Towards macrocyclic ionic liquids: novel ammonium salts based on tetrasubstituted p-tert-butylthiacalix[4]arenes†

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Water-insoluble ionic liquids based on p-tert-butylthiacalix[4]arenes tetrasubstituted at the lower rim with amide and quaternary ammonium groups containing alkyl, phenyl, phthalimide, glycine, alanine and glycylglycine groups in cone and 1,3-alternate conformations were synthesized. It was established that macrocycles containing quaternary ammonium fragments with alkyl, phenyl and ester groups at the nitrogen atom in cone conformation melt lower by 8–31°C than 1,3-alternate stereoisomers. It was shown that the introduction of the bis(trifluoromethylsulfonyl)imide anion as a counterion in the structure of quaternary ammonium salts based on thiacalix[4]arenes led to a substantial decrease in the melting point of the above salts.

Introduction

Synthesis of ionic liquids for extraction and determination of organic compounds is one of the promising areas of investigation in modern organic chemistry.1–7 Water-insoluble solvents have recently been widely used for extraction and separation of biologically significant compounds but they have some technological disadvantages and do not often meet modern environmental standards. The replacement of such solvents is an important applied task. One of the possible solutions to this problem is the use of ionic liquids, e.g., molten salts that are liquids at temperatures below 100 °C. Ionic liquids are mostly non-flammable, synthetically accessible and have negligible vapor pressure; selection of their cations and anions allows adjusting their properties over a wide range. Unique combinations of hydrophobicity and ionic nature, thermal stability and high electrical conductivity of ionic liquids offer new opportunities in the field of organic and analytical chemistry, catalysis and electrochemistry.8–12 The development of approaches to creation of new high-performance systems for the extraction and separation of various compounds based on ionic liquids and functionalized macrocycles, e.g., cyclodextrins, cucurbit[n]urils, (thia)calix[n]arenes, pillar[n]arenes, crown ethers is of great interest.13–17

There are two basic approaches to the creation of such systems: (1) synthesis of the macrocyclic compounds soluble in ionic liquids, and (2) design of ionic liquids containing macrocyclic fragment as their cation or anion (Fig. 1).

Despite large synthetic and conformational diversity of (thia)calix[4]arenes as molecular building platform,18–24 there are only

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few examples of the synthesis of ionic liquids based on them. It should be noted that the macrocyclic ionic liquids described in the literature belong to the pyridinium and imidazolium derivatives. Synthesis of ionic liquids based on quaternary ammonium salt is one of the most important tasks in modern organic chemistry. Ease of synthesis, low cost and non-toxicity are the advantages of quaternary ammonium fragments. According to the examples in the literature of ionic liquids and (thia)calixarenes, we can assume that the introduction of quaternary ammonium fragments at the lower rim of \( \text{p-tert-butylthiacalix[4]arene} \) may be promising for the synthesis of macroyclic ionic liquids capable of the molecular recognition of target species.

In this work, the synthesis of \( \text{p-tert-butylthiacalix[4]arene} \) tetrasubstituted at the lower rim with quaternary ammonium groups in cone and 1,3-alternate conformations as potential ionic liquids is described.

Results and discussion

Synthesis of \( \text{p-tert-butylthiacalix[4]arene} \) containing quaternary ammonium groups

To synthesize ionic liquids based on the \( \text{p-tert-butylthiacalix[4]arene} \) containing quaternary ammonium groups, the reaction of the compounds 1-4 with different alkylating reagents in acetonitrile under reflux has been studied. Alkyl iodides and alkyl bromides were selected as highly reactive alkylating agents. Iodomethane and iodoethane as two simplest homologues were chosen. Based on these compounds, we can verify previously described in the literature suggestion that the increase in the length of the alkyl substituent led to decrease of the melting point. According to the literature, it was also assumed that the introduction of planar \( \pi \)-aromatic ring systems and the ester groups at the lower rim of the macrocycle could result in the synthesis of tetraalkylammonium derivatives of \( \text{p-tert-butylthiacalix[4]arene} \) in cone and 1,3-alternate conformations with low melting points. Thus, benzyl bromide, ethyl bromoacetate and pentyl bromoacetate were used from this consideration. It is interesting to note that in case of iodomethane and iodoethane the reaction was carried out at room temperature because alkyl iodides are more reactive than alkyl bromides.

It was found that the reactivity of the macrocycles 2 and 4 containing tertiary amino groups with ethyl substituents at the lower rim was lower than the reactivity of the thiacalix[4]arenes 1 and 3 with tertiary amino groups with methyl substituents. Probably, this is due to steric hindrance at the amino nitrogen atom. The increase of reaction time from 8 to 48 hours led to the increase in the length of the alkyl substituent. This is due to the decrease of the melting point. According to the literature, it was also assumed that the introduction of planar \( \pi \)-aromatic ring systems and the ester groups at the lower rim of the macrocycle could result in the synthesis of tetraalkylammonium derivatives of \( \text{p-tert-butylthiacalix[4]arene} \) in cone and 1,3-alternate conformations with low melting points. Thus, benzyl bromide, ethyl bromoacetate and pentyl bromoacetate were used from this consideration. It is interesting to note that in case of iodomethane and iodoethane the reaction was carried out at room temperature because alkyl iodides are more reactive than alkyl bromides.

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Scheme 1 Reagents and conditions: \( i - \text{R-Hal, CH}_3\text{CN, reflux.} \)
reflux resulted in formation of the products only in the case of the compounds 1 and 3 containing tertiary amino groups with N,N-dimethyl substituents at the lower rim in cone and 1,3-alternate conformations. The compounds 13 and 30 were synthesized with excellent yields\textsuperscript{a} (Scheme 1). According to the \textsuperscript{1}H NMR spectroscopy, the mixture of differently substituted products difficult for separation was obtained for the macrocycles 2 and 4 containing tertiary amine groups with N,N-diethyl substituents at the lower rim. The increase of the reaction time up to 40 hours did not lead to the formation of the target products. Probably, reactivity of the macrocycles 2 and 4 is reduced by steric hindrance in tertiary amino groups with N,N-diethyl substituents against that of the compounds 1 and 3 containing tertiary amino groups with methyl substituents.

Melting point is one of main characteristics of ionic liquids (see Table 1 for the synthesized macrocycles 5–21 (cone) and 22–38 (1,3-alternate)). Conformation changes and length of the alkyl substituents led to a slight decrease in the melting point up to 40 °C in contrast to 5–7 °C predicted in the literature.\textsuperscript{a} However, main goal has not been achieved. All the obtained salts 5–21 (cone) and 22–38 (1,3-alternate) melt above 100 °C except the macrocycle 35 containing pentyl acetate fragment.

