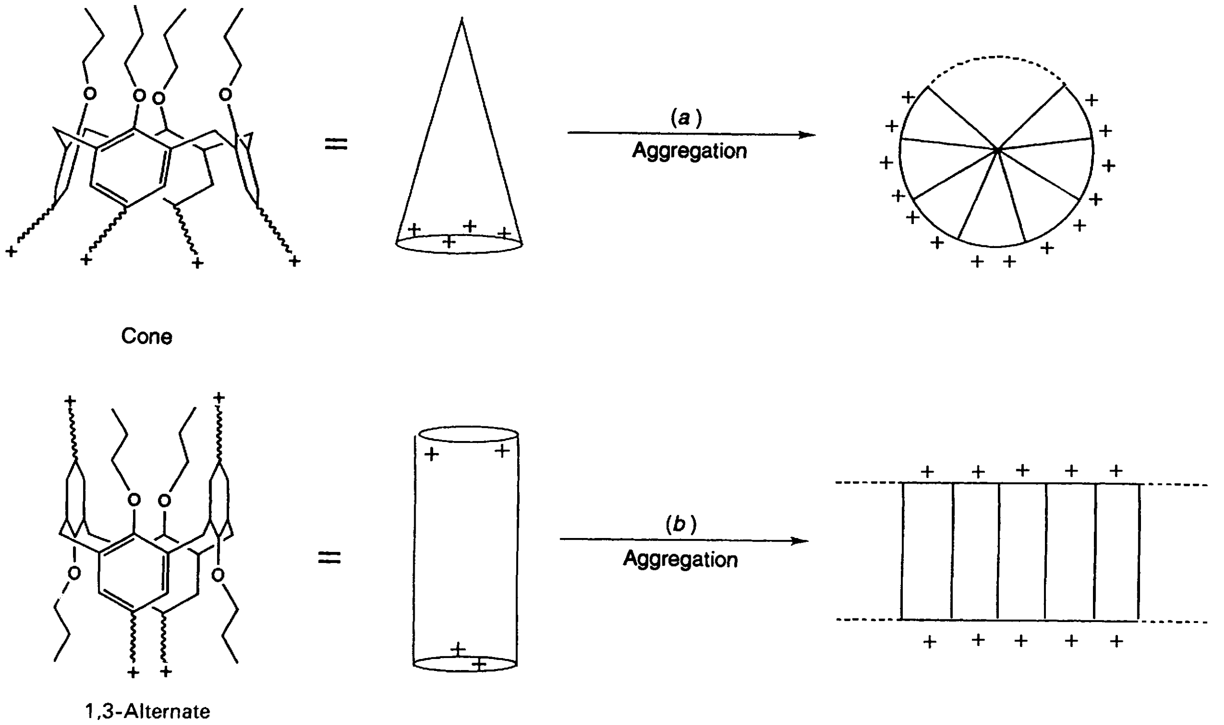

Fig. 1 Expected aggregation modes of cone-shaped cone-**1** (or $\mathbf{2}_n$) (*a*) and cylindrical 1,3-alternate-**1** (or $\mathbf{2}_n$) (*b*)

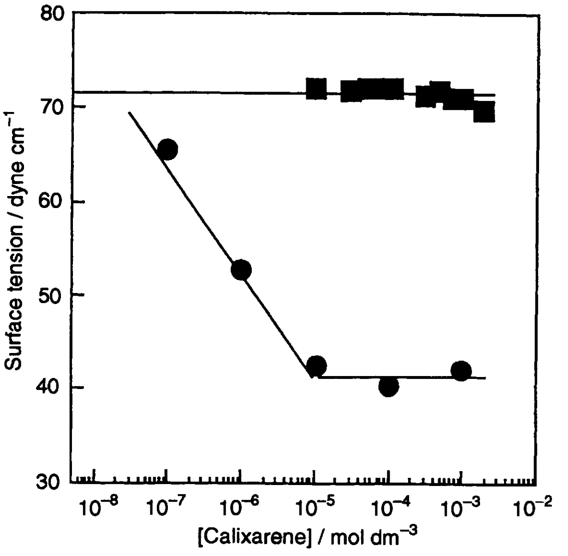

Fig. 2 Surface tension *vs.* concentration of **1** at 17 °C: (■) 1,3-alternate-**1**; (●) cone-**1**

