

Dendritic Host Molecules with a Polycationic Core and an Outer Shell of Dodecyl Groups

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The synthesis of a topologically new type of dendrimer is presented in which a permanently positively charged core is decorated with a shell that is apolar and aliphatic in nature. The novel polyionic dendrimers were successfully applied as hosts for a predefined number of anionic guests, as is shown for the dye methyl orange. The aliphatic periphery of the dendrimers efficiently shields the ion pairs and renders the

dendrimers fully soluble in organic solvents that are as apolar as hexane and, furthermore, provides them with an interesting phase behavior that appears not to be sensitive to the type of anion associated with it.

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Introduction

Applications of dendrimers can be found in many scientific fields, for example, in photochemistry,^[1] nanoscience,^[2] homogeneous catalysis,^[3] and host–guest chemistry.^[4] The large diversity of functional dendrimers can be explained by considering their unique branched structure consisting of three distinctive segments; the core, the dendritic shell, and the periphery with multiple end groups. The controlled stepwise synthesis of dendrimers allows selective functionalization of each of the segments of the dendritic structure. Functionalities can either be introduced by means of covalent incorporation of a functional moiety in one of the segments, or otherwise, by means of noncovalent interaction of the dendrimer with functional “guests”. The internal voids between the dendritic branches can accommodate guest molecules,^[5] which makes dendrimers good candidates as container molecules for binding and delivery of multiple substrate molecules.^[6] A first example of a dendritic container molecule is the “dendritic box” reported by Meijer and coworkers, which involves a poly(propyleneimine) dendrimer that physically entraps substrate molecules in its internal voids.^[7] More recently, our group introduced ionic core, shell dendrimers that consist of a rigid polyionic core decorated with a soft condensed shell of Fréchet-type polybenzyl aryl ether dendrons (Figure 1).^[8] These polyionic dendrimers were successfully applied as container molecules for various anionic (in)organic substrate molecules. The permanent charges in the dendrimer core predefine the

number of guest molecules that are bound by these dendrimers. This property allows the formation of well-defined dendritic assemblies with a discrete number of reversibly bound functional moieties as diverse as dyes,^[8] homogeneous catalysts,^[9] and fullerenes.^[10] In these host–guest systems, the functional guest molecules are positioned with their anionic (anchoring) group towards the ammonium sites in the core of the dendrimer.^[11] As a consequence of

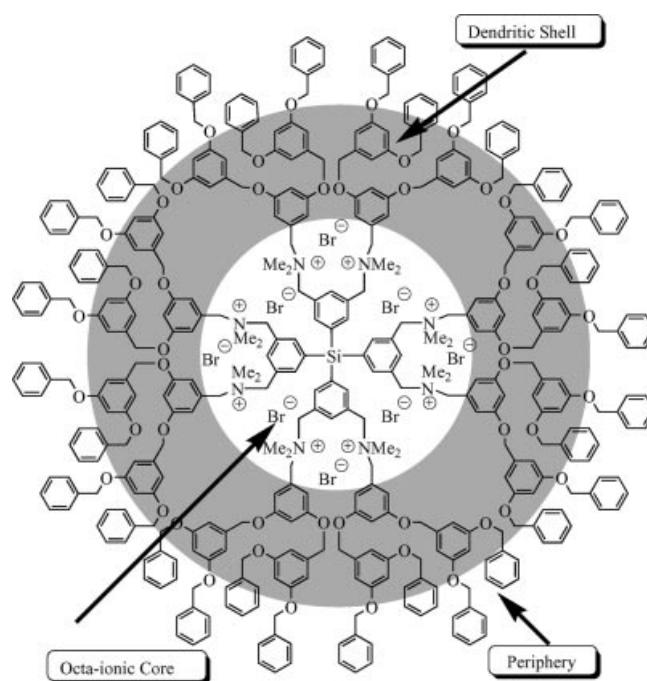


Figure 1. A core–shell dendrimer that bears an octacationic core with bromide anions as counterions, a polybenzyl aryl ether shell, and a periphery of benzyl end groups.

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this binding mode, the rest of the guest molecule is either sticking outside the dendritic structure or is located in the voids of the dendritic structure depending on the length of the molecule and the thickness of the dendritic shell. Interestingly, functional groups that are embedded by a dendritic shell can experience a (a)polar nanoenvironment created by the dendritic structure, which may influence the properties of the functional head group.^[12]

In the present study, we changed the Fréchet-type^[13] polybenzyl aryl ether shell of the dendrimers (Figure 1) to a Percec-type^[14] shell with apolar (dodecyl) end groups (Figure 2). By selectively varying the nature of the dendritic shell around the polyionic core moiety, we aim to modify the physical properties of the dendrimer while leaving the host–guest binding properties unaffected. Through the long aliphatic tails, the resulting polyionic dendrimers [1]Br₈ and [2]Br₄ (Figure 2) can be expected to be soluble in apolar solvents and to more effectively shield a bound functional guest. To investigate whether the novel apolar shell influences the host–guest properties of the dendrimer, the bind-

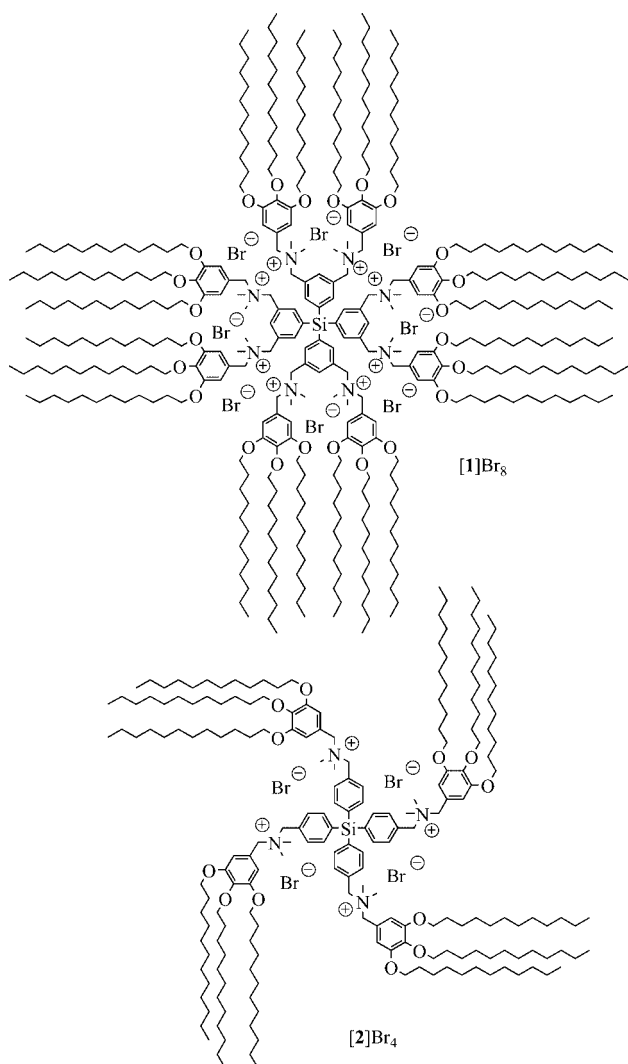


Figure 2. Dendritic molecules [1]Br₈ and [2]Br₄ bearing a polyionic core and an outer shell of dodecyl groups.

ing properties of these dendrimers were studied by means of their interaction with the anionic dye methyl orange (MO).

