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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, ester, phthalimide, glycine, alanine and glycyglycine 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.

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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

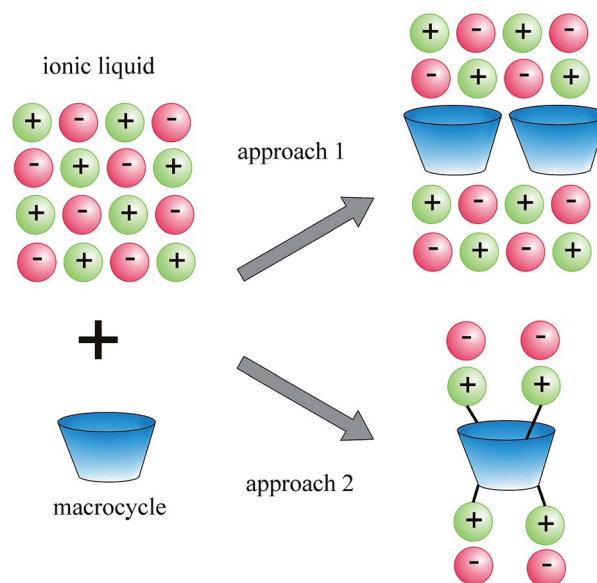


Fig. 1 Two basic approaches to the creation of macrocyclic ionic liquids based on ionic liquids and macrocyclic compounds.

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few examples of the synthesis of ionic liquids based on them.^{7,25} It should be noted that the macrocyclic ionic liquids described in the literature^{7,25,26} 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.²⁷ Ease of synthesis, low cost and non-toxicity are the advantages of quaternary ammonium fragments. According to the examples in the literature of chemistry of ionic liquids^{28–34} and (thia)calixarenes,^{1–7,35} we can assume that the introduction of quaternary ammonium fragments at the lower rim of *p*-*tert*-butylthiacalix[4]arene may be promising for the synthesis of macrocyclic ionic liquids capable to the molecular recognition of target species.

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

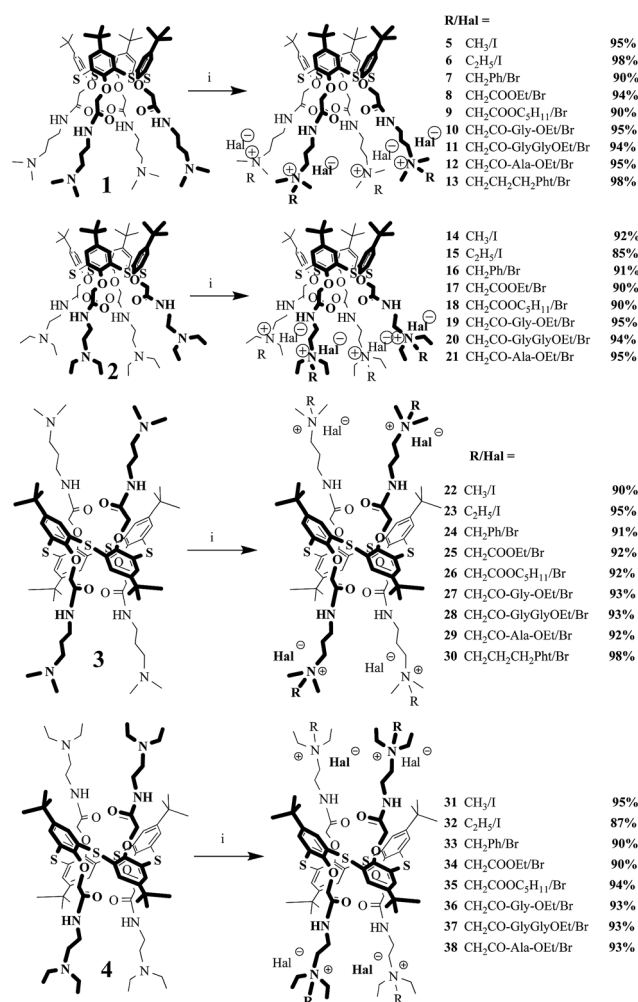
Results and discussion

Synthesis of *p*-*tert*-butylthiacalix[4]arenes containing quaternary ammonium groups

To synthesize ionic liquids based on the *p*-*tert*-butylthiacalix[4]arenes 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 suggestion³⁶ that the increase in the length of the alkyl substituent led to decrease of the melting point. According to the literature,³⁶ it was also assumed that the introduction of planar π -aromatic ring systems and the ester groups at the lower rim of the macrocycle could result in the synthesis of tetraalkylammonium derivatives of *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 compounds **5–9**, **14–18**, **22–26** and **31–35** with 85–98% yields (Scheme 1). It should be noted that all the synthesized macrocycles **5–9**, **14–18**, **22–26** and **31–35** are water-soluble. The solubility of the thiacalix[4]arenes **5–9** and **14–18** in cone conformation was much higher than that of the 1,3-alternate stereoisomers **22–26** and **31–35**.

To synthesize ionic liquids able to recognize various substrates, starting from low molecular compounds to bio-macromolecules, synthesis of the quaternary ammonium salts



Scheme 1 Reagents and conditions: i – R-Hal, CH₃CN, reflux.

based on *p*-*tert*-butylthiacalix[4]arenes containing peptide and phthalimide fragments has been performed. *N*-Bromoacetyl-glycine ethyl ester, *N*-bromoacetyl-glycylglycine ethyl ester, *N*-bromoacetyl-L-alanine ethyl ester and *N*-(3-bromopropyl) phthalimide were chosen as alkylating reagents. The presence of α -amino acid groups in the structure of *p*-*tert*-butylthiacalix[4]arenes is necessary for increasing the efficiency of interaction of the macrocycles with biomacromolecules (proteins and DNA) based on the formation of hydrogen bonds. The introduction of phthalimide groups in the structure of macrocycles is also of great interest because the compounds with phthalimide fragments can be used as intercalators for interaction with DNA or for detection of proteins by hydrophobic interactions.³⁷

The interaction of ethyl esters of *N*-bromoacetyl-glycine, *N*-bromoacetyl-glycylglycine and *N*-bromoacetyl-alanine with aminothiacalix[4]arenes **1–4** containing methyl and ethyl groups at the nitrogen atom in cone and 1,3-alternate conformations was studied earlier. Quaternary ammonium salts **10–12**, **19–21**, **27–29** and **36–38** with amino acid and peptide groups were obtained³⁸ (Scheme 1).