### Table 1 Melting points (°C) of the macrocycles 5–21 (cone) and 22–38 (1,3-alternate)

<table>
<thead>
<tr>
<th>R/Hal⁻</th>
<th>NH(CH(_2))(_3)N(CH(_3))(_2)R Cone 1,3-Alternate</th>
<th>NH(CH(_2))(_3)N(CH(_2))(_3)R Cone 1,3-Alternate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)/I</td>
<td>192 (5)</td>
<td>197 (22)</td>
</tr>
<tr>
<td>C(_2)H(_5)/I</td>
<td>165 (6)</td>
<td>215 (23)</td>
</tr>
<tr>
<td>CH(_3)Ph/Br</td>
<td>135 (7)</td>
<td>150 (24)</td>
</tr>
<tr>
<td>CH(_2)COOCH(_3)/H(_2)/Br</td>
<td>112 (8)</td>
<td>123 (25)</td>
</tr>
<tr>
<td>CH(_2)COOCH(_3)/H(_2)/Br</td>
<td>106 (9)</td>
<td>103 (26)</td>
</tr>
<tr>
<td>CH(_2)CO-Gly-OEt/Br</td>
<td>114 (10)</td>
<td>112 (27)</td>
</tr>
<tr>
<td>CH(_2)CO-Gly-OEt/Br</td>
<td>113 (11)</td>
<td>120 (28)</td>
</tr>
<tr>
<td>CH(_2)CO-Ala-OEt/Br</td>
<td>116 (12)</td>
<td>118 (29)</td>
</tr>
<tr>
<td>CH(_2)CH(_2)Phl/Br</td>
<td>152 (13)</td>
<td>154 (30)</td>
</tr>
</tbody>
</table>

Melting point of the products obtained from the reaction of compounds 5–21 with lithium bis(trifluoromethylsulfonyl)imide anions have identical multiplicity and exert very similar chemical shifts. It can be explained that these compounds are able to form solvent-separated ion pairs in solution.

**Synthesis of ionic liquids based on p-tert-butylthiacalix[4]arenes containing alkyl, ester, aromatic, peptide and phthalimide fragments**

As shown in the literature\textsuperscript{a} replacement of the halide ions by bis(trifluoromethylsulfonyl)imide ions considerably decreased melting point. This can be explained by the fact that the increase in the size of anions decreased symmetry of the molecule obtained\textsuperscript{a} (Fig. 2). Thus, the synthesis of the compounds 5–38 with lithium bis(trifluoromethylsulfonyl)imide in water at room temperature was next step of the work (Scheme 2, Fig. 2).

The structure and composition of the synthesized compounds 39–72 were determined by \textsuperscript{1}H and \textsuperscript{13}C NMR, IR spectroscopy, mass spectrometry and elemental analysis. The \textsuperscript{13}C NMR spectrum of the compounds 39–72 exhibits a quartet at 120 ppm; these signals correspond to anion N(SO\(_2\))\(_2\) (Fig. S67–S100, ESI\textsuperscript{†}).

The configuration of p-tert-butylthiacalix[4]arenes can be studied by two-dimensional NMR spectroscopy. However, the configuration of the compounds 5–72 can be also determined by one-dimensional \textsuperscript{1}H NMR spectroscopy based on specific proton signals.

The conformational differentiation of the cone and 1,3-alternate stereoisomers of the p-tert-butylthiacalix[4]arenes tetrafluoromethylsulfonyl)imide anions have identical multiplicity and exert very similar chemical shifts. It can be explained that these compounds are able to form solvent-separated ion pairs in solution.
Melting points of the synthesized thiacalix[4]arenes 39–72 are presented in Table 2. One can see (Tables 1 and 2) that the replacement of halide ions by bis(trifluoromethylsulfonyl)imide ions leads to significant decrease in the melting points of the thiacalix[4]arenes studied. All the synthesized macrocycles 39–72 containing bis(trifluoromethylsulfonyl)imide anions melt below 100 °C, except the product 56 (Table 2).

One can see (Table 2) that stereoisomerism of the macrocycles 39–43, 48–52, 56–60, 65–69 has an impact on their melting points. In the case of the cone (39–43, 48–52)
stereoisomers, their melting points are lower by 8–31 °C against those of the thiacalix[4]arenes \([56-60, 65-69]\) in 1,3-alternate conformation. It is well known that packing density of the molecules in the crystal lattice is a major factor affecting the melting point of the substance. More symmetrical molecules have denser packing in crystal and higher melting point. Obviously, molecular symmetry of the cone \((39-43, 48-52)\) stereoisomers results in maximal spatial separation of the bulk lipophilic tert-butyl charged ammonium groups and hence in decrease of the packing density and appropriate reduction of their melting point. On the other hand, in the case of the symmetric 1,3-alternate \([56-60, 65-69]\) stereoisomers that show higher melting points, alternation of tert-butyl and ammonium groups at adjacent aryl fragments led to denser packing of the molecules. However, the introduction of additional amide groups with amino acid residues \((\text{Gly, Ala})\) in the structure of thiacalix[4]arene compared to the macrocycles \([39-43, 48-52, 56-60, 65-69]\) decreased influence of the macrocycle configuration on their melting points. Obviously, peptide groups able to form hydrogen bonds contribute to the formation of denser packing of the molecules in the crystal. It can be assumed that two opposite factors influence melting points of the thiacalix[4]arenes depending on the structure of macrocycles, i.e., conformation (melting points of the stereoisomers decrease in the range: 1,3-alternate, cone) and presence of the proton-donating \((-\text{NH})\) and proton-accepting (carbonyl) groups (melting points are increased due to the formation of associates). This results in the fact that melting points of the macrocycles \([44-47, 53-55, 61-64, 70-72]\) in cone and 1,3-alternate conformations are slightly different.

Increasing length of the alkyl substituent of the macrocycle by one \(\text{CH}_2-\) group leads to decrease of the melting point by 8–9 °C in good agreement with the literature.\(^{36}\) It should also be noted that the compound 43 containing pentoxy carbonylmethylene groups at the lower rim in cone conformation has the lowest melting point (35 °C). This corresponds closely to the hypothesis about the influence of the ester groups on the melting points of the target products.

Thermal stability and ionic conductivity have been established for the compound 43 with the lowest melting point. Thermal stability of the compound 43 toward pyrolysis was investigated by thermogravimetric analysis (Fig. S201, ESI†).

The 5 wt% loss temperature \((T_d)\) of the compound 43 under nitrogen was equal to 293.5 °C indicating its high thermal stability. It is known that macrocyclic ionic liquids have lower ionic conductivity in comparison with their non-macrocyclic analogues.\(^{26}\) The ionic conductivity of the compound 43 was evaluated by ac impedance spectroscopy. The ionic conductivity of compound 43 in the bulk state at 324 K was found to be \(6.00 \times 10^{-7} \text{ S cm}^{-1}\) (Fig. 3) corresponded to moderate ionic conductivity. Fig. 3 shows low- \((120 \text{ Hz})\) and high-frequency \((500 \text{ kHz})\) electrical conductivity exhibiting exponential increase with the temperature. The activation energy for the high-frequency conductivity \(E_{A1} = 0.69 \text{ eV}\) is approx. twofold less than that of the low-frequency conductivity \((E_{A2} = 1.24 \text{ eV})\). This behavior of the activation energy was also observed for other organic semiconductors\(^{42}\) and is usually associated with the processes of the hopping of charge carriers in an inhomogeneous conducting medium. This model supposes the current in organic semiconductors generated by hopping carriers between polyconjugated areas from one to another limited by dielectric barrier created by disordered (non-conjugated) structure. Small activation energy values are typical for the occurrence of carriers within interface area and manifest themselves in the measurements at a high frequency, while measuring at the DC and low frequencies give substantially higher values of the activation energy associated probably with the above barrier hopping between coupling fragments.