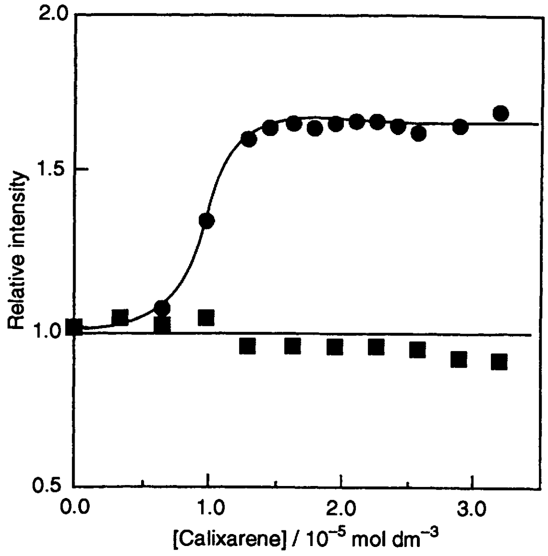

Fig. 3 Fluorescence intensity of 2-anilinonaphthalene (1.00×10^{-6} mol dm^{-3}) at 450 nm *vs.* concentration of **1** : 30 °C; excitation wavelength 315 nm; (■) and (●) as Fig. 2

the fluorescence intensity of a hydrophobic probe, 2-anilinonaphthalene in the presence of **1**. It is seen from this Figure that in the presence of cone-**1** the fluorescence intensity abruptly increases at 1.0×10^{-5} mol dm^{-3} whereas in the presence of 1,3-alternate-**1** the fluorescence intensity remains constant. The light-scattering measurement of aqueous **1** established that cone-**1** (0.010 mol dm^{-3}) aggregates into particles with a 20–40 Å diameter. Examination of CPK molecular models suggests that the length of the long axis of cone-**1** is about 15 Å and that of the short axis about 10 Å. Thus, each particle should consist of several (probably, < ten) molecules. In contrast, we could not find any particle for 1,3-alternate-**1** (0.010 mol dm^{-3}) detectable by the light-scattering method. The fact that even a particle with a 20 Å diameter cannot be found for 1,3-alternate-**1** allows us to conclude that 1,3-alternate-**1** exists discretely as a monomer even at 0.010 mol dm^{-3}. We consider that the interaction among cylindrical hydrophobic surfaces of 1,3-alternate-**1** is not strong enough to maintain the lamellar structure. The foregoing findings consistently support the view that the cone-shaped cone-**1** forms micellar aggregates at around 10^{-5} mol dm^{-3} whereas cylindrical 1,3-alternate-**1** does not form such aggregates up to 10^{-2} mol dm^{-3}. The difference implies that the aggregation mode is well regulated by the surface shape of calix[4]arene conformers.

To facilitate the aggregation in water we introduced aliphatic chains between the calix[4]arene and the four N^+Me_3 groups. The last step in the synthesis of $\mathbf{2}_n$ is methylation of dimethylamino groups by methyl iodide. We attempted several methods to exchange I^- in the products with Cl^- but to

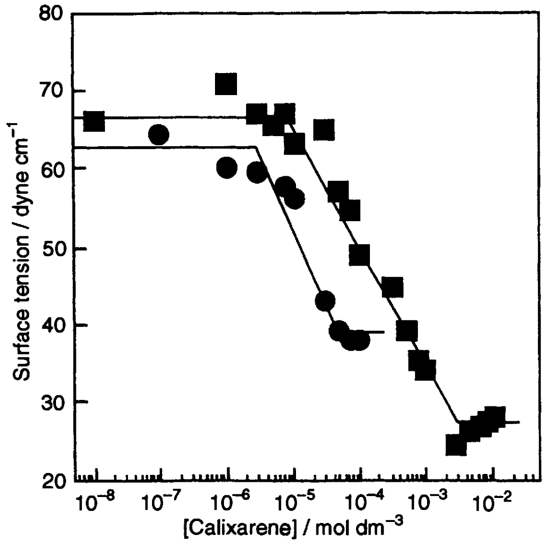

Fig. 4 Surface tension *vs.* concentration of $\mathbf{2}_4$ at 25 °C: (■) 1,3-alternate $\mathbf{2}_4$; (●) cone $\mathbf{2}_4$