It is interesting to note that the reaction of the amines **1–4** with *N*-(3-bromopropyl)phthalimide in acetonitrile under 8 h

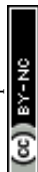


Table 1 Melting points (°C) of the macrocycles 5–21 (cone) and 22–38 (1,3-alternate)

R/Hal [−]	NH(CH ₂) ₃ N ⁺ (CH ₃) ₂ R		NH(CH ₂) ₂ N ⁺ (C ₂ H ₅) ₂ R	
	Cone	1,3-Alternate	Cone	1,3-Alternate
CH ₃ /I	192 (5)	197 (22)	159 (14)	156 (31)
C ₂ H ₅ /I	165 (6)	215 (23)	163 (15)	173 (32)
CH ₂ Ph/Br	135 (7)	150 (24)	139 (16)	131 (33)
CH ₂ COOC ₂ H ₅ /Br	112 (8)	123 (25)	118 (17)	115 (34)
CH ₂ COOC ₅ H ₁₁ /Br	106 (9)	103 (26)	135 (18)	88 (35)
CH ₂ CO-Gly-OEt/Br	114 (10)	112 (27)	111 (19)	114 (36)
CH ₂ CO-GlyGlyOEt/Br	113 (11)	120 (28)	120 (20)	124 (37)
CH ₂ CO-Ala-OEt/Br	116 (12)	118 (29)	116 (21)	118 (38)
CH ₂ CH ₂ CH ₂ Pht/Br	152 (13)	154 (30)	—	—

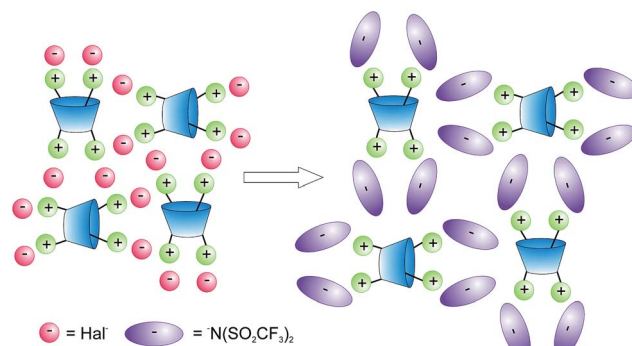
reflux resulted in formation of the products only in the case of the compounds **1** and **3** containing tertiary amino groups with *N,N*-dimethyl substituents at the lower rim in cone and 1,3-alternate conformations. The compounds **13** and **30** were synthesized with excellent yields³⁸ (Scheme 1). According to the ¹H NMR spectroscopy, the mixture of differently substituted products difficult for separation was obtained for the macrocycles **2** and **4** containing tertiary amino 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 is agreement with the literature.³⁶ Introduction of benzyl and ester groups in the structure of macrocycles decreased the melting points by 30–40 °C, in contrast to 5–7 °C predicted in the literature.³⁶ 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.

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

As shown in the literature³⁹ 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 obtained³⁹ (Fig. 2). Thus, the study of the interaction 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 the ¹H and ¹³C NMR, IR spectroscopy, mass spectrometry and elemental analysis. The ¹³C NMR spectrum of the compounds 39–72 exhibits a quartet

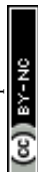
**Fig. 2** Possible scheme of the changes of crystal packing of the *p*-tert-butylthiacalix[4]arene ammonium salts at the replacement of halide ions by bis(trifluoromethylsulfonyl)imide ions.

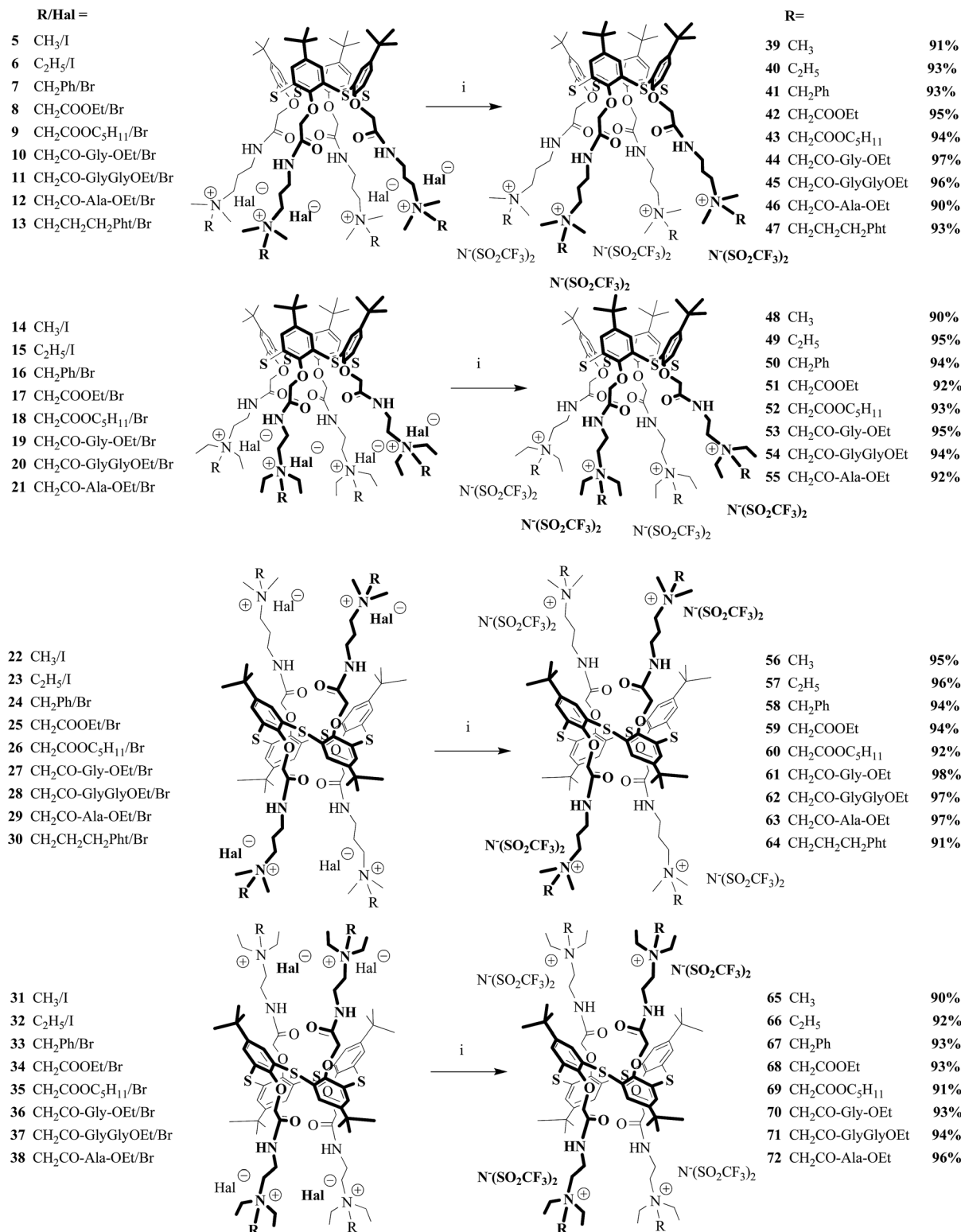
at 120 ppm; these signals correspond to anion [−]N(SO₂CF₃)₂ (Fig. S67–S100, ESI†).