Several examples exist of neutral dendritic compounds that are covalently functionalized at the periphery with long aliphatic tails attached to gallic acid like building blocks.^[14–16] Studies on the thermotropic properties of these dendrimers revealed interesting phase behaviors for this type of dendrimer. We have, therefore, also studied the phase behavior of novel polyionic dendrimers [1]Br₈ and [2]Br₄, and their MO assemblies. Additionally, di- and monoionic wedges [3]Br₂ and [4]Br were prepared, which show structural resemblance to one quarter of the polyionic dendrimers (Figure 3). The properties of [3]Br₂ and [4]Br were subsequently analyzed and compared with those of polyionic dendrimers [1]Br₈ and [2]Br₄.

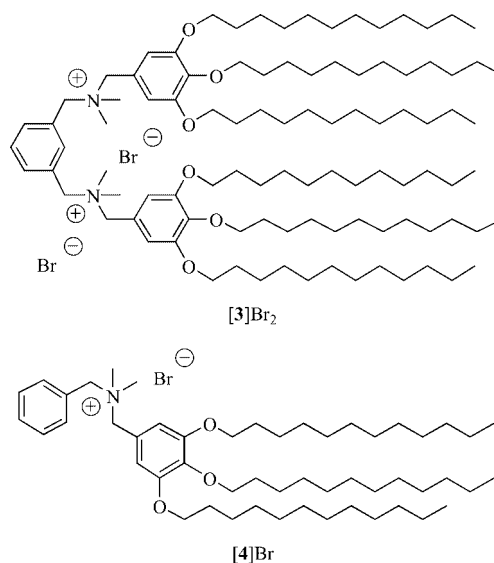


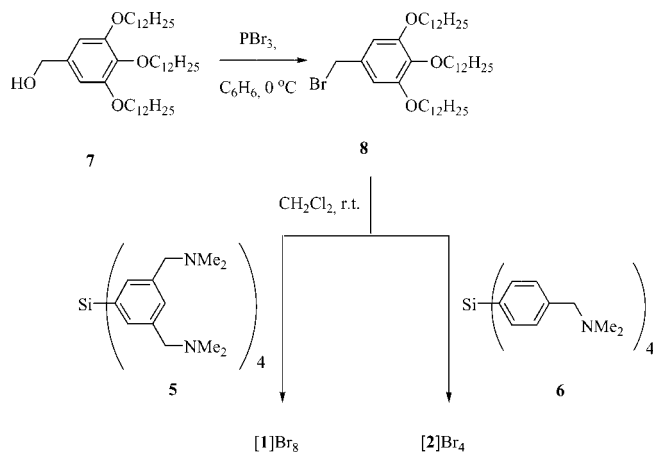
Figure 3. Dendritic wedges [3]Br₂ and [4]Br with a di- or monoionic focal point.

Results and Discussion

Synthesis and Characterization of Ionic Core-Shell Dendrimers [1]Br₈ and [2]Br₄

Dendrimers [1]Br₈ and [2]Br₄ were prepared by using a convergent synthetic route starting from the core molecules tetrakis(3,5-bis[(dimethylamino)methyl]phenyl)silane [Si(NCN)₄; **5**], tetrakis(4-[(dimethylamino)methyl]phenyl)silane [Si(CN)₄; **6**], and 3,4,5-tridodecyloxybenzyl bromide (**8**) (Scheme 1).^[17] Core molecules Si(NCN)₄ (**5**) and Si(CN)₄ (**6**) were prepared according to literature procedures^[8,18] and **8** was synthesized from 3,4,5-tridodecyl-oxybenzyl alcohol (**7**)^[14] (Scheme 1). A solution of **7** in benzene was treated with PBr₃, which afforded **8** as a white solid in 94% isolated yield. The benzylic bromide group of **8** was allowed to react with amino-functionalized core molecules **5** and **6**, which afforded the quaternized molecules [1]Br₈ and [2]Br₄, respectively. A slight excess of **8** was used to ensure full quaternization of the oligo(amino) cores.

The excess amount of unreacted **8** was easily removed by washing the crude products with acetone to afford **[1]Br₈** (74% yield) and **[2]Br₄** (80% yield) as waxy white solids.



Scheme 1. Convergent synthesis for polyionic core, shell dendrimers **[1]Br₈** and **[2]Br₄**.

The NMR spectroscopic, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis data of **[1]Br₈** and **[2]Br₄** are in full agreement with their proposed structures (see Figure 6 for ¹H NMR spectrum of **[1]Br₈**). In the ESI-MS spectra of **[1]Br₈** and **[2]Br₄**, characteristic ion peaks were observed that correspond to the polycationic dendritic backbone with a variable number of bromide counterions. The spectrum recorded for **[1]Br₈** (MW = 6585.2) showed several characteristic fragment ion peaks at $m/z = 3213.8$ (calcd. for **[[1]Br₆]²⁺** 3212.7), 2115.7 (calcd. for **[[1]Br₅]³⁺** 2115.2), and 1566.8 (calcd. for **[[1]Br₄]⁴⁺** 1566.4) (Figure 4). The spectrum recorded for **[2]Br₄** (MW = 3460.8) showed typical fragment ions at $m/z = 1650.7$ (calcd. for **[[2]Br₂]²⁺** 1650.5) and 1073.9 (calcd. for **[[2]Br]³⁺** 1073.7). In the mass spectra of both **[1]Br₈** and **[2]Br₄**, the 3,4,5-tridodecyloxybenzyl cation was observed at $m/z = 643.8$ (calcd. 644.1). Furthermore, peaks were observed that can be attributed to dimeric clustered species derived from **[1]Br₈** and **[2]Br₄**, that is, $m/z = 2554.9$ (calcd. for **[2 × [1]Br₈ - 5Br]⁵⁺** 2554.2) and 2228.0 (calcd. for **[2 × [2]Br₄ - 3Br]³⁺** 2227.3), respectively. These characteristic ion peaks in the mass spectra unequivocally point to the formation of dendritic molecules **[1]Br₈** and **[2]Br₄**.

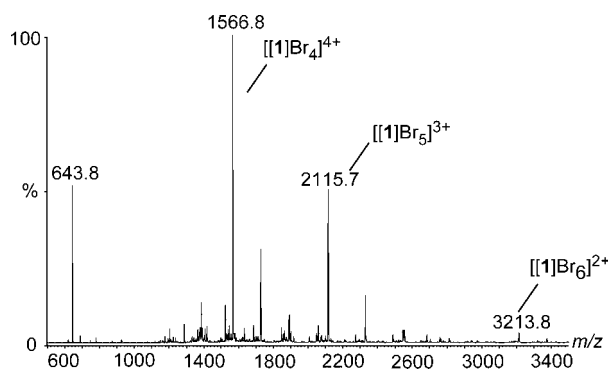


Figure 4. ESI-MS spectrum of octaionic dendrimer **[1]Br₈**.