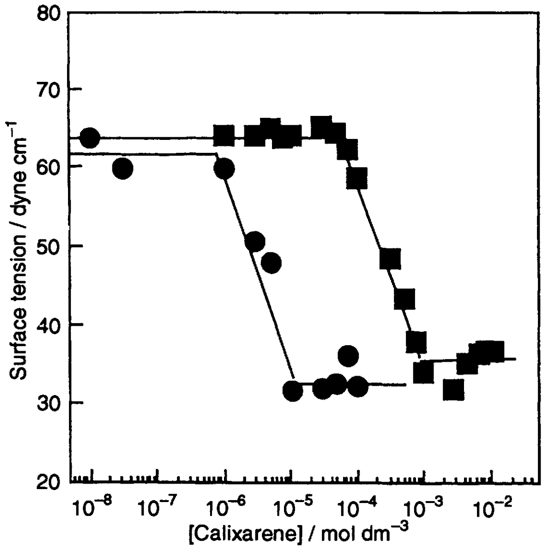

Fig. 5 Surface tension *vs.* concentration of $\mathbf{2}_6$ at 25 °C: (■) 1,3-alternate $\mathbf{2}_6$; (●) cone $\mathbf{2}_6$

completely replace I$^-$ with Cl$^-$ and to isolate the hygroscopic chloride salts was very difficult. Hence, we used the iodide salts for examination of the aggregation properties. Unfortunately, a fluorescence method cannot be applied to iodide-containing $\mathbf{2}_n$ because of the fluorescence quenching I$^-$. We thus estimated their aggregation properties by surface tension and light scattering. The results are summarized in Figs. 4–6 and Tables 1 and 2.

It is seen from Figs. 4–6 that in $\mathbf{2}_n$ both the cone and 1,3-alternate isomers form aggregates in water. The critical aggregate concentrations (CACs) become lower with increasing aliphatic chain length and the CAC values for the cone isomers are always lower than those for the corresponding 1,3-alternate isomers (Table 1). Thus, the CAC for cone-$\mathbf{2}_{11}$ (5.5 × 10^{-7} mol dm^{-3}) is lower by about four orders of magnitude than that for 1,3-alternate-$\mathbf{2}_4$ (3.0 × 10^{-3} mol dm^{-3}) and by about two orders of magnitude than that for 1,3-alternate-$\mathbf{2}_{11}$. These results consistently indicate that the cone-$\mathbf{2}_n$ isomers with a cone-shaped hydrophobic surface are more cohesive intermolecularly than the 1,3-alternate-$\mathbf{2}_n$ isomers with a cylindrical hydrophobic surface.

Table 1 Critical aggregation concentrations (mol dm^{-3}) of **1** and $\mathbf{2}_n$ determined by a surface tension method at 25 °C

	Conformation	
Calix[4]arene	Cone	1,3-Alternate
1[a]	1.0 × 10^{-5}	—[c]
1[b]	1.0 × 10^{-5}	—[c]
$\mathbf{2}_4$	5.0 × 10^{-5}	3.0 × 10^{-3}
$\mathbf{2}_6$	1.0 × 10^{-5}	1.0 × 10^{-3}
$\mathbf{2}_{11}$	5.5 × 10^{-7}	3.0 × 10^{-5}

[a] 17 °C. [b] Determined by a fluorescence method using 2-aminonaphthalene at 30 °C. [c] The CAC could not be detected.

Table 2 Average particle sizes (Å) of **1** and $\mathbf{2}_n$ determined by a dynamic light-scattering method at 30 °C[a]

	Particle size	
Calix[4]arene	Cone	1,3-Alternate
1	30	—[b]
$\mathbf{2}_4$	760	420
$\mathbf{2}_6$	680	930
$\mathbf{2}_{11}$	1150	1460

[a] 1.00 × 10^{-2} mol dm^{-3} for **1**, $\mathbf{2}_4$ and $\mathbf{2}_6$; 1.00 × 10^{-4} mol dm^{-3} for $\mathbf{2}_{11}$. [b] The aggregated particle could not be detected.