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 ¹H 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 tetrasubstituted at the lower rim can be recognized by chemical shifts of the *tert*-butyl group, aromatic ring, oxymethylene and amide protons in the ¹H NMR spectra (Table S1, ESI†). In the compounds 22–38 and 56–72 in the 1,3-alternate conformation, the protons of the –OCH₂– and amide groups are located in the shielded zone of neighboring aromatic rings of the macrocycle, and their signals in the ¹H NMR spectrum are recorded at stronger fields (3.96–4.20 and 8.01–8.38 ppm, respectively) than those of the macrocycles 5–21 and 39–55 in cone conformation (4.79–5.03 and 8.23–9.13 ppm, respectively). The chemical shifts of the aromatic protons depend less on the conformation of the macrocyclic cavity. They drift by only 0.19–0.25 ppm upfield from cone 5–21 and 39–55 (7.30–7.45 ppm) to 1,3-alternate 22–38 and 56–72 (7.59–7.61 ppm) stereoisomers. This is an evidence of the shielding effect of neighboring aryl fragments in the cone stereoisomer on the aryl protons of macrocycle ring. The protons of the *tert*-butyl groups of the cone stereoisomers 5–21 and 39–55 were found at a stronger field (1.07–1.12 ppm) against corresponding proton signals of the 1,3-alternate stereoisomers 22–38 and 56–72 (1.19–1.22 ppm). This effect is probably due to the spatial location of the *tert*-butyl groups of the 1,3-alternate stereoisomer shielded by neighboring fragments of the macrocycle.

It should be noted that the proton signals in the ¹H NMR spectra of the quaternary ammonium salts 5–38 (Table S1, Fig. S1–S16, ESI†) containing halide anions, and the proton signals of initial salts 39–72 (Table S1, Fig. S17–S50, ESI†) containing 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.





Scheme 2 Reagents and conditions: i – Li⁺N[−](SO₂CF₃)₂, H₂O.

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 anions 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)



Table 2 Melting points (°C) of the macrocycles 39–55 (cone) and 56–72 (1,3-alternate)

R	NH(CH ₂) ₃ N ⁺ (CH ₃) ₂ R*N(SO ₂ CF ₃) ₂ [−]		NH(CH ₂) ₂ N ⁺ (C ₂ H ₅) ₂ R*N(SO ₂ CF ₃) ₂ [−]	
	Cone	1,3-Alternate	Cone	1,3-Alternate
CH ₃	87 (39)	106 (56)	72 (48)	83 (65)
C ₂ H ₅	71 (40)	96 (57)	68 (49)	79 (66)
CH ₂ Ph	56 (41)	87 (58)	60 (50)	76 (67)
CH ₂ COOC ₂ H ₅	45 (42)	53 (59)	43 (51)	58 (68)
CH ₂ COOC ₅ H ₁₁	35 (43)	47 (60)	39 (52)	49 (69)
CH ₂ CO-Gly-OEt	63 (44)	73 (61)	66 (53)	62 (70)
CH ₂ CO-GlyGlyOEt	69 (45)	76 (62)	64 (54)	64 (71)
CH ₂ CO-Ala-OEt	56 (46)	60 (63)	63 (55)	62 (72)
CH ₂ CH ₂ CH ₂ Pht	83 (47)	87 (64)	—	—

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 and 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 (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 (–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 CH₂– 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*₅) 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 × 10^{−7} S × cm^{−1} (Fig. 3) corresponded to moderate ionic conductivity. Fig. 3 shows low- (120 Hz) and high-frequency (500 kHz) electrical conductivity exhibiting exponential increase with the temperature. The activation energy for the high-frequency conductivity *E*_{A1} = 0.69 eV is approx. twofold less than that of the low-frequency conductivity (*E*_{A2} = 1.24 eV). This behavior of the activation energy was also observed for other organic semiconductors⁴² 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.

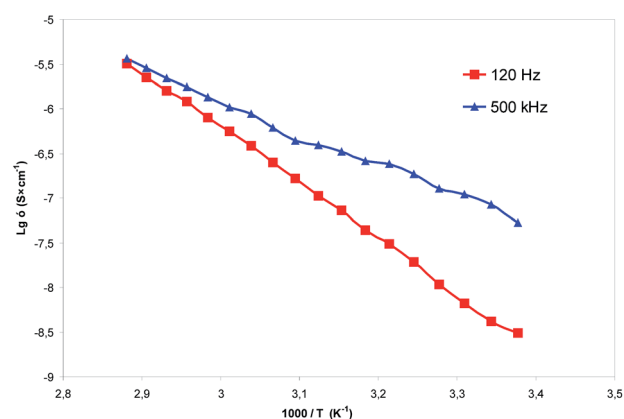


Fig. 3 Ionic conductivity of the thiacalix[4]arene cone 43.



Conclusions

Thus, water-soluble and water-insoluble *p*-*tert*-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 ^1H 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(trifluoromethylsulfonyl)imide 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. Macrocylic 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 substrates, *e.g.*, biomacromolecules and cations of heavy and transition metals.

Experimental

General

The ^1H and ^{13}C NMR spectra of compounds (3–5% solution in CDCl_3 , $(\text{CD}_3)_2\text{SO}$) were recorded on 400 MHz and 100 MHz Bruker Avance 400 spectrometer using CDCl_3 and $(\text{CD}_3)_2\text{SO}$ 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 $\sim 10^{-6}\text{ g ml}^{-1}$).

Melting points were determined using Boetius Block apparatus. The purity of the compounds was monitored by melting, boiling points, ^1H 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 – 4 mm.