Synthesis and Characterization of **[3]Br₂** and **[4]Br**

In addition to the synthesis of the two polyionic dendrimers, diionic wedge **[3]Br₂** and monoionic wedge **[4]Br** were synthesized (Figure 3). Quantitative quaternization of 1,3-bis[(dimethylamino)methyl]benzene and *N,N*-dimethylbenzylamine with a slight excess of dendron **8** afforded compounds **[3]Br₂** (yield 45%) and **[4]Br** (71% yield), respectively, as white solids. The NMR spectroscopic data of **[3]Br₂** and **[4]Br** are in agreement with their proposed structures and confirm the quantitative quaternization of the amino groups.

Synthesis and Characterization of Dendrimer/Methyl Orange Host–Guest Assemblies

To investigate whether the apolar shell around the polyionic core influences the host–guest properties of the novel polyionic dendrimers, the binding properties of cationic dendritic moieties **[1]⁸⁺**, **[2]⁴⁺**, **[3]²⁺**, and **[4]⁺** were studied by using methyl orange (MO) as a guest molecule.^[19] The binding studies were performed according to a standard procedure that was developed earlier in our group.^[8] A biphasic system consisting of a slight excess of MO (Na[MO]) in deionized water and a solution of ionic dendritic molecules **[1]Br₈**, **[2]Br₄**, **[3]Br₂**, or **[4]Br** in dichloromethane was used to exchange the bromide anions of the dendritic molecules for MO. Thorough mixing of the biphasic system gave rise to an instantaneous colorization of the organic phase. Because Na[MO] is insoluble in dichloromethane, the color change indicated that anion exchange had occurred. The orange organic layer was separated and repeatedly washed with deionized water to remove sodium bromide. The orange-colored assemblies obtained by this procedure were analyzed with ¹H and ¹³C{¹H} NMR spectroscopy, and ESI-MS. ¹H NMR spectroscopic analysis of the assemblies allowed the determination of the stoichiometry of the ion exchange procedure, that is, the ratio of MO to dendritic host. Specific peak integration in the ¹H NMR spectra showed that in all four experiments stoichiometric exchange of the bromide anions had been achieved (Table 1); the assemblies are correctly formulated as **[1][MO]₈**, **[2][MO]₄**, **[3][MO]₂**, and **[4][MO]** (Figure 5). Moreover, when an excess of MO was used in the exchange procedure, the formation of the assemblies with higher MO contents was not observed. The maximum amount of MO that is accommodated by the novel core–shell dendrimers is, therefore, predefined by the number of ammonium sites comprised in the core of the dendritic compounds. A sim-

Table 1. The number of MO anions accommodated by polycationic dendritic molecules **[1]⁸⁺** and **[2]⁴⁺** and cationic wedges **[3]²⁺** and **[4]⁺** as determined by ¹H NMR spectroscopy.

| Host–guest assembly | MO/Host |
|----------------------------|---------|
| [1][MO]₈ | 7.60 |
| [2][MO]₄ | 3.95 |
| [3][MO]₂ | 1.98 |
| [4][MO] | 1.03 |

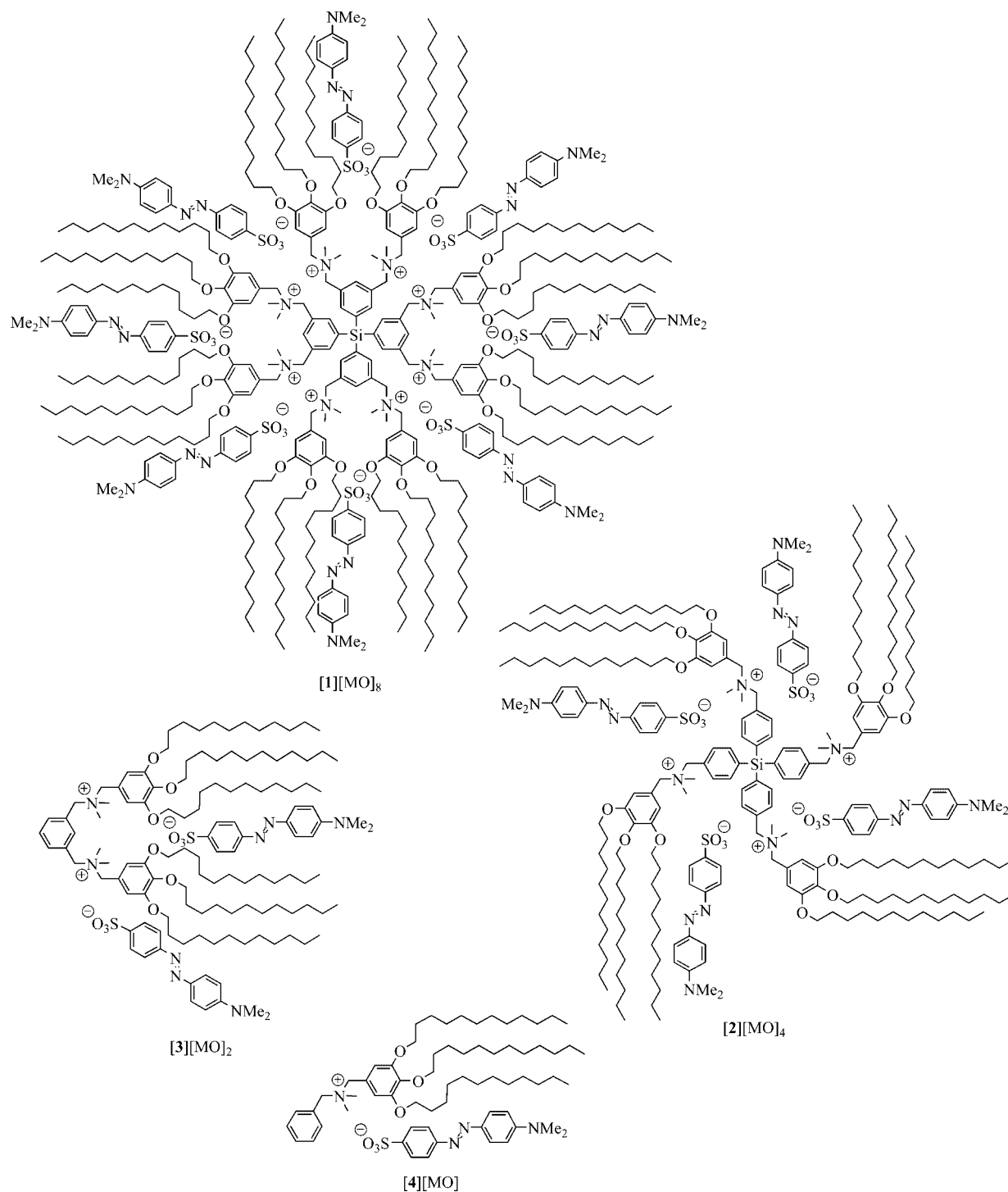


Figure 5. MO assemblies [1][MO]₈, [2][MO]₄, [3][MO]₂, and [4][MO].

ilar behavior was earlier observed for ionic core, shell dendrimers with a shell of polybenzyl aryl ether dendrons.^[8] The binding stoichiometry of the ionic core-shell dendrimers is, therefore, not altered by the presence of long aliphatic groups at the periphery.