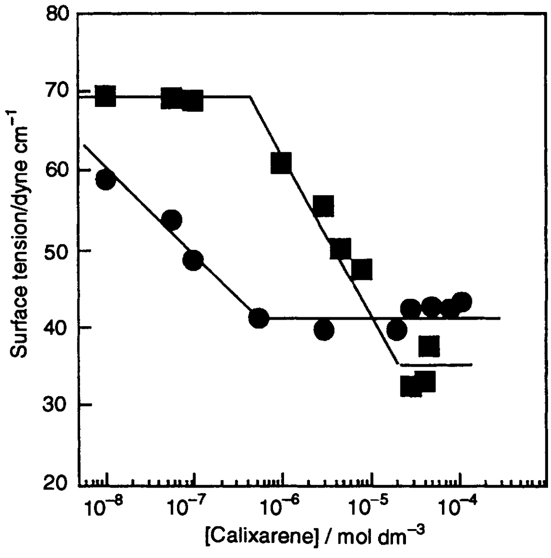

Fig. 6 Surface tension *vs.* concentration of $\mathbf{2}_{11}$ at 25 °C: (■) 1,3-alternate $\mathbf{2}_{11}$; (●) cone $\mathbf{2}_{11}$

The results of the light-scattering experiments are summarized in Table 2. In $\mathbf{2}_n$ we detected particles much larger than those for cone-**1** ranging from 424 to 1464 Å which change depending on the core structure and the aliphatic chain length. Careful examination of Table 2 reveals that in $\mathbf{2}_4$ the cone isomer aggregates into a particle larger than the 1,3-alternate isomer whereas in $\mathbf{2}_6$ and $\mathbf{2}_{11}$ the 1,3-alternate isomers aggregate into particles larger than the cone isomers. The inversion in the particle size implies that the aggregation mode of $\mathbf{2}_4$ is more or less similar to that of **1** whereas the aggregation mode of $\mathbf{2}_6$ and $\mathbf{2}_{11}$ is somewhat different from that of **1**. The working hypothesis of the present investigation is that inferring from their monomer shape, the cone isomer favourably forms a globular micelle whereas the 1,3-alternate isomer favourably forms a two-dimensional lamella. The two-dimensional lamella should have a molecular weight greater than the globular micelle but the maintenance of such gigantic aggregates should

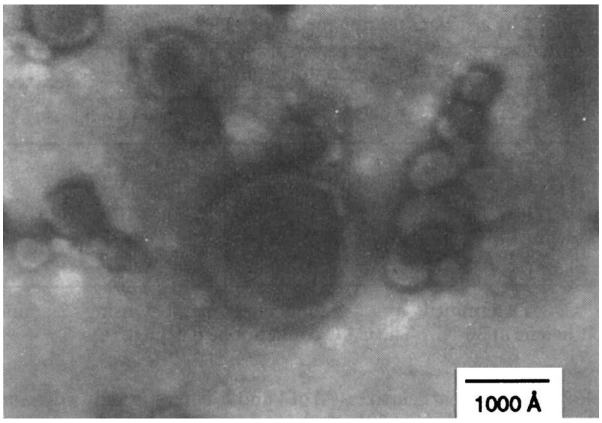

Fig. 7 Electron micrograph of 1,3-alternate-$\mathbf{2}_{11}$ vesicles; the sample solution was sonicated in the presence of uranyl acetate

be energetically difficult unless the monomer has a sufficient hydrophobic surface. This situation is reflected by an inverse in the molecular weight: although the 1,3-alternate isomers of **1** and $\mathbf{2}_4$ have a cylindrical molecular shape, the hydrophobic surface is not wide enough to maintain the lamella structure, whereas those of $\mathbf{2}_6$ and $\mathbf{2}_{11}$ are sufficiently hydrophobic and probably form lamellas with high molecular weights.

To obtain further insights into the aggregation mode of $\mathbf{2}_{11}$ we observed directly the aggregates by an electron microscope. This study was stimulated by electron-microscopic observations of bilayer membranes and bolaamphiphile membranes.[2,20,21] Fig. 7 shows a TEM picture of the 1,3-alternate-$\mathbf{2}_{11}$ aggregate. The sample was prepared by sonication of $\mathbf{2}_{11}$ in the presence of uranyl acetate. It is clearly seen from this picture that 1,3-alternate-$\mathbf{2}_{11}$ forms vesicular aggregates with a 1000–2000 Å diameter. The vesicular size is compatible with that determined by a light-scattering method (average particle 1460 Å). The thickness of the lamella is *ca.* 100 Å. Examination of CPK molecular models suggests that when the $[CH_2]_{11}$ chains in $\mathbf{2}_{11}$ adopt an extended zigzag conformation, the length of the long axis is 44 Å. We thus consider that the lamella consist of two layers but the resolution was not high enough to observe directly the two layers. In contrast, such a stable aggregate detectable by electron microscopy was not found for cone-$\mathbf{2}_{11}$. In addition, we carried out DSC studies of cone-$\mathbf{2}_{11}$ and 1,3-alternate-$\mathbf{2}_{11}$. 1,3-Alternate-$\mathbf{2}_{11}$ gave an exothermic peak (ΔH 120 kJ mol^{-1}) at 34 °C, indicating that 1,3-alternate-$\mathbf{2}_{11}$ forms oriented stable aggregates. For cone-$\mathbf{2}_{11}$, on the other hand, we could not observe such a DSC peak at 5–120 °C, suggesting that cone-$\mathbf{2}_{11}$ exists as thermodynamically stable aggregates like a globular micelle.