![Fig. 3 Ionic conductivity of the thiacalix[4]arene cone 43.](image-url)

**Table 2** Melting points \(^\circ\text{C}\) of the macrocycles 39–55 (cone) and 56–72 (1,3-alternate)

<table>
<thead>
<tr>
<th>R</th>
<th>NH((\text{CH}_2))_2N'((\text{CH}_2)_nR*\text{R'}(\text{SO}_2\text{CF}_3)_2^-</th>
<th>NH((\text{CH}_2))_2N'((\text{CH}_2)_n\text{R'}(\text{SO}_2\text{CF}_3)_2^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3</td>
<td>87 (39)</td>
<td>106 (56)</td>
</tr>
<tr>
<td>C2H5</td>
<td>71 (40)</td>
<td>96 (57)</td>
</tr>
<tr>
<td>CH3Ph</td>
<td>56 (41)</td>
<td>87 (58)</td>
</tr>
<tr>
<td>CH3COOC2H5</td>
<td>45 (42)</td>
<td>53 (59)</td>
</tr>
<tr>
<td>CH3COOC2H5</td>
<td>45 (42)</td>
<td>53 (59)</td>
</tr>
<tr>
<td>CH3CO-Gly-OEt</td>
<td>63 (44)</td>
<td>73 (61)</td>
</tr>
<tr>
<td>CH3CO-Gly-OEt</td>
<td>63 (44)</td>
<td>73 (61)</td>
</tr>
<tr>
<td>CH3CO-Ala-OEt</td>
<td>56 (46)</td>
<td>60 (63)</td>
</tr>
<tr>
<td>CH3CH2CH2Ph</td>
<td>83 (47)</td>
<td>87 (64)</td>
</tr>
<tr>
<td></td>
<td>Cone</td>
<td>1,3-Alternate</td>
</tr>
<tr>
<td></td>
<td>72 (48)</td>
<td>83 (65)</td>
</tr>
<tr>
<td></td>
<td>68 (49)</td>
<td>79 (66)</td>
</tr>
<tr>
<td></td>
<td>60 (50)</td>
<td>76 (67)</td>
</tr>
<tr>
<td></td>
<td>43 (51)</td>
<td>58 (68)</td>
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<tr>
<td></td>
<td>39 (52)</td>
<td>49 (69)</td>
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<td></td>
<td>66 (53)</td>
<td>62 (70)</td>
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<td></td>
<td>64 (54)</td>
<td>64 (71)</td>
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<tr>
<td></td>
<td>63 (55)</td>
<td>62 (72)</td>
</tr>
<tr>
<td></td>
<td>Cone</td>
<td>1,3-Alternate</td>
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<tr>
<td></td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
Conclusions

Thus, water-soluble and water-insoluble p-tet-butylthiacalix[4]arenes tetrasubstituted at the lower rim with amide and quaternary ammonium groups with alkyl, ester, amino acid, peptide and phthalimide fragments in cone and 1,3-alternate conformation were synthesized. The structure and composition of the synthesized macrocycles were determined by the physical methods, i.e., the $^1$H and $^{13}$C NMR, IR spectroscopy, MALDI TOF and ESI mass spectrometry and elemental analysis. It was found that the replacement of halide ions in the synthesized macrocycles by bis(trifluoromethyl)sulfonylimide ions led to water-insoluble salts with melting points below 100 °C. It was shown that the macrocycles containing quaternary ammonium fragments with alkyl, phenyl and ester groups at the nitrogen atom in cone conformation melt lower by 8–31 °C than 1,3-alternate stereoisomers. Macrocyclic water-insoluble ionic liquids synthesized in this work showed high thermal stability and moderate ionic conductivity. These salts can be used in the sensor assemblies for the molecular recognition of the target substances, e.g., biomacromolecules and cations of heavy and transition metals.

Experimental

General

The $^1$H and $^{13}$C NMR spectra of compounds (3–5% solution in CDCl$_3$, (CD$_3)_2$SO) were recorded on 400 MHz and 100 MHz Bruker Avance 400 spectrometer using CDCl$_3$ and (CD$_3)_2$SO as internal standard.

The IR spectra were recorded on Spectrum 400 (Perkin Elmer) IR spectrometer. The IR spectra from 4000 to 400 cm$^{-1}$ were considered in this analysis. The spectra were measured with 4 cm$^{-1}$ resolution and 14 scans co-addition.

Elemental analysis was performed on Perkin-Elmer 2400 Series II instruments.

Mass spectra (MALDI-TOF) were recorded on Ultraflex III mass spectrometer in the 4-nitroaniline matrix.

Mass spectra (ESI) were recorded on an AmaZonX mass spectrometer (Bruker Daltonik GmbH, Germany). The drying gas was nitrogen at 300 °C. The capillary voltage was 4.5 kV. The samples were dissolved in acetonitrile (concentration $\sim 10^{-6}$ g ml$^{-1}$).

Melting points were determined using Boetius Block apparatus. The purity of the compounds was monitored by melting, boiling points, $^1$H NMR and thin layer chromatography (TLC) on 200 μm UV 254 silica gel plate using UV-light (254 nm).

Conductivity measurements were performed on the RLC-meter E7-20 in “sandwich” type cell at frequencies of 120 Hz and 500 kHz at temperatures range from room temperature to 74 °C. The sample size was 1 cm$^2$, thickness $\sim 4$ mm.

In this work, the following reagents and solvents were used: acetonitrile (chemical pure), benzyl bromide (chemical pure), lithium bis(trifluoromethansulfonylimide (Acros Organic), N-(3-bromopropyl)phthalimide (Acros Organic), distilled water, iodomethane (Acros Organic), 2-propyl bromoacetate (chemical pure).

N-Bromoacetyl-glycine ethyl ester, N-bromoacetyl-glycyl-glycine ethyl ester, N-bromoacetyl-L-alanine ethyl ester were synthesized according to the literature procedure.  
5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dime-thylaminomethyl)carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene (cone 1) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(2',2'-diethylammonium)methyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene (cone 2) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dime-thylaminomethyl)carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene (cone 1,3-alternate 3) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(2',2'-diethylammonium)methyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene (cone 1,3-alternate 4) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-trimethyl)-ammoniumpropyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 6) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-benzylammoniumpropyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 7) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-ethyl)ammoniumpropyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 8) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-ethyl)ammoniumpropyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 10) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-ethoxy]carbonylmethyl)amidocarboxylmethyl)ammoniumpropyl]carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 11) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-{[ethoxycarbonylmethyl]amidocarboxylmethyl)ammoniumpropyl}carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 12) was synthesized according to the literature procedure.

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-{[ethoxycarbonylmethyl]amidocarboxylmethyl)ammoniumpropyl}carbamoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (cone 13) was synthesized according to the literature procedure.


5,11,17,23-Tetra-2-tert-butyl-25,26,27,28-tetrakis[N(3',3'-dimethyl-3'-(ethoxycarbonylmethyl)amidocarbonylmethyl)ammonium]methyl]carbomoyl]methoxy]-2,8,14,20-tetra[thiacalix[4]arene tetrabromide (1,3-alternate 27) was synthesized according to the literature procedure.