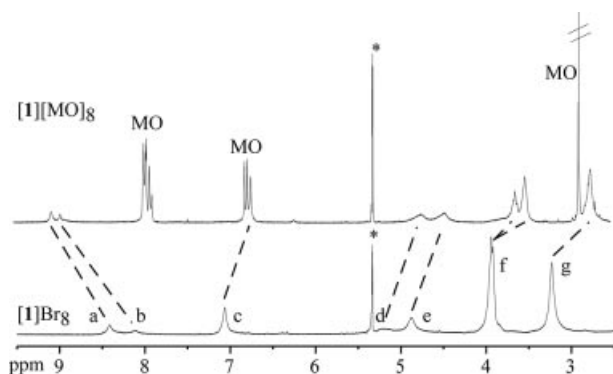
¹H NMR spectroscopic analysis furthermore allowed the determination of the positioning of the MO anions with respect to the dendritic backbone (Table 2). The ¹H NMR

spectra of octaionic dendrimer [1]Br₈ and its corresponding MO assembly [1][MO]₈ are shown in Figure 6.

Upfield shifts (0.2–0.4 ppm) were found for protons in the core of dendrimer [1]⁸⁺ upon introduction of MO, [NMe₂ grouping (g), benzylic protons (d, e), and aromatic protons of the dendritic wedge (c)], whereas strong downfield shifts of 0.5–0.7 ppm were observed for the Ar-H of the tetraphenylsilane core unit (a, b). Similar changes in the

Table 2. Selected ^1H NMR spectroscopic data of the cationic host in [1]Br₈, [2]Br₄, [3]Br₂, and [4]Br, and their corresponding MO assemblies in CD₂Cl₂ (10⁻³ M) at room temperature.

| Compound | ArH _{core} or ArH _{focal} | CH ₂ NCH ₂ Ar | NMe ₂ | ArH _{shell} | OCH ₂ |
|----------------------|---|-------------------------------------|------------------|----------------------|------------------|
| [1]Br ₈ | 8.40, 8.10 | 5.16, 4.85 | 3.21 | 7.05 | 3.95 |
| [1][MO] ₈ | 8.85, 8.75 | 4.78, 4.53 | 2.92 | 6.66 | 3.74, 3.64 |
| [2]Br ₄ | 7.84, 7.24 | 5.34, 4.88 | 3.15 | 6.85 | 3.97 |
| [2][MO] ₄ | 7.81, 7.26 | 5.15, 4.71 | 2.97 | 6.71 | 3.84, 3.74 |
| [3]Br ₂ | 8.62, 7.83, 7.57 | 5.14, 4.83 | 3.15 | 6.86 | 3.98 |
| [3][MO] ₂ | 8.51, 7.52 | 4.95, 4.71 | 3.07 | 6.73 | 3.91, 3.84 |
| [4]Br | 7.64, 7.52 | 5.01, 4.96 | 3.09 | 6.84 | 3.99 |
| [4][MO] | 7.56, 7.48 | 4.82, 4.81 | 3.01 | 6.81 | 3.92 |

Figure 6. The ^1H NMR spectra of dendrimer [1]Br₈ (bottom) and the corresponding MO assembly [1][MO]₈ (top). Spectra were recorded in [D₂]dichloromethane, * denotes residual solvent peak.

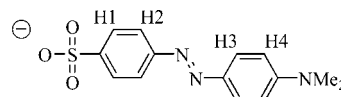
chemical shift values were found for tetraionic dendrimer [2]Br₄ upon formation of dendritic MO assembly [2][MO]₄. The changes in the chemical shift values were, however, smaller than those found for octaionic dendrimer [1][MO]₈. For the tetraphenylsilane core of [2]Br₄, the chemical shift values are unaffected upon formation of the MO assembly. Remarkably, the ^1H NMR spectra of dendritic MO assemblies [1][MO]₈ and [2][MO]₄ show two poorly resolved triplets with a 2:1 ratio for the upfield shifted OCH₂ protons (f) of the dodecyl tails, whereas original dendrimers [1]Br₈ and [2]Br₄ show one broad signal.

In addition, small shifts were observed for the protons of the MO guests, more specifically the protons *ortho* to the sulfonato grouping (see H1 in Table 3). These aryl protons shift upfield (0.04–0.08 ppm) in the presence of the polycationic dendrimers and downfield (0.08–0.1 ppm) in the presence of the di- and monocationic wedge. The peaks of the other aryl protons (H2–H4) and the dimethylamino group (NMe₂) of the MO guest hardly shift in the presence of the cationic host molecules.

The diagnostic shifts observed for the cationic host moieties and MO in the NMR spectra of [1][MO]₈, [2][MO]₄, [3][MO]₂, and [4][MO] show that the MO guests are indeed bound to the (dendritic) host molecules. The strong shifts of the protons of the ammonium sites of the host molecules strongly indicate that the sulfonato group of the MO guest is located nearby the cationic site(s) of the host molecules. In the case of dendritic MO assemblies [1][MO]₈ and

Table 3. Selected ^1H NMR spectroscopic data of the anionic guest in MO assemblies [1][MO]₈, [2][MO]₄, [3][MO]₂, and [4][MO] and the tetrabutylammonium salt of MO in CD₂Cl₂ (10⁻³ M) at room temperature.

| Compound | H1 | H2 | H3 | H4 | NMe ₂ |
|-------------------------|------|------|------|------|------------------|
| [Bu ₄ N][MO] | 7.87 | 7.78 | 7.86 | 6.77 | 3.08 |
| [1][MO] ₈ | 7.83 | 7.75 | 7.82 | 6.71 | 3.05 |
| [2][MO] ₄ | 7.81 | 7.77 | 7.81 | 6.72 | 3.05 |
| [3][MO] ₂ | 7.95 | 7.81 | 7.86 | 6.77 | 3.10 |
| [4][MO] | 7.97 | 7.79 | 7.85 | 6.76 | 3.08 |



[2][MO]₄, MO is expected to fill up the internal voids of the dendritic hosts to afford a more congested molecular structure. The separation of the OCH₂ peaks of [1][MO]₈ and [2][MO]₄ may be due to a restricted mobility of the dendritic shell. A congested dendritic structure would prevent MO from penetrating as deeply into the dendritic structure as the bromide anions, which explains the downfield shifts observed for the tetraphenylsilane core of dendritic MO assembly [1][MO]₈. The idea of a more congested shell is supported by the results obtained with less-congested assembly [2][MO]₄, and wedges [3][MO]₂ and [4][MO].^[20] The introduction of MO guests gives smaller shifts of the protons nearby the cationic site(s), and smaller or, in the case of [4][MO], no separation of the OCH₂ peaks. As a result of the “open” structure of [3][MO]₂ and [4][MO], the signals of the protons of the aryl groups at the focal point (ArH_{focal}) shift upfield instead of downfield as was observed for assembly [1][MO]₈.