Conclusions

The present study demonstrates that the aggregation properties of amphiphiles are profoundly affected by the change in the molecular shape. In tetra-cationic amphiphiles with a calix[4]arene core, the cone isomers are always more cohesive than the 1,3-alternate isomers and 1,3-alternate-**1** cannot form as aggregate whereas 1,3-alternate $\mathbf{2}_{11}$ can form stable vesicles. The difference in the aggregation properties is reasonably explained by the difference in the molecular shape: that is, the cone isomers have a cone shape which is favourable to the formation of a globular micelle and the 1,3-alternate isomers have a cylindrical shape which is favourable to the formation of a lamella. It is known that calix[4]arene conformers can be modified by various substituents[3–13,22–24] and some of them are useful as a 'core' in starburst dendrimers.[25] We believe, therefore, that the basic skeleton of calix[4]arene conformers is useful for the design of a new surface shape, which will eventually lead to the regulation of the three-dimensional architecture of molecular assemblies.

Experimental

Preparation of cone- and 1,3-alternate-5,11,17,23-tetrakis(chloromethyl)-25,26,27,28-tetrapropoxycalix[4]arene (cone-**3** and 1,3-alternate-**3**, respectively) were described previously.[26–29] Since the preparation methods for the cone and 1,3-alternate isomers are similar to each other, we here describe the preparation methods for the cone isomers and simply record the analytical data for the 1,3-alternate isomers.

5,11,17,23-Tetrakis(trimethylammoniomethyl)-25,26,27,28-tetrapropoxycalix[4]arene tetrachloride (1)

Cone-**3** (500 mg; 0.64 mmol) was dissolved in dimethylformamide (DMF) (50 cm^3). To this solution was introduced trimethylamine (gas) for 1 h at room temperature. The precipitate was collected by filtration, washed with chloroform and dried *in vacuo*. Cone-**1**: yield 37%, mp (decomp.) > 235 °C; δ_H[D_2O; 3-trimethylsilylpropanesulfonic acid, sodium salt (DSS) standard; 25 °C; 250 MHz] 1.03 (12 H, t, CCH_3), 2.01 (8 H, m, CH_2 in Pr), 2.91 [36 H, s, $N(CH_3)_3$], 3.44 and 4.57 (4 H each, d each, $ArCH_2Ar$), 4.01 (8 H, t, OCH_2), 4.23 (8 H, s, NCH_2) and 6.97 (8 H, s, ArH) (Found: C, 64.65; H, 8.1; N, 5.35. $C_{56}H_{88}Cl_4N_4O_4{\cdot}H_2O$ requires C, 64.59; H, 8.73; N, 5.38%). The treatment of 1,3-alternate-**3** in a similar manner gave 1,3-alternate-**1**: yield 12%, mp (decomp.) > 269 °C; δ_H(D_2O; DSS standard; 25 °C; 250 MHz) 0.89 (12 H, t, CCH_3), 1.56 (8 H, m, CH_2 in Pr), 3.02 [36 H, s, $N(CH_3)_3$], 3.72 (8 H, t, OCH_2), 3.95 (8 H, s, NCH_2), 4.35 (8 H, s, $ArCH_2Ar$) and 7.36 (8 H, s, ArH) (Found: C, 63.9; H, 8.4; N, 5.2. $C_{56}H_{88}Cl_4N_4O_4{\cdot}2H_2O$ requires C, 63.49; H, 8.77; N, 5.29%). The water content in these samples has been confirmed by a Karl–Fischer titration.