In this work, the following reagents and solvents were used: acetonitrile (chemical pure), benzyl bromide (chemical pure), lithium bis(trifluoromethanesulfonyl)imide (Acros Organic), *N*-(3-bromopropyl)phthalimide (Acros Organic), distilled water, iodomethane (Acros Organic), iodoethane (Acros Organic), ethyl bromoacetate (Acros Organic), pentyl 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.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethylaminopropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (cone 1) was synthesized according to the literature procedure.⁴⁰

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethylaminoethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (cone 2) was synthesized according to the literature procedure.⁴⁰

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethylaminopropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate 3) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethylaminoethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate 4) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3',3'-trimethyl)-ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (cone 5) was synthesized according to the literature procedure.⁴⁰

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-ethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (cone 6) was synthesized according to the literature procedure.⁴¹

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-benzyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 7) was synthesized according to the literature procedure.⁴⁰

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-(ethoxycarbonylmethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 8) was synthesized according to the literature procedure.⁴¹

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((ethoxycarbonylmethyl)amidocarbonylmethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 10) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((ethoxycarbonylmethyl)amidocarbonylmethyl)amidocarbonylmethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 11) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((ethoxycarbonyl[*S*-methyl)methyl)amidocarbonylmethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 12) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-{3''-propylphthalimide}ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 13) was synthesized according to the literature procedure.⁴¹

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2'-methyl-2',2'-diethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (cone 14) was synthesized according to the literature procedure.⁴⁰



5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-{[(ethoxycarbonylmethyl)amidocarbonylmethyl]ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 19) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-{[(ethoxycarbonylmethyl)amidocarbonylmethyl]ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 20) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-{[(ethoxycarbonyl[*S*-methyl]methyl)amidocarbonylmethyl]ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 21) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dime-thyl-3'-{[(ethoxycarbonylmethyl)amidocarbonylmethyl]ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 27) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dime-thyl-3'-{[(ethoxycarbonylmethyl)amidocarbonylmethyl]ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 28) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dime-thyl-3'-{[(ethoxycarbonyl[*S*-methyl]methyl)amidocarbonylmethyl]ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 29) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-die-thyl-2'-{[(ethoxycarbonylmethyl)amidocarbonylmethyl]ammoni-umethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 36) was synthesized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-die-thyl-2'-{[(ethoxycarbonylmethyl)amidocarbonylmethyl]amidocarbon-ylmethyl]ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetrabromide (1,3-alternate 37) was synthe-sized according to the literature procedure.³⁸

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-die-thyl-2'-{[(ethoxycarbonyl[*S*-methyl]methyl)amidocarbonylmethyl]ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 38) was synthesized according to the literature procedure.³⁸

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

The compounds 1–4 (0.10 g, 0.08×10^{-3} mol) were dissolved in 2 ml of acetonitrile in the round bottom flask equipped with magnetic stirrer and a reflux condenser. Iodomethane, iodoethane, ethyl bromoacetate, pentyl bromoacetate, or benzyl bromide (0.32×10^{-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.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dime-thyl-3'-{[(ethoxycarbonylmethyl)ammoniumpropyl]carbomoyl-methoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 9). Yield: 0.12 g (90%), mp 106 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 0.87 (t, ³J_{HH} = 6.9 Hz, 12H, CH₂CH₃), 1.08 (s, 36H, (CH₃)₃C), 1.27–1.31 (m, 16H, O(CH₂)₂CH₂C₂H₅, O(CH₂)₃-CH₂CH₃), 1.60 (m, 8H, OCH₂CH₂C₃H₇), 1.95 (m, 8H, -NCH₂-CH₂CH₂NH), 3.22–3.25 (s, 32H, (CH₃)₂N⁺, -NCH₂CH₂CH₂NH), 3.60 (m, 8H, NCH₂CH₂CH₂NH), 4.14 (t, ³J_{HH} = 6.9 Hz, 8H, OCH₂C₄H₉), 4.51 (s, 8H, N⁺CH₂CO), 4.82 (s, 8H, OCH₂CO), 7.39 (s, 8H, ArH), 8.56 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-*d*₆) δ: 168.23, 164.79, 157.94, 146.70, 134.42, 128.06, 74.25, 65.74, 62.44, 60.58, 51.01, 35.25, 33.90, 30.67, 27.45, 27.33, 22.53, 21.68, 13.82. El. anal. calcd for C₉₆H₁₅₆Br₄N₈O₁₆S₄: C 54.23%, H 7.40%, N 5.27%, S 6.03%. Found: C 54.48%, H 7.64%, N 5.52%, S 6.24%. MS (ESI): calcd for [M – 2Br]²⁺ *m/z* = 983.2, [M – 3Br]³⁺ *m/z* = 628.8, [M – 4Br]⁴⁺ *m/z* = 451.6, found *m/z* = 983.4, 628.7, 451.6. IR ν_{max}: 1663, 1742 (C=O), 2956, 3349 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2',2'-triethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetra-thiacalix[4]arene tetraiodide (cone 15). Yield: 0.10 g (85%), mp 163 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 1.11 (s, 36H, (CH₃)₃C), 1.41 (t, ³J_{HH} = 7.1 Hz, 36H, CH₃CH₂-), 3.57 (q, ³J_{HH} = 7.1 Hz, 24H, -CH₂CH₃), 3.66 (m, 8H, -NCH₂CH₂NH), 3.94 (m, 8H, NCH₂CH₂NH), 4.99 (s, 8H, OCH₂CO), 7.34 (s, 8H, ArH), 8.82 (t, ³J_{HH} = 5.9 Hz, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-*d*₆) δ: 169.76, 157.13, 147.73, 134.91, 128.17, 73.99, 55.82, 54.15, 34.31, 33.68, 31.11, 8.29. El. anal. calcd for C₈₀H₁₃₂I₄N₈O₈S₄: C 48.78%, H 6.75%, N 5.69%, S 6.51%. Found: C 48.59%, H 6.66%, N 5.51%, S 6.42%. MS (ESI): calcd for [M – 2I]²⁺ *m/z* = 858.0, [M – 3I]³⁺ *m/z* = 529.7, [M – 4I]⁴⁺ *m/z* = 365.5, found *m/z* = 857.9, 529.6, 365.4. IR ν_{max}: 1669 (C=O), 2955, 3317 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-die-thyl-2'-benzyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 16). Yield: 0.12 g (91%), mp 139 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 1.10 (s, 36H, (CH₃)₃C), 1.44 (t, ³J_{HH} = 6.7 Hz, 24H, CH₃CH₂-), 3.50 (q, ³J_{HH} = 6.7 Hz, 16H, -CH₂CH₃), 3.63 (m, 8H, -NCH₂CH₂NH), 4.10 (m, 8H, NCH₂CH₂NH), 4.92 (s, 8H, N⁺CH₂Ph), 5.03 (s, 8H, OCH₂CO), 7.32 (s, 8H, ArH), 7.36–7.40 (m, 8H, Ar'H), 7.64 (m, 12H, Ar'H), 9.08 (t, ³J_{HH} = 5.7 Hz, 4H, CONH). ¹³C NMR (100 MHz, 298 K, CDCl₃) δ: 169.89, 157.44, 147.45, 134.85, 132.89, 130.61, 129.38, 128.30, 127.09, 73.98, 62.04, 55.80, 53.91, 34.27, 33.72, 31.11, 8.70. El. anal. calcd for C₁₀₀H₁₄₀Br₄N₈O₈S₄: C 59.16%, H 6.95%, N 5.52%, S 6.32%. Found: C 59.35%, H 6.72%, N 5.23%, S 6.47%. MS (ESI): calcd for [M – 2Br]²⁺ *m/z* = 935.2, [M – 3Br]³⁺ *m/z* = 596.8, [M – 4Br]⁴⁺ *m/z* = 427.6, found *m/z* = 935.4, 596.7, 427.7. IR ν_{max}: 1670 (C=O), 2960, 3320 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-die-thyl-2'-{[(ethoxycarbonylmethyl)ammoniummethyl]carbomoyl-methoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 17). Yield: 0.12 g (90%), mp 118 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 1.10 (s, 36H, (CH₃)₃C), 1.29 (t, ³J_{HH} = 7.1 Hz, 12H OCH₂CH₃), 1.46 (t, ³J_{HH} = 7.0 Hz, 24H, CH₃CH₂-), 3.88–4.03 (m,