To gain more insight into the molecular structures of MO assemblies [1][MO]₈ and [2][MO]₄, molecular mechanics calculations (MMFF94) were performed.^[21] The calculated structure of [1][MO]₈ (5.1 × 4.8 × 4.5 nm) consists of a spherical dendritic backbone that accommodates eight MO guests. Assembly [2][MO]₄ bears four MO guests and comprises a less congested disc-shaped structure (5.0 × 4.3 × 1.9 nm) (Figure 7). The dodecyl groups of the outer shell were set to an all-*trans* conformation prior to the optimization of the molecular structure. Though the dodecyl groups retain their *trans* conformation, the aliphatic

tails can easily adopt various alternative conformations at room temperature. The calculated structures depicted in Figure 7 should therefore be considered as “fully stretched” structures of $[1][MO]_8$ and $[2][MO]_4$. In assemblies $[1][MO]_8$ and $[2][MO]_4$, the sulfonato groups of the MO guests are located nearby the ammonium sites in the core of the dendritic backbone and the MO guests of assembly $[1][MO]_8$ are embedded by the dendritic host. These observations are fully consistent with the results obtained by NMR spectroscopy.

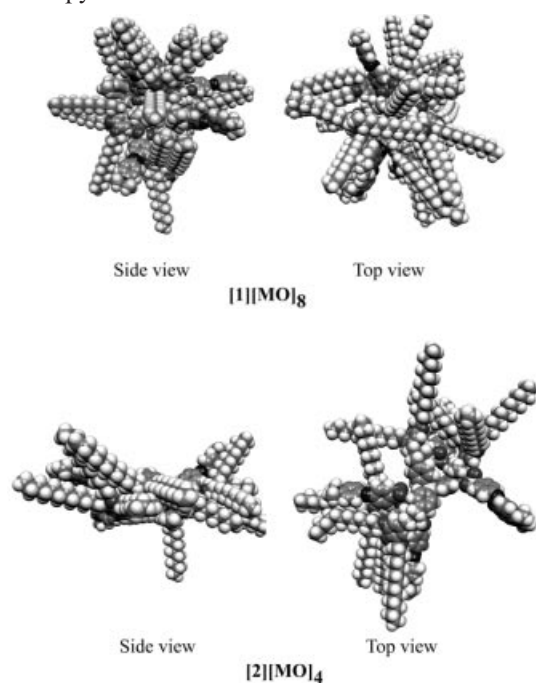


Figure 7. Space filling models of the calculated molecular structures of dendritic MO assemblies $[1][MO]_8$ and $[2][MO]_4$ (side and top view).

Solubility Properties

The earlier reported polyionic polybenzyl aryl ether dendrimers are soluble in chlorinated hydrocarbons and toluene, but are insoluble in hexane.^[8] The fact that dendrimers $[1]Br_8$ and $[2]Br_4$, as well as their corresponding MO assemblies $[1][MO]_8$ and $[2][MO]_4$, are soluble in apolar solvents like hexane implies an excellent shielding of the ion pairs in the core by the aliphatic groups. Solubility studies in hexane showed that the solubility of the MO assemblies decreases going from $[1][MO]_8$, $[2][MO]_4$, $[3][MO]_2$ to $[4][MO]$. For comparison, the tetrabutylammonium salt of MO is very poorly soluble in hexane, which is most probably due to the less efficient shielding of the ion pair. These observations clearly demonstrate the influence of the shell on the solubility profile of the core-shell dendrimers.

Phase Behavior

The incorporation of liquid crystalline fragments in a dendritic structure offers interesting possibilities for the

construction of macromolecules with specific physical properties and has thus been actively studied.^[15,16,22] Several systems have been reported in which 3,4,5-tridodecyloxybenzyl groups are appended to the periphery as mesogenic units, similar to the compounds described here. This, together with the fact that some examples of *ionic* liquid-crystalline dendrimers have been reported,^[16,23] prompted us to study the phase behavior of our polyionic dendrimers, the model compounds, and the MO assemblies. An initial study of the phase behavior of dendrimers $[1]Br_8$ and $[2]Br_4$ and wedges $[3]Br_2$ and $[4]Br$ was performed by using thermal optical polarization microscopy (TOPM) and differential scanning calorimetry (DSC). In addition, the thermal stability of these compounds was studied by thermogravimetric analysis (TGA).

Ionic core-shell dendrimers $[1]Br_8$ and $[2]Br_4$ are waxy and malleable solids, which show birefringent domains under the polarization microscope that become more fluid at higher temperatures. An irreversible transition to an isotropic liquid occurs at temperatures of 170 and 176 °C for $[1]Br_8$ and $[2]Br_4$, respectively. Accordingly, the DSC traces of dendrimers $[1]Br_8$ and $[2]Br_4$ do not show any reversible transitions in the 20–190 °C range. TGA shows that the irreversible transitions are caused by thermal decomposition of $[1]Br_8$ and $[2]Br_4$ ($T_{dec} = 170$ and 176 °C, respectively). Similar irreversible isotropization was observed for dendritic wedge $[3]Br_2$ ($T_{dec} = 175$ °C). In the case of $[4]Br$, however, the anisotropic phase does restore itself again upon cooling of the isotropic liquid. Indeed, the DSC shows one phase transition at 137 °C ($\Delta H = 44.9$ kJ mol⁻¹) in good agreement with the observations made under the microscope. According to TGA, thermal decomposition of $[4]Br$ occurs at 145 °C.

To study the influence of the MO guest molecules on the phase behavior of the corresponding dendrimer assemblies, $[1][MO]_8$ and $[2][MO]_4$ were also analyzed by TOPM and DSC. Dendritic MO assemblies $[1][MO]_8$ and $[2][MO]_4$ both show birefringence at room temperature. Upon heating, the malleable specimens gradually become more fluid, while the anisotropy remains. Isotropic liquids are irreversibly formed at 120 and 160 °C, respectively. The phase behavior of dendrimers $[1]Br_8$ and $[2]Br_4$ is, therefore, not substantially changed upon the incorporation of MO. The only effect that is observed is that the introduction of MO anions causes a decrease in the thermal stability by 16 and 50 °C for $[1]Br_8$ and $[2]Br_4$, respectively. In the case of host-guest assemblies $[1][MO]_8$ and $[2][MO]_4$ based on dendrimers $[1]Br_8$ and $[2]Br_4$, the properties are predominated by the dendritic backbone, that is, the MO guest molecules are subjected to the properties of the dendritic backbone. These findings are supported by the solubility profiles earlier observed for MO assemblies $[1][MO]_8$ and $[2][MO]_4$, which are very similar to those of dendrimers $[1]Br_8$ and $[2]Br_4$.