5,11,17,23-Tetra-2-tert-butyl-25,26,27,28-tetrakis[N(3',3'-dimethyl-3'-(ethoxycarbonylmethyl)amidocarbonylmethyl)ammonium]methyl]carbomoyl]methoxy]-2,8,14,20-tetra[thiacalix[4]arene tetrabromide (1,3-alternate 28) was synthesized according to the literature procedure.

5,11,17,23-Tetra-2-tert-butyl-25,26,27,28-tetrakis[N(3',3'-dimethyl-3'-(ethoxycarbonylmethyl)amidocarbonylmethyl)ammonium]methyl]carbomoyl]methoxy]-2,8,14,20-tetra[thiacalix[4]arene tetrabromide (1,3-alternate 29) was synthesized according to the literature procedure.


General procedure for the synthesis of compounds 9, 15-18, 22-26, 31-35

The compounds 1-4 (0.10 g, 0.08 x 10^{-3} mol) were dissolved in 2 ml of acetonitrile in the round bottom flask equipped with magnetic stirrer and a reflux condenser. Iodomethane, iodooctane, ethyl bromoacetate, pentyl bromoacetate, or benzyl bromide (0.32 x 10^{-3} mol) was added. The reaction mixture was refluxed for 48 h. The solvent was removed under reduced pressure. The precipitate was dried under reduced pressure over phosphorus pentoxide.
32H, –CH2CH3, –NCH2CH2NH, 8H, NCH2CH2NH), 4.24 (q, 3JHH = 7.1 Hz, 12H, O(CH2)3C), 1.91 (s, 36H, (CH3)3C), 1.25–1.33 (m, 16H, O(CH2)2CH2C(CH3)3), 1.44 (t, 3JHH = 7.1 Hz, 12H, O(CH2)3C), 1.63 (m, 8H, OCH2CH2CH2CH3), 3.88–3.97 (m, 32H, –N(CH2)3N+), –NCH2CH2NH, –NCH2CH2NH, –NCH2CH2NH), 4.14 (t, 3JHH = 6.8 Hz, 8H, OCH2CH2C(CH3)3), 4.70 (s, 8H, NCH2CH2NH), 4.93 (s, 8H, OCH2CO), 7.30 (s, 8H, ArH), 9.01 (br, s, 4H, CONH). 

13C NMR (100 MHz, 298 K, DMSO-d6): δ = 169.88, 165.85, 170.36, 174.11, 134.82, 128.22, 73.90, 66.91, 57.63, 56.76, 55.91, 34.25, 33.31, 31.09, 29.77, 27.75, 22.90, 13.91, 8.78. El. anal. calcd for C100H164Br4N8O16S4: C 55.04%, H 7.57%, N 5.13%, S 5.88%. Found: C 54.99%, H 7.53%, N 5.48%, S 5.58%. MS (ESI): calcd for [M – 4Br]4+: m/z = 438.6, found m/z = 438.0. IR: νmax: 3530, 2954, 2350, 1730, 1275, 1126, 1096, 1024, 1009, 984, 879, 807. 

Yield: 0.12 g (90%), mp 197 °C. 

1H NMR (400 MHz, 298 K, DMSO-d6): δ = 1.21 (s, 36H, (CH3)3C), 1.91 (m, 8H, –NCH2CH2CH2NH), 3.17 (s, 36H, (CH3)3N+), 3.32 (m, 8H, –NCH2CH2CH2NH), 3.60 (m, 8H, –NCH2CH2CH2NH), 3.98 (s, 8H, OCH2CO), 7.60 (s, 8H, ArH), 8.01 (t, 3JHH = 5.2 Hz, 4H, CONH). 

13C NMR (100 MHz, 298 K, DMSO-d6): δ = 167.37, 157.02, 146.08, 132.95, 127.61, 70.96, 63.23, 52.23, 35.31, 33.89, 30.78, 22.86. El. anal. calcd for C27H114BrN4O16S4: C 45.65%, H 6.29%, N 6.03%, S 6.90%. Found: C 46.40%, H 5.89%, N 5.60%, S 6.00%. MS (MALDI TOF): calcd for [M – 1 – 4H]4+: m/z = 1730.7, found m/z = 1730.2. IR νmax: 1660 (C=O), 2955, 3292 (NH).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetraakis[N(3',3',3'-trimethylammoniumpropyl)carbomethoxy]-2,8,14,20-tetrathiaticalix[4]arene tetrabromide (1,3-alternate 22). Yield: 0.12 g (90%), mp 197 °C. 

1H NMR (400 MHz, 298 K, DMSO-d6): δ = 1.21 (s, 36H, (CH3)3C), 1.24 (t, 3JHH = 7.1 Hz, 12H, O(CH2)3C), 1.88 (m, 8H, –NCH2CH2CH2NH), 3.01 (s, 24H, (CH3)3N+), 3.19 (m, 8H, –NCH2CH2CH2NH), 3.29 (m, 8H, OCH2CH2CH2NH), 3.35 (q, 3JHH = 7.2 Hz, 8H, N(CH2)3C), 3.99 (s, 8H, OCH2CO), 7.60 (s, 8H, ArH), 8.03 (br, s, 4H, CONH). 

13C NMR (100 MHz, 298 K, DMSO-d6): δ = 167.37, 157.06, 146.04, 133.00, 127.56, 70.84, 60.23, 58.59, 49.60, 35.80, 33.88, 30.78, 22.44, 7.84. El. anal. calcd for C72H212BrN8O32: C 47.70%, H 6.53%, N 5.86%, S 6.70%. Found: C 47.53%, H 6.52%, N 5.56%, S 6.64%. MS (MALDI TOF): calcd for [M – 1 – 4H]4+: m/z = 1786.8, found m/z = 1786.5. IR νmax: 1653 (C=O), 2958, 3335 (NH).
6.5 Hz, 16H, −CH2CH3), 3.49 (m, 8H, NCH2CH2NH), 4.05 (s, 8H, OCH2CO), 7.61 (s, 8H, ArH), 8.18 (t, 3JHH = 5.5 Hz, 4H, CONH).

13C NMR (100 MHz, 298 K, DMSO-d6) δ: 168.03, 156.80, 146.08, 132.95, 127.51, 76.13, 70.51, 65.99, 62.12, 56.83, 56.16, 47.02, 33.91, 32.13, 30.87, 26.70, 25.36, 7.46. El. anal. calcld for C37H40N2O8S4: C 70.76%, H 5.63%, S 6.70%. Found: C 70.67%, H 5.56%, S 6.70%. MS (ESI): calcd for [M + Br−]2+: 436.5, found m/z = 436.5. IR max: 3427.3. IR max: 1675 (C=O), 2954, 3194 (N-H).