32H, $-\text{CH}_2\text{CH}_3$, $-\text{NCH}_2\text{CH}_2\text{NH}$, 8H, $\text{NCH}_2\text{CH}_2\text{NH}$), 4.24 (q, $^3J_{\text{HH}} = 7.1$ Hz, 8H, OCH_2CH_3), 4.75 (s, 8H, $\text{N}^+\text{CH}_2\text{CO}$), 4.97 (s, 8H, OCH_2CO), 7.33 (s, 8H, ArH), 9.03 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, CDCl_3) δ : 169.97, 164.50, 157.34, 147.56, 134.84, 128.27, 73.95, 62.90, 57.49, 56.71, 56.23, 34.26, 33.71, 31.08, 14.02, 8.56. El. anal. calcd for $\text{C}_{88}\text{H}_{140}\text{Br}_4\text{N}_8\text{O}_{16}\text{S}_4$: C 52.48%, H 6.53%, N 5.86%, S 6.70%. Found: C 52.65%, H 6.71%, N 6.01%, S 6.27%. MS (ESI): calcd for $[\text{M} - 3\text{Br}^-]^{3+} m/z = 591.3$, $[\text{M} - 4\text{Br}^-]^{4+} m/z = 423.5$, found $m/z = 591.5$, 423.5. IR ν_{max} : 1666, 1740 (C=O), 2958, 3322 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(pentoxycarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (cone 18). Yield: 0.11 g (90%), mp 135 °C. ^1H NMR (400 MHz, 298 K, CDCl_3) δ : 0.88 (t, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{O}(\text{CH}_2)_4\text{CH}_3$), 1.09 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.26–1.33 (m, 16H, $\text{O}(\text{CH}_2)_3\text{CH}_2\text{CH}_3$, $\text{O}(\text{CH}_2)_2\text{CH}_2\text{C}_2\text{H}_5$), 1.44 (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, $\text{CH}_3\text{CH}_2\text{N}^+$), 1.63 (m, 8H, $\text{OCH}_2\text{CH}_2\text{C}_3\text{H}_7$), 3.88–3.97 (m, 32H, $-\text{N}^+\text{CH}_2\text{CH}_3$, $-\text{NCH}_2\text{CH}_2\text{NH}$, $-\text{NCH}_2\text{CH}_2\text{NH}$), 4.14 (t, $^3J_{\text{HH}} = 6.8$ Hz, 8H, $\text{OCH}_2\text{C}_4\text{H}_9$), 4.70 (s, 8H, $\text{N}^+\text{CH}_2\text{CO}$), 4.93 (s, 8H, OCH_2CO), 7.30 (s, 8H, ArH), 9.01 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, CDCl_3) δ : 169.88, 164.55, 157.40, 147.51, 134.82, 128.22, 73.90, 66.91, 57.63, 56.76, 55.91, 34.25, 33.81, 31.09, 27.97, 27.75, 22.90, 13.91, 8.78. El. anal. calcd for $\text{C}_{100}\text{H}_{164}\text{Br}_4\text{N}_8\text{O}_{16}\text{S}_4$: C 55.04%, H 7.57%, N 5.13%, S 5.88%. Found: C 54.99%, H 7.53%, N 4.98%, S 5.63%. MS (ESI): calcd for $[\text{M} - 4\text{Br}^-]^{4+} m/z = 465.6$, found $m/z = 465.6$. IR ν_{max} : 1670, 1741 (C=O), 2956, 3320 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-trimethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (1,3-alternate 22). Yield: 0.12 g (90%), mp 197 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.21 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.91 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.17 (s, 36H, $(\text{CH}_3)_3\text{N}^+$), 3.32 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.60 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.98 (s, 8H, OCH_2CO), 7.60 (s, 8H, ArH), 8.01 (t, $^3J_{\text{HH}} = 5.2$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.37, 157.02, 146.08, 132.95, 127.61, 70.96, 63.23, 52.23, 35.81, 33.89, 30.78, 22.86. El. anal. calcd for $\text{C}_{72}\text{H}_{116}\text{I}_4\text{N}_8\text{O}_8\text{S}_4$: C 46.55%, 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 $[\text{M} - \text{I}^-]^{+} m/z = 1730.7$, found $m/z = 1730.2$. IR ν_{max} : 1660 (C=O), 2955, 3292 (NH).