Conclusions

We have presented the synthesis of a topologically new type of dendrimer in which a permanently positively

charged core is covered by a peripheral shell that is apolar and fully aliphatic in nature. Owing to the presence of the ammonium groups in the core, these dendrimers can be used as hosts for a predefined number of anionic guests, as was shown for MO. The aliphatic periphery renders the dendrimers soluble in organic solvents that are as apolar as hexane. The binding properties of the core are not influenced by this aliphatic shell in comparison to a more polar shell like, for example, Fréchet-type polybenzyl aryl ether wedges. Remarkably, the phase behavior of these dendrimers appear not to be sensitive to the type of anions that are associated with them, as was exemplified for MO whose macroscopic properties, but not its functional properties, are “overruled” by that of the dendritic host. In this respect, this class of dendrimers can be regarded as versatile hosts for anionic functional guests. As a result of their topology, they may, furthermore, be of interest as highly charged nancontainers or reactors in apolar media.

Experimental Section

General Remarks: All solvents were carefully dried and distilled prior to use. Compounds **5**,^[18] **6**,^[8] and **7**^[14] were prepared according to reported procedures. ¹H and ¹³C{¹H} NMR spectroscopic measurements were carried out with a Varian Mercury or Inova spectrometer (200 and 300 MHz, respectively) at 25 °C and chemical shifts (δ) are given in ppm relative to the residual solvent peak. Differential scanning calorimetry was performed by using a Mettler DSC 12E with the samples in sealed aluminium pans (heating rate 10 °Cmin⁻¹). Thermogravimetry was performed with a Perkin–Elmer TGS-2 thermogravimetric system under a nitrogen atmosphere (heating rate 10 °Cmin⁻¹). Thermal optical polarization microscopy was carried out with a Leitz Metallux 3 polarization microscope provided with a Linkam THMS 600 hot stage and a Linkam TMS 91 temperature controller. Elemental analyses were performed by Dornis und Kolbe, Mühlheim a/d Ruhr, Germany. Time-of-flight electrospray ionization mass spectra were recorded with a Micromass LC-TOF mass spectrometer operating in the positive ion mode by the department of Biomolecular Mass Spectrometry, Utrecht University. In all experiments, dendrimer samples at a concentration of 10–20 μ M were introduced into the electrospray needles. The nanospray needle potential was typically set to 1300 V and the cone voltage to 60 V. The source block temperature was set to 80 °C.

3,4,5-Tridodecyloxybenzyl Bromide (8): To a solution of 3,4,5-tridodecyloxybenzyl alcohol (**7**) (40.26 g, 61 mmol) in benzene (250 mL) at 0 °C was added dropwise a solution of PBr₃ (1.99 mL, 21 mmol) in benzene (50 mL) under a nitrogen atmosphere. The solution was warmed to room temperature and stirred overnight. At the point where NMR spectroscopic and TLC (hexanes/dichloromethane, 1:1) analysis indicated full consumption of alcohol **7**, the yellowish reaction mixture was poured into iced water (250 mL), whereupon CH₂Cl₂ (100 mL) was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 \times 50 mL). The combined organic layers were washed with H₂O (200 mL), dried with MgSO₄, filtered, and concentrated in vacuo to give **8** as a white powder (41.39 g, 57 mmol, 94%). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 6.57 (s, 2 H, ArH), 4.43 (s, 2 H, CH₂Br), 3.96 (m, 6 H, OCH₂), 1.76 (m, 6 H, OCH₂CH₂), 1.27 (m, 54 H, 9 \times CH₂), 0.88 (m, 9 H, CH₃) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃, 25 °C): δ = 153.2, 138.4, 132.5, 107.5, 73.5, 69.1, 34.6, 31.9,

30.3, 29.7, 29.6, 26.1, 22.7, 14.1 ppm. C₄₃H₇₉BrO₃ (723.99): calcd C 71.34, H 11.00; found C 71.45, H 11.12.

[1]Br₈: A mixture of Si(NCN)₄ (**5**; 150 mg, 0.19 mmol) and **8** (1.20 g, 1.66 mmol) in CH₂Cl₂ (150 mL) was stirred for 24 h at room temperature. The slightly yellow solution was concentrated in vacuo and excess **8** was removed by washing with acetone (5 \times 50 mL) to afford [1]Br₈ as a yellow–white waxy solid (0.91 g, 0.14 mmol, 74%). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 8.40 [s, 8 H, ArH(core)], 8.10 [s, 4 H, ArH(core)], 7.05 [s, 16 H, ArH(shell)], 5.16 [s, 16 H, NCH₂(shell)], 4.85 [s, 16 H, CH₂N(core)], 3.95 (br. signal, 48 H, OCH₂), 3.21 [s, 48 H, N(CH₃)₂], 1.68 (m, 48 H, OCH₂CH₂), 1.40 (m, 48 H, OCH₂CH₂CH₂), 1.26 (m, 384 H, 8 \times CH₂), 0.88 (m, 72 H, CH₃) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃, 25 °C): δ = 153.5, 143.4, 140.2, 129.3, 122.0, 112.0, 73.6, 69.8, 67.5, 48.9, 32.1, 31.9, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 26.3, 22.8, 14.2 ppm. ESI-MS: m/z = 3213.8 (3212.7 calcd. for [[1]Br₆]²⁺), 2554.9 (2554.2 calcd. for [2 \times [1]Br₈ - 5Br]⁵⁺), 2115.7 (2115.2 calcd. for [[1]Br₅]³⁺), 1566.8 (1566.2 calcd. for [[1]Br₄]⁴⁺), 643.8 (644.1 calcd. for [C₄₃H₇₉O₃]⁺). C₃₉₂H₇₀₈Br₈N₈O₂₄Si (6585.17): calcd. C 71.50, H 10.84, N 1.70; found C 71.81, H 10.76, N 1.64.