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetakis[N(3’-2’,2’-diethyl-2’-benzylammoniumpropl)]carbomoylmethoxy]-2,8,14,20-tetra-thiaclix[4]arene tetrabromide (1,3-alternate 33). Yield: 0.11 g (90%), mp 173 °C. 1H NMR (400 MHz, 298 K, DMSO-d6) δ: 1.22 (s, 36H, (CH3)3C), 1.23 (t, 3JHH = 7.1 Hz, 3H, CH2CH3), 3.15 (m, 8H, −NCH2CH2NH), 3.31 (q, 3JHH = 7.1 Hz, 4H, −CH2CH3), 3.47 (m, 8H, NCH2CH2NH), 4.03 (s, 8H, OCH2CO), 7.61 (s, 8H, ArH), 8.13 (t, 3JHH = 5.3 Hz, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6) δ: 167.98, 156.74, 146.14, 132.94, 127.58, 70.46, 53.52, 53.43, 39.31, 31.84, 30.74. El. anal. calcld for C37H40N2O8S4: C 70.03%, H 5.56%, S 6.70%. Found: C 69.92%, H 5.57%, S 6.79. MS (ESI): calcd for [M + Br−]2+: 436.5, found m/z = 436.5. IR max: 1675 (C=O), 2954, 3261 (N-H).
NCH2CH2CH2NH), 3.05 (s, 36H, (CH3)2N), 3.25 (m, 8H, NCH2CH2CH2NH), 3.27 (m, 8H, NCH2CH2CH2NH), 4.82 (s, 8H, OCH2CO), 7.40 (s, 8H, ArH), 8.49 (t, JHH = 5.2 Hz, 4H, CONH).

13C NMR (100 MHz, 298 K, DMSO-d6): 168.26, 157.99, 146.80, 134.42, 128.02, 119.96 (q), 74.22, 63.40, 52.28, 35.38, 33.91, 30.69, 22.83. El. anal. calcld for C39H35F24N12O32S12: C 38.89%, H 4.73%, N 6.80%, S 15.57%. Found: C 39.03%, H 5.02%, N 6.53%, S 15.12%. MS (MALDI TOF): calcld for [M – N\(^{+}\)(SO\(_{2}\)CF\(_{3}\)\(_{2}\)]\(^{4+}\)/m/z = 2188.55, found m/z = 2189.4. IR \(\nu_{max}\) 1669 (C=O), 2965, 3327 (NH).

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetraakis[N(3',3'-dimethyl-3'-ethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetraethylcalix[4]arene tetra[bis(trifluoromethylsulfonylimide) (cone 40). Yield: 0.10 g (93%), mp 71 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): 1.08 (s, 36H, (CH3)2C), 1.22 (t, JHH = 7.0 Hz, 12H, N\(^{+}\)CH2CH2CH2N), 1.87 (m, 8H, –NCH2CH2CH2N), 2.97 (2H, (CH3)2N\(_{2}\)), 3.23 (m, 8H, –NCH2CH2CH2N), 3.29 (q, JHH = 7.2 Hz, 8H, N\(^{+}\)CH2CH2CH2N), 3.32 (m, 8H, N\(^{+}\)CH2CH2CH2N), 3.48 (s, 8H, OCH2CO), 7.40 (s, 8H, ArH), 8.49 (br. s, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6): 168.24, 157.94, 146.78, 134.43, 127.99, 119.67 (q), 74.17, 60.33, 54.65, 49.53, 35.39, 33.91, 30.67, 22.35, 7.74. El. anal. calcld for C39H35F24N12O32S12: C 39.93%, H 4.95%, N 6.65%, S 15.23%. Found: C 39.37%, H 5.00%, N 6.76%, S 14.89%. MS (MALDI TOF): calcld for [M – N\(^{+}\)(SO\(_{2}\)CF\(_{3}\)\(_{2}\)]\(^{4+}\)/m/z = 2244.6, found m/z = 2244.8. IR \(\nu_{max}\) 1671 (C=O), 2965, 3328 (NH).

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetraakis[N(3',3'-dimethyl-3'-benzyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetraethylcalix[4]arene tetra[bis(trifluoromethylsulfonylimide) (cone 41). Yield: 0.10 g (93%), mp 56 °C. 1H NMR (400 MHz, 298 K, CDCl3): 1.10 (s, 36H, (CH3)2C), 2.23 (m, 8H, –NCH2CH2CH2N), 2.98 (s, 24H, (CH3)2N\(_{2}\)), 3.50 (m, 8H, –NCH2CH2CH2N), 3.53 (m, 8H, N\(^{+}\)CH2CH2CH2N), 4.42 (s, 8H, N\(^{+}\)CH2CH2N), 4.91 (s, 8H, OCH2CO), 7.35 (s, 8H, ArH), 7.43 (m, 20H, ArH), 8.29 (br. s, 4H, CONH). 13C NMR (100 MHz, 298 K, CDCl3): 169.24, 157.30, 147.80, 134.97, 132.85, 131.06, 124.93, 127.87, 126.49, 119.94 (q), 74.26, 68.37, 63.07, 49.46, 36.20, 34.38, 31.04, 23.01. El. anal. calcld for C40H36F24N12O32S12: C 45.01%, H 4.79%, N 6.60%, S 13.87%. Found: C 45.03%, H 4.69%, N 5.84%, S 14.04%. MS (MALDI TOF): calcld for [M – N\(^{+}\)(SO\(_{2}\)CF\(_{3}\)\(_{2}\)]\(^{4+}\)/m/z = 2492.6, found m/z = 2493.3. IR \(\nu_{max}\) 1665 (C=O), 2961, 3328 (NH).

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetraakis[N(3',3'-dimethyl-3'-{(ethoxycarbonyl)methyl}amidocarbonylpropyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetraethylcalix[4]arene tetra[bis(trifluoromethylsulfonylimide) (cone 42). Yield: 0.11 g (97%), mp 55 °C. 1H NMR (400 MHz, 298 K, CDCl3): 1.11 (s, 36H, (CH3)2C), 1.26 [t, JHH = 7.1 Hz, 12H, 12H, (CH3)2C], 2.14 (m, 8H, –NCH2CH2CH2N), 3.34 (s, 24H, (CH3)2N\(_{2}\)), 3.47 (m, 8H, –NCH2CH2CH2N), 3.72 (m, 8H, N\(^{+}\)CH2CH2CH2N), 4.42 (s, 8H, N\(^{+}\)CH2CH2N), 4.91 (s, 8H, OCH2CO), 7.35 (s, 8H, ArH), 7.43 (m, 20H, ArH), 8.29 (br. s, 4H, CONH). 13C NMR (100 MHz, 298 K, CDCl3): 169.24, 157.30, 147.80, 134.97, 132.85, 131.06, 124.93, 127.87, 126.49, 119.94 (q), 74.26, 68.37, 63.07, 49.46, 36.20, 34.38, 31.04, 23.01. El. anal. calcld for C41H38F24N12O32S12: C 45.01%, H 4.79%, N 6.60%, S 13.87%. Found: C 45.03%, H 4.69%, N 5.84%, S 14.04%. MS (MALDI TOF): calcld for [M – N\(^{+}\)(SO\(_{2}\)CF\(_{3}\)\(_{2}\)]\(^{4+}\)/m/z = 2492.6, found m/z = 2493.3. IR \(\nu_{max}\) 1665 (C=O), 2961, 3328 (NH).
5,11,17,23-Tetra-tetra-butyl-25,26,27,28-tetrakis[N-(2',2',2'-triethylammonium)carboxyloxymethyl]calix[4]arene tetra[trifluoromethylsulfonylimide] (cone 46). Yield: 0.12 g (90%), mp 72 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): 1.08 (s, 36H, (CH3)3C), 1.19 (t, 3JHH = 7.1 Hz, 12H, CH2CH3), 1.31 (d, 3JHH = 7.3 Hz, 12H, CH2CH3), 1.92 (m, 8H, NHCH2CH2N3), 3.16 (s, 12H, (CH3)N3), 3.23 (m, 8H, NHCH2CH2N3), 3.48 (m, 8H, NHCH2CH2N3), 4.06 (s, 8H, N′CH3CO), 4.09 (m, 8H, CH3CH2O), 7.36 (s, 8H, ArH), 8.40 (br. s, 8H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6): 169.75, 169.20, 163.93, 156.72, 148.19, 142.94, 139.0, 135.06, 127.73, 119.89 (q), 73.89, 62.97, 56.99, 53.32, 30.66, 24.14, 22.61, 16.63, 15.32. El. anal. calcd for C108H156F24N20O40S12: C 40.34%, H 4.89%, N 8.71%, S 13.67%. Found: C 40.56%, H 4.83%, N 8.95%, S 13.81%. MS (ESI): calcd for [M – 4N-(SO2CF3)3]1+ m/z = 580.7, found m/z = 567.5, 580.5. IR vmax = 1674 (C=O), 2963, 3314 (NH).