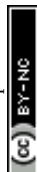
5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-ethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (1,3-alternate 23). Yield: 0.14 g (95%), mp 215 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.21 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.24 (t, $^3J_{\text{HH}} = 7.1$ Hz, 12H, $\text{N}^+\text{CH}_2\text{CH}_3$), 1.88 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.01 (s, 24H, $(\text{CH}_3)_2\text{N}^+$), 3.19 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.29 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.35 (q, $^3J_{\text{HH}} = 7.2$ Hz, 8H, $\text{N}^+\text{CH}_2\text{CH}_3$), 3.99 (s, 8H, OCH_2CO), 7.60 (s, 8H, ArH), 8.03 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) 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 $\text{C}_{76}\text{H}_{124}\text{I}_4\text{N}_8\text{O}_8\text{S}_4$: 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 $[\text{M} - \text{I}^-]^{+} m/z = 1786.8$, found $m/z = 1786.5$. IR ν_{max} : 1653 (C=O), 2958, 3335 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-benzyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 24). Yield: 0.12 g (91%), mp 150 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.20 (s, 36H, $(\text{CH}_3)_3\text{C}$), 2.05 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.00 (s, 24H, $(\text{CH}_3)_2\text{N}^+$), 3.21 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.37 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 4.01 (s, 8H, OCH_2CO), 4.60 (s, 8H, $\text{N}^+\text{CH}_2\text{Ph}$), 7.52 (m, 12H, Ar'H), 7.59 (m, 8H, Ar'H), 7.60 (s, 8H, ArH), 8.10 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.44, 157.03, 146.06, 133.12, 132.95, 130.29, 128.89, 128.00, 127.57, 70.90, 65.91, 61.12, 49.22, 35.86, 33.87, 30.79, 22.63. El. anal. calcd for $\text{C}_{96}\text{H}_{132}\text{Br}_4\text{N}_8\text{O}_8\text{S}_4$: C 58.41%, H 6.74%, N 5.68%, S 6.50%. Found: C 58.75%, H 6.62%, N 6.01%, S 6.37%. MS (MALDI TOF): calcd for $[\text{M} - \text{Br}^-]^{+} m/z = 1245.7$, found $m/z = 1245.8$. IR ν_{max} : 1664 (C=O), 2955, 3287 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-(ethoxycarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 25). Yield: 0.13 g (92%), mp 123 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.20 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.25 (t, $^3J_{\text{HH}} = 7.1$ Hz, 12H, OCH_2CH_3), 1.91 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.17 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.22 (s, 24H, $(\text{CH}_3)_2\text{N}^+$), 4.00 (s, 8H, OCH_2CO), 4.55 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 4.24 (q, $^3J_{\text{HH}} = 7.2$ Hz, 8H, $\text{N}^+\text{CH}_2\text{CH}_3$), 4.47 (s, 8H, $\text{N}^+\text{CH}_2\text{CO}$), 7.60 (s, 8H, ArH), 8.05 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.39, 164.85, 157.40, 146.19, 133.26, 127.82, 70.89, 62.30, 62.00, 60.54, 51.12, 35.69, 33.85, 30.77, 22.44, 13.85. El. anal. calcd for $\text{C}_{84}\text{H}_{132}\text{Br}_4\text{N}_8\text{O}_{16}\text{S}_4$: C 51.53%, H 6.80%, N 5.72%, S 6.55%. Found: C 51.49%, H 6.58%, N 5.55%, S 6.64%. MS (ESI): calcd for $[\text{M} - 4\text{Br}^-]^{4+} m/z = 409.6$, found $m/z = 409.5$. IR ν_{max} : 1666, 1742 (C=O), 2958, 3300 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-(pentoxycarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 26). Yield: 0.13 g (92%), mp 103 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 0.87 (t, $^3J_{\text{HH}} = 6.9$ Hz, 12H CH_2CH_3), 1.20 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.27–1.33 (m, 16H, $\text{O}(\text{CH}_2)_2\text{CH}_2\text{C}_2\text{H}_5$, $\text{O}(\text{CH}_2)_3\text{CH}_2\text{CH}_3$), 1.62 (m, 8H, $\text{OCH}_2\text{CH}_2\text{C}_3\text{H}_7$), 1.92 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.18 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.35 (s, 24H, $(\text{CH}_3)_2\text{N}^+$), 3.56 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}$), 3.98 (s, 8H, OCH_2CO), 4.17 (t, $^3J_{\text{HH}} = 6.6$ Hz, 4H, $\text{OCH}_2\text{C}_4\text{H}_9$), 4.50 (s, 8H, $\text{N}^+\text{CH}_2\text{CO}$), 7.60 (s, 8H, ArH), 8.06 (t, $^3J_{\text{HH}} = 5.4$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.37, 164.77, 157.10, 146.01, 133.03, 127.54, 70.94, 65.80, 62.36, 60.53, 51.12, 35.70, 33.84, 30.78, 27.44, 27.36, 22.55, 21.66, 13.79. El. anal. calcd for $\text{C}_{96}\text{H}_{156}\text{Br}_4\text{N}_8\text{O}_{16}\text{S}_4$: C 54.23%, H 7.40%, N 5.27%, S 6.03%. Found: C 54.12%, H 7.54%, N 5.38%, S 5.96%. MS (ESI): calcd for $[\text{M} - 2\text{Br}^-]^{2+} m/z = 983.2$, $[\text{M} - 3\text{Br}^-]^{3+} m/z = 628.8$, $[\text{M} - 4\text{Br}^-]^{4+} m/z = 451.6$, found $m/z = 982.4$, 628.9, 451.6. IR ν_{max} : 1665, 1742 (C=O), 2954, 3300 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2'-methyl-2',2'-diethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (1,3-alternate 31). Yield: 0.13 g (95%), mp 156 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.22 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.27 (t, $^3J_{\text{HH}} = 6.5$ Hz, 24H, $(\text{CH}_3\text{CH}_2-)$), 2.98 (s, 12H, $(\text{CH}_3)_2\text{N}^+$), 3.21 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{NH}$), 3.39 (q, $^3J_{\text{HH}} =$