5,11,17,23-Tetrakis(trimethylammoniobutyloxymethyl)-25,26,-27,28-tetrapropoxycalix[4]arene tetraiodide ($\mathbf{2}_4$)

N,*N*-Dimethylaminobutan-1-ol (0.85 cm^3; 5.12 mmol) and potassium *tert*-butoxide (690 mg; 6.14 mmol) were dispersed into THF (20 cm^3) and the mixture was stirred for 30 min at room temperature. Cone-**3** (500 mg; 0.64 mmol) was added and then the reaction mixture was refluxed for one day under a nitrogen stream. After cooling, the mixture was diluted with aqueous 5% $NaHCO_3$ solution (100 cm^3). After cooling in an ice-bath, the organic layer was separated, washed with NaCl-saturated water and dried over $MgSO_4$. The concentration of this solution *in vacuo* resulted in a yellow oil. The product was used without further purification for quaternization with methyl iodide (2.0 cm^3; 6.18 mmol) in DMF (20 cm^3) at room temperature for 12 h. The solution was concentrated *in vacuo* to dryness, the residue being purified by column chromatography (Sephadex LH-20, methanol). Cone-$\mathbf{2}_4$: yield 74%, mp 146–149 °C; δ_H(CD_3OD; Me_4Si; 25 °C; 250 MHz) 1.03 (12 H, t, CCH_3), 1.64 (8 H, m, CH_2 in Pr), 1.93 (16 H, m, $OC[CH_2]_2$), 3.17 [36 H, s, $N(CH_3)_3$], 3.39 (8 H, t, NCH_2), 3.44 (8 H, t, OCH_2) 3.55 and 4.49 (4 H each, d each, $ArCH_2Ar$), 3.86 (8 H, t, OCH_2 in Pr) and 4.19 (8 H, s, $ArCH_2$), 6.67 (8 H, s, ArH) (Found: C, 53.5; H, 7.2; N, 3.0. $C_{72}H_{120}I_4N_4O_8{\cdot}1.2C_6H_{14}$ requires C, 53.05; H, 7.63; N, 3.13%). The treatment of 1,3-alternate-**3** in a similar manner gave 1,3-alternate-$\mathbf{2}_4$: yield 62%, mp (decomp.) > 245 °C; δ_H(CD_3OD; Me_4Si; 25 °C; 250 MHz) 0.90 (12 H, t, CCH_3), 1.54 (8 H, m, CH_2 in Pr), 1.72 (8 H, m, CH_2CN), 1.85 (8 H, m, $OCCH_2$), 3.15 [36 H, s, $N(CH_3)_3$], 3.41 (8 H, t NCH_2), 3.49 (8 H, t, OCH_2), 3.55 (8 H, t, OCH_2 in Pr), 3.68 (8 H, s, $ArCH_2Ar$), 4.35 (8 H, s, $ArCH_2$) and 7.01 (8 H, s, ArH) (Found: C, 51.8; H, 7.15; N, 3.1. $C_{72}H_{120}I_4N_4O_8$ requires C, 51.55; H, 7.22; N, 3.34%).

5,11,17,23-Tetrakis(trimethylammoniohexyloxymethyl)-25,26,-27,28-tetrapropoxycalix[4]arene tetraiodide ($\mathbf{2}_6$)

Cone-$\mathbf{2}_6$ was synthesized by the reaction of cone-**3** and *N*,*N*-dimethylaminohexan-1-ol followed by quaterization with methyl iodide in a manner similar to that described for $\mathbf{2}_4$: yield 67%, mp 132–135 °C; δ_H(CD_3OD; Me_4Si standard; 25 °C; 250 MHz) 1.03 (12 H, t, CCH_3), 1.46 (16 H, m, $OCC[CH_2]_2$), 1.60 (8 H, m, CH_2 in Pr), 1.81 (8 H, m, $OCCH_2$), 1.99 (8 H, m, $NCCH_2$), 3.14 [36 H, s, $N(CH_3)_3$], 3.34 (8 H, t, NCH_2), 3.38 (8 H, t, OCH_2), 3.40 and 4.49 (4 H each, d each, $ArCH_2Ar$), 3.86 (8 H, t, OCH_2 in Pr), 4.14 (8 H, s, $ArCH_2$) and 6.74 (8 H, s, ArH) (Found: C, 54.4; H, 7.63; N, 2.9. $C_{80}H_{136}I_4N_4O_8\cdot0.7C_6H_{14}$ requires C, 53.31; H, 7.91; N, 3.01%). The treatment of 1,3-alternate-**3** in a similar manner gave 1,3-alternate-$\mathbf{2}_6$: yield 74%, mp 125–128 °C; δ_H(CD_3OD, Me_4Si standard; 25 °C; 250 MHz) 0.91 (12 H, t, CCH_3), 1.45 (16 H, m, $OCC[CH_2]_2$), 1.50 (8 H, t, CH_2 in Pr), 1.62 (8 H, m, $OCCH_2$), 1.80 (8 H, m, $NCCH_2$), 3.07 [36 H, s, $N(CH_3)_3$], 3.50 (8 H, t, NCH_2), 3.39 (8 H, t, OCH_2), 3.48 (8 H, t, OCH_2 in Pr), 3.66 (8 H, s, $ArCH_2Ar$), 4.32 (8 H, s, $ArCH_2$) and 6.99 (8 H, s, ArH) (Found: C, 53.8; H, 7.6; N, 3.0. $C_{80}H_{136}I_4N_4O_8$ requires C, 53.69: H, 7.68; N, 3.13%).