5,11,17,23-Tetra-tetra-butyl-25,26,27,28-tetrakis[N-(2',2'-diethylbenzylammonium)carboxyloxymethyl]calix[4]arene tetra[trifluoromethylsulfonylimide] (cone 50). Yield: 0.12 g (94%), mp 60 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): 1.10 (s, 36H, (CH3)3C), 1.39 (t, 3JHH = 7.1 Hz, 24H, (CH2CH3)), 3.24 (q, 3JHH = 6.9 Hz, 16H, –CH2CH3), 3.39 (t, 3JHH = 7.1 Hz, 8H, –NCH2CH2NH), 3.93 (m, 8H, N′CH3CN), 4.43 (s, 8H, N′CH2Ph), 4.95 (s, 8H, OCH3CO), 7.35 (s, 8H, ArH), 7.41–7.46 (m, 20H, Ar′H). 8.51 (br. s, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6): 169.90, 156.78, 148.04, 135.0, 132.36, 131.06, 129.62, 127.82, 126.19, 119.74 (q), 73.85, 61.56, 51.18, 53.70, 34.18, 32.78, 31.02, 7.83. El. anal. calcd for C108H156F24N20O40S12: C 40.34%, H 4.89%, N 8.71%, S 13.67%. Found: C 40.51%, H 4.69%, N 7.08%, S 12.64%. MS (ESI): calcd for [M – 4N-(SO2CF3)3]1+ m/z = 427.4, found m/z = 424.7. IR vmax = 1672 (C=O), 2967, 3330 (NH).
CH3CH2N+), 1.57 (m, 8H, OCH2CH2CH2), 3.52–3.60 (m, 32H, –NCH2CH3, –NCH2CH2NH, –NCH2CH2NH), 4.10 (t, JHH = 7.3 Hz, 12H, CH2CH3), 1.31 (t, JHH = 7.2 Hz, 4H, OCH2CH2CH2), 3.48–3.61 (m, 24H, NHCH2CH2N+, NCH2CH2N+), 3.63 (m, 8H, NHCH2CH2NH), 4.09 (s, 8H, N+CH2CO), 4.11 (m, 8H, CH2CH2O–), 2.47 (m, 4H, CH2CH3), 4.84 (s, 8H, OCH2CO), 7.40 (s, 8H, ArH), 8.81 (br. s, 4H, NHCH2CH2NH), 9.23 [d, JHH = 6.7 Hz, 4H, CONH]. 13C NMR (100 MHz, 298 K, DMSO-d6) δ: 171.74, 168.94, 162.97, 157.56, 146.83, 134.55, 127.82, 119.46 (q), 73.98, 60.75, 56.15, 55.17, 55.07, 47.64, 33.95, 32.90, 30.55, 16.56, 13.96, 7.35. El. anal. calec for C104H160F24N32O48S12: C 41.85%, H 5.20%, N 7.23%, S 12.42%. Found: C 42.01%, H 5.74%, N 7.43%, S 12.17%. MS (ESI): calced for [M – 4N–(SO2CF3)2]+ m/z = 494.6, found m/z = 494.3. IR 1680 (C=O), 3663 (N-H).

5,11,17,23-Tetra-t-butyl-25,26,27,28-tetraakis[N′(2′,2′-diethyl-2′-[(ethoxy carbonyl)methyl][S-methyl]methylamidocarbonyl methyl ammonium]carbonylmethoxy]-2,8,14,20-tetra(naphthacil) [4]arene tetra[bis(trifluoromethylsulfonylimide) (cone 55). Yield: 0.12 g (96%), mp 96 ºC. 1H NMR (400 MHz, 298 K, DMSO-d6) δ: 1.21 (s, 36H, (CH3)3C), 1.24 (t, JHH = 7.0 Hz, 12H, CH2CH2O–), 1.87 (m, 8H, –NCH2CH2NH), 2.99 (s, 24H, (CH3)3C), 3.19 (m, 8H, –NCH2CH2NH), 3.24 (m, 8H, NHCH2CH2NH), 3.33 (q, JHH = 7.1 Hz, 8H, N+CH2CO), 4.00 (s, 8H, OCH2CO), 7.60 (s, 8H, ArH), 8.03 (br. s, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6) δ: 167.18, 157.05, 145.99, 133.07, 127.45, 119.90 (q), 73.72, 60.28, 58.67, 44.99, 35.32, 33.85, 30.75, 22.43, 7.76. El. anal. calec for C74H112F42N26O50S12: C 82.20%, H 4.45%, N 6.65%, S 15.23%. Found: C 83.48%, H 4.06%, N 6.37%, S 13.16%. MS (MALDI TOF): calced for [M – N′-(SO2CF3)2]++ m/z = 2190.4, found m/z = 2190.1. IR max: 1669 (C=O), 3663 (N-H).
N+CH2CO), 7.59 (s, 8H, ArH), 8.02 (br. s, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6): δ 176.40, 164.74, 157.11, 146.00, 132.97, 127.54, 119.46 (q), 70.93, 62.32, 61.86, 60.54, 51.21, 35.68, 33.83, 30.73, 22.52, 13.75. El. anal. calcld. for C20H112F2N10O12S12: C 40.05%, H 4.82%, N 6.09%, S 13.95%. Found: C 39.75%, H 5.19%, N 5.85%, S 13.66%. MS (MALDI TOF): calcld. for [M – N(SO2CF3)3]+ m/z = 695.0, [M – 4N(SO2CF3)3]+ m/z = 695.0. IR max: 1667, 1749 (C=O). View Article Online