[2]Br₄: A mixture of Si(CN)₄ (**6**) (400 mg, 0.71 mmol) and **8** (2.31 g, 3.19 mmol) in CH₂Cl₂ (150 mL) was stirred for 24 h at room temperature. The slightly yellow solution was concentrated in vacuo and excess **8** was removed by washing with acetone (5 \times 50 mL). Product [2]Br₄ was obtained as a white powder (1.95 g, 0.56 mmol, 80%). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 7.84 [d, ³J_{H,H} = 7.2 Hz, 8 H, ArH(core)], 7.24 [d, ³J_{H,H} = 7.5 Hz, 8 H, ArH(core)], 6.85 [s, 8 H, ArH(wedge)], 5.34 [s, 8 H, NCH₂(shell)], 4.88 [s, 8 H, CH₂N(core)], 3.97 (br. signal, 24 H, OCH₂), 3.15 [br. s, 24 H, N(CH₃)₂], 1.72 (m, 24 H, OCH₂CH₂), 1.46 (m, 24 H, OCH₂CH₂CH₂), 1.27 (m, 192 H, 8 \times CH₂), 0.87 (t, ³J_{H,H} = 6.6 Hz, 36 H, CH₃) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃, 25 °C): δ = 153.5, 140.4, 136.6, 133.3, 129.8, 121.6, 111.9, 73.5, 69.7, 69.1, 67.2, 48.4, 31.9, 30.4, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 26.1, 22.6, 14.0 ppm. ESI-MS: m/z = 2228.0 (2227.3 calcd. for [2 \times [2]Br₄ - 3Br]³⁺), 1650.7 (1650.5 calcd. for [[2]Br₂]²⁺), 1073.9 (1073.7 calcd. for [[2]Br]³⁺), 643.8 (644.1 calcd. for [C₄₃H₇₉O₃]⁺). C₂₀₈H₃₆₄Br₄N₄O₁₂Si (3460.84): calcd. C 72.19, H 10.60, N 1.62, Br 9.24; found C 72.11, H 10.64, N 1.57, Br 9.34.

[3]Br₂: A mixture of 1,3-bis[(dimethylamino)methyl]benzene (33 mg, 0.17 mmol) and **8** (260 mg, 0.36 mmol) in CH₂Cl₂ (40 mL) was stirred at room temperature for 24 h. The colorless solution was concentrated in vacuo, and the crude product was purified by two consecutive precipitations from CH₂Cl₂ by adding acetone. Product [3]Br₂ was obtained as a white powder (130 mg, 0.08 mmol, 46%). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 8.62 [s, 1 H, ArH(core)], 7.83 [d, ³J_{H,H} = 7.6 Hz, 2 H, ArH(core)], 7.57 [t, ³J_{H,H} = 7.8 Hz, 1 H, ArH(core)], 6.86 [s, 4 H, ArH(wedge)], 5.14 [s, 4 H, NCH₂(shell)], 4.83 (s, 4 H, CH₂N), 3.98 (br. signal, 12 H, OCH₂), 3.15 [s, 12 H, N(CH₃)₂], 1.75 (m, 12 H, OCH₂CH₂), 1.27 (m, 108 H, 9 \times CH₂), 0.88 (t, ³J_{H,H} = 6.6 Hz, 18 H, CH₃) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃, 25 °C): δ = 153.3, 139.8, 138.5, 135.2, 129.8, 128.7, 121.7, 111.6, 73.4, 69.6, 68.7, 66.9, 65.1, 48.7, 31.9, 30.4, 29.7, 29.6, 29.5, 29.3, 26.2, 26.1, 24.9, 22.6, 14.1 ppm. ESI-MS: m/z = 1560.38 (1560.02 calcd. for [[3]Br]⁺), 1061.80 (1602.79 calcd. for [[3] + CH₃C₆H₂(OC₁₂H₂₅)₃]²⁺), 836.27 (836.39 calcd. for [[3] - CH₂C₆H₂(OC₁₂H₂₅)₃]⁺), 740.24 (740.80 calcd. for [3]²⁺), 644.27 (644.09 calcd. for [CH₂C₆H₂(OC₁₂H₂₅)₃]⁺). C₉₈H₁₇₈Br₂N₂O₆·2H₂O (1676.31): calcd. C 70.22, H 10.94, N 1.67; found C 69.97, H 10.57, N 1.40.

[4]Br: A mixture of dimethylbenzylamine (56 mg, 0.41 mmol) and **8** (286 mg, 0.40 mmol) in CH₂Cl₂ (40 mL) was stirred for 24 h at

room temperature. The colorless solution was concentrated in vacuo, and the crude product was washed with hexanes (40 mL) to give [4]Br as a white powder (250 mg, 0.29 mmol, 71%). ^1H NMR (200 MHz, CD_2Cl_2 , 25 °C): δ = 7.64 [d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, ArH(core)], 7.46 [m, 3 H, ArH(core)], 6.84 [s, 2 H, ArH(wedge)], 5.01 [s, 2 H, NCH_2 (shell)], 4.96 (s, 2 H, CH_2N), 3.99 (br. signal, 6 H, OCH_2), 3.09 [s, 6 H, $\text{N}(\text{CH}_3)_2$], 1.75 (m, 6 H, OCH_2CH_2), 1.48 (m, 6 H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.27 (m, 48 H, $8 \times \text{CH}_2$), 0.88 (t, $^3J_{\text{H,H}} = 6.6$ Hz, 9 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3 , 25 °C): δ = 153.3, 140.0, 133.3, 130.5, 129.0, 127.4, 111.8, 73.4, 69.5, 68.2, 67.3, 48.2, 31.8, 30.3, 29.7, 29.6, 29.6, 29.4, 29.3, 26.1, 26.0, 22.6, 14.0 ppm. ESI-MS: m/z = 1637.77 (1638.49 calcd. for $[2 \times [4]\text{Br} - \text{Br}]^+$), 779.29 (779.19 calcd. for $[4]^+$). $\text{C}_{52}\text{H}_{92}\text{BrNO}_3$ (859.20): calcd. C 72.69, H 10.79, Br 9.30, N 1.63; found C 72.78, H 10.67, Br 9.42, N 1.54.

General Preparation and Characterization of Dendritic MO Assemblies: A solution of methyl orange ($\text{Na}[\text{MO}]$; 43 mg, 151 μmol , 4.5 equiv.) in deionized water (25 mL) was added to a solution of $[2]\text{Br}_4$ (100 mg, 29 μmol) in dichloromethane (25 mL) and the mixture was vigorously stirred overnight at room temperature. The orange-colored dichloromethane layer was separated off and washed with deionized water. The organic layer was then dried with Na_2SO_4 and concentrated in vacuo. The red solid $[2][\text{MO}]_4$ was isolated in 87% yield (110 mg, 25.2 μmol). From the ^1H NMR spectrum, the amount of MO anions in the assemblies was calculated by using specific signal integration (see Table 1).