6.5 Hz, 16H, $-\text{CH}_2\text{CH}_3$), 3.49 (m, 8H, $\text{NCH}_2\text{CH}_2\text{NH}$), 4.05 (s, 8H, OCH_2CO), 7.61 (s, 8H, ArH), 8.18 (t, $^3J_{\text{HH}} = 5.5$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) 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. calcd for $\text{C}_{76}\text{H}_{124}\text{I}_4\text{N}_8\text{O}_8\text{S}_4$: C 47.70%, H 6.53%, N 5.86%, S 6.70%. Found: C 47.54%, H 5.93%, N 6.16%, S 6.17%. MS (ESI): calcd for $[\text{M} - 2\text{I}]^{2+}$ $m/z = 829.3$, $[\text{M} - 3\text{I}]^{3+}$ $m/z = 510.3$, $[\text{M} - 4\text{I}]^{4+}$ $m/z = 351.2$, found $m/z = 829.3$, 510.6, 351.4. IR ν_{max} : 1664 (C=O), 2955, 3300 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(*N*-(2',2'-triethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetraiodide (1,3-alternate 32). Yield: 0.11 g (87%), mp 173 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.22 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.23 (t, $^3J_{\text{HH}} = 7.1$ Hz, 36H, CH_3CH_2-), 3.15 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{NH}$), 3.31 (q, $^3J_{\text{HH}} = 7.1$ Hz, 24H, $-\text{CH}_2\text{CH}_3$), 3.47 (m, 8H, $\text{NCH}_2\text{CH}_2\text{NH}$), 4.03 (s, 8H, OCH_2CO), 7.61 (s, 8H, ArH), 8.13 (t, $^3J_{\text{HH}} = 5.3$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.98, 156.74, 146.14, 132.94, 127.58, 70.46, 53.53, 52.46, 33.91, 31.84, 30.84, 7.04. El. anal. calcd for $\text{C}_{80}\text{H}_{132}\text{I}_4\text{N}_8\text{O}_8\text{S}_4$: C 48.78%, H 6.75%, N 5.69%, S 6.51%. Found: C 49.02%, H 6.58%, N 5.73%, S 6.37%. MS (ESI): calcd for $[\text{M} - 4\text{I}]^{4+}$ $m/z = 365.6$, found $m/z = 365.5$. IR ν_{max} : 1664 (C=O), 2955, 3261 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(benzyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 33). Yield: 0.12 g (90%), mp 131 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.19 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.39 (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, CH_3CH_2-), 3.16 (m, 8H, $\text{NCH}_2\text{CH}_2\text{NH}$), 3.25 (q, $^3J_{\text{HH}} = 7.1$ Hz, 16H, $-\text{CH}_2\text{CH}_3$), 3.62 (m, 8H, $\text{NCH}_2\text{CH}_2\text{NH}$), 4.20 (s, 8H, OCH_2CO), 4.60 (s, 8H, $\text{N}^+\text{CH}_2\text{Ph}$), 7.53 (m, 8H, Ar'H), 7.58 (m, 12H, Ar'H), 7.60 (s, 8H, ArH), 8.38 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 168.07, 157.35, 145.80, 133.44, 132.63, 130.46, 129.15, 127.49, 127.18, 70.84, 60.55, 54.14, 53.19, 33.87, 32.07, 30.89, 7.57. El. anal. calcd for $\text{C}_{100}\text{H}_{140}\text{Br}_4\text{N}_8\text{O}_8\text{S}_4$: C 59.16%, H 6.95%, N 5.52%, S 6.32%. Found: C 58.95%, H 7.05%, N 5.28%, S 6.13%. MS (ESI): calcd for $[\text{M} - 4\text{Br}]^{4+}$ $m/z = 427.6$, found $m/z = 427.3$. IR ν_{max} : 1669 (C=O), 2954, 3194 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(ethoxycarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 34). Yield: 0.12 g (90%), mp 115 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.22 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.26 (t, $^3J_{\text{HH}} = 7.1$ Hz, 12H, OCH_2CH_3), 1.28 (t, $^3J_{\text{HH}} = 7.0$ Hz, 24H, CH_3CH_2-), 3.45–3.65 (m, 32H, $-\text{CH}_2\text{CH}_3$, $-\text{NCH}_2\text{CH}_2\text{NH}$, $-\text{NCH}_2\text{CH}_2\text{NH}$), 4.04 (s, 8H, OCH_2CO), 4.24 (q, $^3J_{\text{HH}} = 7.1$ Hz, 8H, OCH_2CH_3), 4.48 (s, 8H, $\text{N}^+\text{CH}_2\text{CO}$), 7.60 (s, 8H, ArH), 8.27 (t, $^3J_{\text{HH}} = 4.9$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 168.03, 164.24, 156.99, 145.96, 133.08, 127.38, 70.57, 62.13, 55.83, 55.54, 55.08, 33.86, 32.00, 30.87, 13.76, 7.41. El. anal. calcd for $\text{C}_{88}\text{H}_{140}\text{Br}_4\text{N}_8\text{O}_{16}\text{S}_4$: C 52.48%, H 6.53%, N 5.86%, S 6.70%. Found: C 52.64%, H 6.73%, N 6.06%, S 6.33%. MS (ESI): calcd for $[\text{M} - 4\text{Br}]^{4+}$ $m/z = 423.2$, $[\text{M} - 3\text{Br}]^{3+}$ $m/z = 591.4$, $[\text{M} - 2\text{Br}]^{2+}$ $m/z = 927.0$, found $m/z = 423.5$, 591.5, 926.8. IR ν_{max} : 1669, 1741 (C=O), 2957, 3187 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(pentoxycarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 35). Yield: 0.14 g (94%), mp 88 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 0.87 (t, $^3J_{\text{HH}} = 6.6$ Hz, 12H, $-\text{O}(\text{CH}_2)_4\text{CH}_3$), 1.21 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.25–1.32 (m, 16H, $\text{O}(\text{CH}_2)_3\text{CH}_2\text{CH}_3$, $\text{O}(\text{CH}_2)_2\text{CH}_2\text{C}_2\text{H}_5$), 1.28 (t, $^3J_{\text{HH}} = 7.0$ Hz, 24H, $(\text{CH}_3\text{CH}_2\text{N}^+)$), 1.63 (m, 8H, $\text{OCH}_2-\text{CH}_2\text{C}_3\text{H}_7$), 3.45–3.63 (m, 32H, $-\text{N}^+\text{CH}_2\text{CH}_3$, $-\text{NCH}_2\text{CH}_2\text{NH}$, $-\text{NCH}_2\text{CH}_2\text{NH}$), 4.08 (s, 8H, OCH_2CO), 4.18 (t, $^3J_{\text{HH}} = 6.4$ Hz, 8H, $\text{OCH}_2\text{C}_4\text{H}_9$), 4.51 (s, 8H, $\text{N}^+\text{CH}_2\text{CO}$), 7.60 (s, 8H, ArH), 8.29 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.93, 164.44, 157.02, 145.20, 133.11, 127.37, 70.58, 65.69, 55.87, 55.52, 55.05, 33.86, 31.53, 30.87, 27.43, 27.35, 21.66, 13.80, 7.95. El. anal. calcd for $\text{C}_{100}\text{H}_{164}\text{Br}_4\text{N}_8\text{O}_{16}\text{S}_4$: C 55.04%, H 7.57%, N 5.13%, S 5.88%. Found: C 54.96%, H 7.68%, N 5.11%, S 5.94%. MS (ESI): calcd for $[\text{M} - 4\text{Br}]^{4+}$ $m/z = 465.6$, found $m/z = 465.6$. IR ν_{max} : 1669, 1741 (C=O), 2955, 3300 (NH).