5,11,17,23-Tetrakis(trimethylammonioundecycloxymethyl)-25,26,27,28-tetrapropoxycalix[4]arene tetraiodide ($\mathbf{2}_{11}$)

Cone-$\mathbf{2}_{11}$ was synthesized by the reaction of cone-**3** and *N*,*N*-dimethylaminoundecan-1-ol followed by quaterization with methyl iodide in a similar manner to that described for $\mathbf{2}_4$: yield 43%, mp 145–148 °C; δ_H(CD_3OD; Me_4Si standard; 25 °C; 250 MHz) 1.01 (12 H, t, CCH_3), 1.30 (56 H, m, $OCC[CH_2]_7$), 1.53 (16 H, m, CH_2 in Pr, $NCCH_2$), 1.77 (8 H, m, $OCCH_2$), 3.13 [36 H, s, $N(CH_3)_3$], 3.28 (8 H, t, NCH_2), 3.33 (8 H, t, OCH_2), 3.45 and 4.48 (4 H each, d each, $ArCH_2Ar$), 3.84 (8 H, t, OCH_2 in Pr), 4.13 (8 H, s, $ArCH_2$), 6.72 (8 H, s, ArH) (Found: C, 57.5; H, 8.8; N, 2.35. $C_{100}H_{176}I_4N_4O_8\cdot CH_3OH$ requires C, 57.70; H, 8.65; N, 2.67%). The treatment of 1,3-alternate-**3** in a similar manner gave 1,3-alternate-$\mathbf{2}_{11}$: yield 34%, mp 93–95 °C; δ_H(CD_3OD; Me_4Si standard; 25 °C; 250 MHz) 0.96 (12 H, t, CCH_3), 1.33 (56 H, m, $OCC[CH_2]_7$), 1.50–1.70 (24 H, m, CH_2 in Pr, $NCCH_2$, $OCCH_2$), 3.30 [36 H, s, $N(CH_3)_3$], 3.40 (8 H, t, NCH_2), 3.38 (8 H, t, NCH_2), 3.43 (8 H, t, OCH_2), 3.46 (8 H, t, OCH_2 in Pr), 3.63 (8 H, s, $ArCH_2Ar$), 4.31 (8 H, s, $ArCH_2$) and 6.98 (8 H, s, ArH) (Found: C, 57.4; H, 8.8; N, 2.2. $C_{100}H_{176}I_4N_4O_8\cdot1.8CH_3OH$ requires C, 57.45; H, 8.69; N, 2.63%).

Estimation of aggregation properties

Surface tension was estimated by a Wilhelmy method using a Kyowa ESB-IV apparatus. The detail of the method was described previously.[30] The light-scattering measurements were carried out on an Otsuka Electronics DLS-700 apparatus. The fluorescence measurements were carried out on a Hitachi 650-10S spectrophotometer. Electron microscopy (Hitachi H-500 electron microscope) was used for the observation of the aggregates formed from cone- and 1,3-alternate-$\mathbf{2}_{11}$. $\mathbf{2}_{11}$ (1.35 mg; 0.65 mmol) was dispersed into aq 2% uranyl acetate solution (2 cm^3) and the mixture was sonicated with a Branson Sonifer (Model 185) for 2 min at room temperature. The sample was prepared according to the method reported by Kunitake and Okahata.[31] The DSC measurements were carried out on a Seiko SSC/5200 Calorimeter. The concentrations of the aqueous sample solutions were 10–45 mmol dm^{-3} for cone-$\mathbf{2}_{11}$ and 1.0 mmol dm^{-3} for 1,3-alternate-$\mathbf{2}_{11}$.

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