5.11.17.23-Tetra-tet-t-butyl-25,26,27,28-tetakis[N(3′,3′-dimethyl-3′-[(ethoxycarbonylmethyl]amidocarbonylmethyl)ammoniumpropyl]carbomethoxymethoxy]-2,8,14,20-tetraathiacalix[4]arene tetra[bis(trifluoromethylsulfonylimide)l]imide (1,3-alternate 59). Yield: 0.11 g (97%), mp 76 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ 1.18 (t, JHH = 7.1 Hz, 12H, CH3CH2O–), 1.20 (s, 36H, (CH3)2C), 1.93 (m, 8H, NHCH2CH2NH2), 3.22 (s, 12H, (CH3)2N+), 3.49 (m, 8H, NHCH2CH2NH2), 4.03 (s, 8H, OCH2CO), 1.92 (m, 8H, NHCH2CH2NH2), 3.20 (s, 24H, (CH3)3C), 3.67 (t, JHH = 7.1 Hz, 12H, CH3CH2O–), 7.59 (s, 8H, ArH), 8.02 (br. s, 4H, CONH). C 44.93%, H 4.97%, N 7.34%, S 12.56%. MS (ESI): calcld. for [M – 4N−(SO2CF3)3]3+ m/z = 466.6, found m/z = 466.6. IR max: 1180 (COC), 1673 (C=O), 2968, 3374 (N-H).

5.11.17.23-Tetra-tet-t-butyl-25,26,27,28-tetakis[N(3′,3′-dimethyl-3′-[(ethoxycarbonyl)methyl]amidocarbonylmethyl)ammoniumpropyl]carbomethoxymethoxy]-2,8,14,20-tetraathiacalix[4]arene tetra[bis(trifluoromethylsulfonylimide)l]imide (1,3-alternate 60). Yield: 0.14 g (97%), mp 67 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ 1.20 (s, 36H, (CH3)2C), 1.93 (m, 8H, NHCH2CH2CH2N+), 3.18 (s, 12H, (CH3)3C), 3.19 (m, 8H, NHCH2CH2CH2N+), 3.86 (br. s, 8H, NHCH2CO), 3.87 (br. s, 8H, NHCH2CO), 3.97 (s, 8H, OCH2CO), 4.08 (s, 8H, N′CH2CO), 4.09 (q, JHH = 7.1 Hz, 8H, CH3CH2O–), 7.59 (s, 8H, ArH), 8.02 (br. s, 4H, CONH). Found: C 41.00%, H 5.05%, N 5.92%, S 11.66%. MS (ESI): calcld. for [M – 3N−(SO2CF3)3]+ m/z = 791.3, [M – 4N−(SO2CF3)3]+ m/z = 523.5, found m/z = 791.3, 523.6. IR max: 1182 (COC), 1663 (C=O), 2966, 3313 (N-H).

5.11.17.23-Tetra-tet-t-butyl-25,26,27,28-tetakis[N(3′,3′-dimethyl-3′-[(ethoxycarbonyl)methyl]amidocarbonylmethyl)ammoniumpropyl]carbomethoxymethoxy]-2,8,14,20-tetraathiacalix[4]arene tetra[bis(trifluoromethylsulfonylimide)l]imide (1,3-alternate 63). Yield: 0.13 g (97%), mp 67 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ 1.18 (t, JHH = 7.1 Hz, 12H, CH3CH2O–), 1.20 (s, 36H, (CH3)2C), 1.33 (d, JHH = 7.3 Hz, 12H, CH3CH2), 1.93 (m, 8H, NHCH2CH2CH2N+), 3.18 (s, 12H, (CH3)3C), 3.19 (m, 8H, NHCH2CH2CH2N+), 3.51 (m, 8H, NHCH2CH2CH2N+), 4.01 (s, 8H, OCH2CO), 4.09 (s, 8H, N′CH2CO), 4.10 (q, JHH = 7.1 Hz, 8H, CH3CH2O–), 4.30 (m, 4H, CH2CH), 7.59 (s, 8H, ArH), 8.03 (t, JHH = 4.9 Hz, 4H, NHCH2CH2CH2N+), 9.04 (d, JHH = 6.5 Hz, 4H, CONH). C 41.00%, H 5.05%, N 5.92%, S 11.66%. MS (ESI): calcld. for [M – 4N−(SO2CF3)3]+ m/z = 466.6, found m/z = 464.4. IR max: 1180 (COC), 1673 (C=O), 2965, 3357 (N-H).

5.11.17.23-Tetra-tet-t-butyl-25,26,27,28-tetakis[N(3′,3′-dimethyl-3′-[(prop-2-ynyl)carbonyl]methyl)amidocarbonylmethyl)ammoniumpropyl]carbomethoxymethoxy]-2,8,14,20-tetraathiacalix[4]arene tetra[bis(trifluoromethylsulfonylimide)l]imide (1,3-alternate 66). Yield: 0.13 g (91%), mp 87 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ 1.21 (s, 36H, (CH3)2C), 1.88 (m, 8H, CH2CH2CH2Pht), 2.05 (m, 8H, NHCH2CH2CH2N+), 2.99 (s, 2H, (CH3)2C), 3.17 (m, 8H, NHCH2CH2CH2N+), 3.29 (m, 8H, CH2CHCH2Pht), 3.39 (m, 8H, NHCH2CH2CH2N+), 3.67 (t, JHH = 6.2 Hz, 8H, CH2CHCH2Pht), 3.99 (s, 8H, OCH2CO), 7.60 (s, 8H, ArH), 7.84–7.89 (m, 16H, Pht), 8.04 (t, JHH = 5.3 Hz, 4H, NHCH2CH2CH2N+). C 41.00%, H 5.05%, N 5.92%, S 11.66%. MS (ESI): calcld. for [M – 4N−(SO2CF3)3]+ m/z = 466.6, found m/z = 464.4. IR max: 1180 (COC), 1673 (C=O), 2965, 3357 (N-H).
5.11,17-Tetra-tert-butyl-25,26,27,28-tetrakis[2-(2'-methyl-2',2'-diethyl)ammoniummethyl]carboxymethoxy]-2,8,14,20-tetra- thiadialic[4]arene tetra[bis(trifluoromethylsulfonylimide)] (1,3-alttrane 65). Yield: 0.12 g (90%), mp 83 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ: 1.22 (s, 36H, (CH3)3C), 1.26 (t, JHH = 7.1 Hz, 24H, (CH2)3), 3.02 (s, 12H, (CH3)2N), 3.21 (m, 8H, -NCH2CH2NH), 3.37 (q, JHH = 7.1 Hz, 16H, -CH2CH2), 3.48 (m, 8H, NCH2CH2NH), 4.05 (s, 8H, OCH2CO), 7.60 (s, 8H, ArH), 8.17 (t, JHH = 5.6 Hz, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6): δ: 168.02, 156.89, 146.04, 132.99, 127.49, 117.85 (q), 70.54, 56.87, 56.16, 46.96, 33.88, 32.13, 30.84, 7.39. El. anal. calecd for C8sH132F24N12O24S12: C 40.92%, H 5.15%, N 6.53%, S 12.68%. MS (ESI): calecd for [M - 4N-(SO2CF3)2]+ m/z = 365.5, found m/z = 365.4. IR vmax: 1670 (C = O), 2969, 3374 (NH).