[1][MO]₈: ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 8.85 [s, 8 H, ArH(core)], 8.75 [s, 4 H, ArH(core)], 7.83 [d, $^3J_{\text{H,H}} = 8.1$ Hz, 16 H, ArH(MO)], 7.82 [d, $^3J_{\text{H,H}} = 9.3$ Hz, 16 H, ArH(MO)], 7.75 [d, $^3J_{\text{H,H}} = 8.1$ Hz, 16 H, ArH(MO)], 6.71 [d, $^3J_{\text{H,H}} = 9.3$ Hz, 16 H, ArH(MO)], 6.66 [s, 16 H, ArH(wedge)], 4.78 [s, 16 H, NCH_2 (shell)], 4.53 (s, 16 H, CH_2N), 3.74 (t, 16 H, OCH_2), 3.64 (t, 32 H, OCH_2), 3.05 [s, 48 H, $\text{N}(\text{CH}_3)_2$ (MO)], 2.92 [s, 48 H, $\text{N}(\text{CH}_3)_2$], 1.54 (m, 48 H, OCH_2CH_2), 1.23 (m, 432 H, $9 \times \text{CH}_2$), 0.86 (m, 72 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 154.0, 153.9, 153.3, 148.5, 144.1, 140.3, 129.7, 127.1, 125.7, 122.6, 111.9, 74.0, 69.9, 49.4, 40.6, 32.6, 32.5, 31.0, 30.1, 30.0, 26.9, 26.7, 23.3, 14.5 ppm. ESI-MS: m/z = 2487.6 (2489.22 calcd. for $[[1][\text{MO}]_5]^{3+}$), 1790.25 (1790.83 calcd. for $[[1][\text{MO}]_4]^{4+}$), 1950.77 (1952.11 calcd. for $[[1][\text{MO}]_4 + \text{CH}_3\text{C}_6\text{H}_2(\text{OC}_{12}\text{H}_{25})_3]^{4+}$), 606.87 (608.69 calcd. for $[[\text{MO}]_2]^+$), 301.91 (304.35 calcd. for $[\text{MO}]^+$).

[2][MO]₄: ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 7.99 [d, $^3J_{\text{H,H}} = 8.4$ Hz, 8 H, ArH(MO)], 7.81 [d, $^3J_{\text{H,H}} = 9.0$ Hz, 16 H, ArH(MO) and ArH(core)], 7.77 [d, $^3J_{\text{H,H}} = 8.7$ Hz, 8 H, ArH(MO)], 7.26 [br. signal, 8 H, ArH(core)], 6.72 [d, $^3J_{\text{H,H}} = 9.0$ Hz, 8 H, ArH(MO)], 6.68 [s, 8 H, ArH(wedge)], 5.15 (s, 8 H, NCH_2), 4.71 (s, 8 H, CH_2N), 3.84 (t, 8 H, OCH_2), 3.74 (t, 16 H, OCH_2), 3.05 [s, 24 H, $\text{N}(\text{CH}_3)_2$ (MO)], 2.97 [s, 24 H, $\text{N}(\text{CH}_3)_2$], 1.62 (m, 24 H, OCH_2CH_2), 1.22 (m, 216 H, $9 \times \text{CH}_2$), 0.86 (m, 36 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 153.9, 153.8, 153.2, 148.3, 143.9, 140.1, 137.3, 133.9, 130.5, 127.1, 125.6, 122.7, 122.5, 111.9, 73.9, 69.7, 48.4, 40.6, 32.5, 30.9, 30.4, 30.3, 30.2, 30.0, 26.9, 26.7, 23.3, 14.5 ppm. ESI-MS: m/z = 1874.9 (1875.0 calcd. for $[[2][\text{MO}]_2]^{2+}$), 1148.6 (1148.5 calcd. for $[[2][\text{MO}]_3]^{3+}$), 785.4 (785.3 calcd. for $[2]^{4+}$).

[3][MO]₂: ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 8.51 [s, 1 H, ArH(core)], 7.95 [d, $^3J_{\text{H,H}} = 8.1$ Hz, 4 H, ArH(MO)], 7.86 [d, $^3J_{\text{H,H}} = 9.3$ Hz, 4 H, ArH(MO)], 7.81 [d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H, ArH(MO)], 7.52 [t, $^3J_{\text{H,H}} = 7.6$ Hz, 3 H, ArH(core)], 6.77 [d, $^3J_{\text{H,H}} = 9.0$ Hz, 4 H, ArH(MO)], 6.73 [s, 4 H, ArH(wedge)], 4.95 [s, 4 H, NCH_2 (shell)], 4.71 (s, 4 H, CH_2N), 3.91 (t, 4 H, OCH_2), 3.84 (t, 8 H, OCH_2), 3.10 [s, 12 H, $\text{N}(\text{CH}_3)_2$ (MO)], 3.07 [s, 12 H, $\text{N}(\text{CH}_3)_2$],

1.69 (m, 12 H, OCH_2CH_2), 1.25 (m, 108 H, $9 \times \text{CH}_2$), 0.89 (m, 18 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 154.0, 153.3, 148.2, 144.1, 140.4, 135.7, 129.5, 127.2, 125.7, 122.5, 122.4, 111.9, 100.6, 73.9, 69.8, 49.3, 40.6, 32.5, 30.9, 30.4, 30.3, 30.2, 30.1, 30.0, 26.8, 26.7, 23.3, 14.5 ppm. ESI-MS: m/z = 2429.8 (2429.9 calcd. for $[[3][\text{MO}] + \text{CH}_3\text{C}_6\text{H}_2(\text{OC}_{12}\text{H}_{25})_3]^{3+}$), 1784.4 (1784.8 calcd. for $[[3][\text{MO}]^+]$), 836.8 (836.4 calcd. for $[[3] - \text{CH}_2\text{C}_6\text{H}_2(\text{OC}_{12}\text{H}_{25})_3]^{3+}$), 740.1 (740.2 calcd. for $[3]^{2+}$), 644.6 (644.1 calcd. for $[\text{CH}_2\text{C}_6\text{H}_2(\text{OC}_{12}\text{H}_{25})_3]^{3+}$).

[4][MO]: ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 7.97 [d, $^3J_{\text{H,H}} = 9.0$ Hz, 2 H, ArH(MO)], 7.85 [d, $^3J_{\text{H,H}} = 9.3$ Hz, 2 H, ArH(MO)], 7.79 [d, $^3J_{\text{H,H}} = 8.7$ Hz, 2 H, ArH(MO)], 7.56 [m, 2 H, ArH(core)], 7.48 [m, 3 H, ArH(core)], 6.81 [s, 2 H, ArH(wedge)], 6.76 [d, $^3J_{\text{H,H}} = 9.3$ Hz, 2 H, ArH(MO)], 4.82 [s, 2 H, NCH_2 (shell)], 4.81 (s, 2 H, CH_2N), 3.92 (m, 6 H, OCH_2), 3.08 [s, 6 H, $\text{N}(\text{CH}_3)_2$ (MO)], 3.01 [s, 6 H, $\text{N}(\text{CH}_3)_2$], 1.72 (m, 6 H, OCH_2CH_2), 1.43 (m, 6 H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.25 (m, 48 H, $8 \times \text{CH}_2$), 0.86 (m, 9 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CD_2Cl_2 , 25 °C): δ = 154.0, 153.4, 148.5, 144.1, 140.3, 133.9, 131.1, 129.7, 128.2, 127.3, 125.6, 122.7, 122.4, 112.1, 112.0, 73.9, 69.9, 69.5, 68.5, 48.8, 40.6, 32.5, 30.9, 30.3, 30.2, 30.1, 30.0, 26.8, 26.7, 23.3, 14.5 ppm. ESI-MS: m/z = 1861.69 (1862.93 calcd. for $[2 \times [4][\text{MO}] - \text{MO}]^+$), 779.15 (779.29 calcd. for $[4]^+$).

Acknowledgments

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