5.11,17-Tetra-tert-butyl-25,26,27,28-tetrakis[N(2',2'-diethyl-benzyl)ammoniummethyl]carboxymethoxy]-2,8,14,20-tetra- thiadialic[4]arene tetra[bis(trifluoromethylsulfonylimide)] (1,3-alttrane 66). Yield: 0.11 g (91%), mp 49 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ: 0.87 (t, JHH = 6.6 Hz, 12H, -O(CH2)2CH2), 1.21 (s, 36H, (CH3)3C), 1.27–1.35 (m, 16H, O(CH2)2CH2CH3, OCH2CH2CH2H), 1.28 (t, JHH = 7.0 Hz, 24H, (CH2CH2)2N), 1.65 (m, 8H, O(CH2)2CH2CH3), 3.44–3.65 (m, 32H, -NCH2CH3, -NCH2CH2NH, -NCH2CH2NH), 4.07 (s, 8H, OCH2CO), 4.19 (q, JHH = 6.5 Hz, 8H, OCH2CH3), 4.48 (s, 8H, NCH2CH2NH), 7.69 (s, 8H, ArH), 8.22 (t, JHH = 5.1 Hz, 4H, CONH). 13C NMR (100 MHz, 298 K, DMSO-d6): δ: 168.01, 164.77, 156.91, 146.00, 133.00, 124.57, 119.47 (q), 70.55, 65.90, 55.78, 55.42, 54.99, 33.84, 31.96, 30.83, 27.41, 27.35, 21.66, 13.79, 7.34. El. anal. calecd for C108H164F24N12O32S12: C 43.48%, H 5.54%, N 5.63%, S 12.90%. Found: C 43.71%, H 5.52%, N 5.77%, S 12.68%. MS (ESI): calecd for [M - 4N-(SO2CF3)2]+ m/z = 465.6, found m/z = 465.5. IR vmax: 1671, 1746 (C = O), 2961, 3373 (NH).

5.11,17-Tetra-tert-butyl-25,26,27,28-tetrakis[N(2',2'-diethyl-2'-pentacyclohexylmamylniummethyl]carboxymethoxy)-2,8,14,20-tetra- thiadialic[4]arene tetra[bis(trifluoromethylsulfonylimide)] (1,3-alttrane 70). Yield: 0.13 g (93%), mp 62 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ: 1.20 (t, JHH = 7.1 Hz, 12H, CH2CH2O), 1.21 (s, 36H, (CH3)3C), 1.31 (t, JHH = 7.0 Hz, 24H, CH2CH2N), 3.48 (s, 8H, NHCH2CH2N), 3.53–3.59 (m, 16H, CH2CH2N, NHCH2CH2N), 3.96 (d, JHH = 5.7 Hz, 8H, NHCH2CO), 4.05 (s, 8H, OCH2CO), 4.12 (q, JHH = 6.5 Hz, 8H, OCH2CH3), 7.60 (s, 8H, ArH), 8.22 (t, JHH = 5.4 Hz, 4H, NHCH2CH2N), 9.10 (t, JHH = 5.7 Hz, 4H, NHCH2CO). 13C NMR (100 MHz, 298 K, DMSO-d6): δ: 169.05, 168.06, 163.55, 156.85, 145.92, 132.80, 127.65, 119.46 (q), 70.12, 60.85, 56.37, 55.87, 55.10, 40.71, 33.84, 31.95, 30.82, 14.00, 7.36. El. anal. calecd for C108H16sF24N12O32S12: C 41.85%, H 5.54%, N 5.63%, S 12.90%. Found: C 41.99%, H 5.31%, N 7.24%, S 12.05%. MS (ESI): calecd for [M - 4N-(SO2CF3)2]+ m/z = 480.6, found m/z = 481.0. IR vmax: 1180 (COC), 1685 (C = O), 2967, 3364 (N-H).

5.11,17-Tetra-tert-butyl-25,26,27,28-tetrakis[N(2',2'-diethyl-2'-ethoxy carbonylaminomethyl)mamidocarboxymethyl]ammoniummethyl]carboxymethoxy]-2,8,14,20-tetra- thiadialic[4]arene tetra[bis(trifluoromethylsulfonylimide)] (1,3-alttrane 71). Yield: 0.14 g (94%), mp 64 °C. 1H NMR (400 MHz, 298 K, DMSO-d6): δ: 1.19 (t, JHH = 7.1 Hz, 12H, CH2CH2O), 1.21 (s, 36H, (CH3)3C), 1.30 (t, JHH = 7.1 Hz, 24H, CH2CH2N), 3.44 (m, 8H, NHCH2CH2N), 3.51–3.58 (m, 24H, CH2CH2N, NHCH2CH2N), 3.87 (br. s, 8H, NHCH2CO), 3.88 (br. s, 8H, NHCH2CO), 4.04 (s, 8H, OCH2CO), 4.08 (q, JHH = 7.1 Hz, 8H, CH2CH2CO), 4.09 (s, 8H, NCH2CO), 7.59 (s, 8H, ArH), 8.21 (br. t, 4H, NHCH2CH2N), 8.51 (t, JHH = 5.7 Hz, 4H, CONH), 8.90.
(1H NMR (400 MHz, 298 K, DMSO-d<sub>6</sub>) δ: 1.19 (s, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 12H, <em>CH</em><sub>2</sub>CH<sub>2</sub>O–), 1.21 (s, 36H, <em>CH</em><sub>3</sub>), 1.32 (d, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 12H, <em>CH</em><sub>2</sub>CH), 1.34 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 24H, <em>CH</em><sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.49 (m, 8H, NH<sub>2</sub>CHCH<sub>2</sub>NH<sub>2</sub>CHCH<sub>2</sub>NH), 3.51–3.58 (m, 24H, NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>NH), 4.07 (s, 8H, OCH<sub>2</sub>CO), 4.09–4.11 (m, 16H, N<sub>2</sub>CH<sub>2</sub>CO, CH<sub>2</sub>CH<sub>2</sub>O–), 4.30 (m, 4H, CH<sub>2</sub>CH), 7.60 (s, 8H, ArH), 8.23 (t, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 4H, NHCH<sub>2</sub>NH<sup>+</sup>), 9.11 (d, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, 4H, CONH). <sup>13</sup>C NMR (100 MHz, 298 K, DMSO-d<sub>6</sub>) δ: 171.63, 169.79, 162.83, 156.91, 146.01, 133.00, 127.43, 119.48 (q), 70.54, 60.85, 56.36, 55.93, 55.17, 47.92, 33.84, 31.96, 30.18, 16.53, 13.97, 7.34. El. anal. calc. for [C<sub>135</sub>H<sub>160</sub>F<sub>4</sub>N<sub>36</sub>O<sub>36</sub>S<sub>12</sub>]<sup>+</sup>; C: 51.85%, H: 5.20%, N: 7.23%, S: 12.42%. Found: C: 42.08%, H: 5.38%, N: 6.97%, S: 12.09%. MS (ESI): calc. for [M – 4N<sup>−</sup> (SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sup>+</sup> m/z = 494.6, found m/z = 494.6. IR ν<sub>r</sub> max: 1181 (COC), 1680 (C=O), 2969, 3361 (N-H).

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Notes and references