Procedure for the synthesis of compound 30

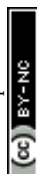
The compound 3 (0.10 g, 0.08×10^{-3} mol) was dissolved in 10 ml of acetonitrile in the round bottom flask equipped with magnetic stirrer and a reflux condenser. *N*-(3-Bromopropyl)phthalimide (0.32×10^{-3} mol) was added. The reaction mixture was refluxed for 8 h. The solvent was removed under reduced pressure. The precipitate was dried under reduced pressure over phosphorus pentoxide.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-{3''-propylphthalimide}ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetrabromide (1,3-alternate 30). Yield: 0.14 g (98%), mp 154 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.20 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.88 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2-\text{Pht}$), 2.06 (m, 8H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}^+$), 3.00 (s, 24H, $(\text{CH}_3)_2\text{N}^+$), 3.17 (m, 8H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}^+$), 3.30 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Pht}$), 3.56 (m, 8H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}^+$), 3.70 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Pht}$), 3.99 (s, 8H, OCH_2CO), 7.60 (s, 8H, ArH), 7.82–7.89 (m, 16H, Pht), 8.05 (t, $^3J_{\text{HH}} = 5.3$ Hz, 4H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}^+$). ^{13}C NMR (100 MHz, 298 K, $\text{DMSO}-d_6$) δ : 167.94, 167.21, 146.00, 134.42, 134.15, 131.66, 127.64, 123.10, 122.96, 58.56, 49.88, 36.15, 34.69, 33.85, 31.89, 31.10, 30.55, 21.60, 20.73. El. anal. calcd for $\text{C}_{112}\text{H}_{144}\text{Br}_4\text{N}_{12}\text{O}_{16}\text{S}_4$: C 56.94%, H 6.14%, N 7.12%, S 5.43%, Br 13.53%. Found: C 56.91%, H 5.85%, N 6.04%, S 5.46%, Br 13.65%. MS (ESI): calcd for $[\text{M} - 4\text{Br}]^{4+}$ $m/z = 510.7$, found $m/z = 510.6$. IR ν_{max} : 1667, 1705 (C=O), 2956, 3315 (N-H).

General procedure for the synthesis of compounds 39–72

The compounds 5–38 (0.10 g) were dissolved in 2 ml of water in the round bottom flask equipped with magnetic stirrer. Lithium bis(trifluoromethylsulfonyl)imide was added in the molar ratio of 1 : 1 taken for each ammonium group. The reaction mixture was stirred for 24 h. The precipitate was filtered and dried under reduced pressure over phosphorus pentoxide.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(*N*-(3',3',3'-trimethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 39). Yield: 0.09 g (91%), mp 87 °C. ^1H NMR (400 MHz, 298 K, $\text{DMSO}-d_6$) δ : 1.08 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.89 (m, 8H,



–NCH₂CH₂CH₂NH), 3.05 (s, 36H, (CH₃)₃N⁺), 3.25 (m, 8H, –NCH₂CH₂CH₂NH), 3.27 (m, 8H, NCH₂CH₂CH₂NH), 4.82 (s, 8H, OCH₂CO), 7.40 (s, 8H, ArH), 8.49 (t, ³J_{HH} = 5.2 Hz, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 168.26, 157.99, 146.80, 134.42, 128.02, 119.96 (q), 74.22, 63.40, 52.29, 35.38, 33.91, 30.69, 22.83. El. anal. calcd for C₈₀H₁₁₆F₂₄N₁₂O₂₄S₁₂: 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): calcd for [M – N[–](SO₂CF₃)₂]⁺ m/z = 2188.5, found m/z = 2189.4. IR ν_{max}: 1669 (C=O), 2965, 3327 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(*N*-(3',3'-dime-thyl-3'-ethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 40). Yield: 0.10 g (93%), mp 71 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.08 (s, 36H, (CH₃)₃C), 1.22 (t, ³J_{HH} = 7.0 Hz, 12H, N⁺CH₂CH₃), 1.87 (m, 8H, –NCH₂CH₂CH₂NH), 2.97 (s, 24H, (CH₃)₂N⁺), 3.23 (m, 8H, –NCH₂CH₂CH₂NH), 3.29 (q, ³J_{HH} = 7.2 Hz, 8H, N⁺CH₂CH₃), 3.32 (m, 8H, NCH₂CH₂CH₂NH), 4.82 (s, 8H, OCH₂CO), 7.40 (s, 8H, ArH), 8.49 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 168.24, 157.94, 146.78, 134.43, 127.99, 119.67 (q), 74.17, 60.33, 58.65, 49.53, 35.39, 33.91, 30.67, 22.35, 7.74. El. anal. calcd for C₈₄H₁₂₄F₂₄N₁₂O₂₄S₁₂: 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): calcd for [M – N[–](SO₂CF₃)₂]⁺ m/z = 2244.6, found m/z = 2244.8. IR ν_{max}: 1671 (C=O), 2965, 3328 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(*N*-(3',3'-dime-thyl-3'-benzyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 41). Yield: 0.10 g (93%), mp 56 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 1.10 (s, 36H, (CH₃)₃C), 2.23 (m, 8H, –NCH₂CH₂CH₂NH), 2.98 (s, 24H, (CH₃)₂N⁺), 3.50 (m, 8H, –NCH₂CH₂CH₂–NH), 3.53 (m, 8H, NCH₂CH₂CH₂NH), 4.42 (s, 8H, N⁺CH₂CO), 4.91 (s, 8H, OCH₂CO), 7.35 (s, 8H, ArH), 7.43 (m, 20H, Ar⁺H), 8.29 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, CDCl₃) δ: 169.24, 157.30, 147.80, 134.97, 132.85, 131.06, 129.43, 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. calcd for C₁₀₄H₁₃₂F₂₄N₁₂O₂₄S₁₂: C 45.01%, H 4.79%, N 6.06%, S 13.87%. Found: C 45.30%, H 4.69%, N 5.84%, S 14.04%. MS (MALDI TOF): calcd for [M – N[–](SO₂CF₃)₂]⁺ m/z = 2492.6, found m/z = 2493.3. IR ν_{max}: 1658 (C=O), 2961, 3328 (NH).

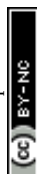
5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dime-thyl-3'-((ethoxycarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 42). Yield: 0.11 g (95%), mp 45 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 1.11 (s, 36H, (CH₃)₃C), 1.30 (t, ³J_{HH} = 7.1 Hz, 12H, OCH₂CH₃), 2.14 (m, 8H, –NCH₂CH₂CH₂–NH), 3.34 (s, 24H, (CH₃)₂N⁺), 3.47 (m, 8H, –NCH₂CH₂CH₂NH), 3.72 (m, 8H, NCH₂CH₂CH₂NH), 4.23 (s, 8H, N⁺CH₂CO), 4.26 (q, ³J_{HH} = 7.0 Hz, 8H, N⁺CH₂CH₃), 4.89 (s, 8H, OCH₂CO), 7.35 (s, 8H, ArH), 8.23 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, CDCl₃) δ: 169.12, 164.07, 157.27, 147.82, 134.87, 119.67 (q), 74.26, 64.50, 62.95, 56.57, 51.42, 35.93, 34.28, 31.05, 29.81, 22.82, 13.71. El. anal. calcd for C₉₂H₁₃₂F₂₄N₁₂O₃₂S₁₂: C 40.05%, H 4.82%, N 6.09%, S 13.95%. Found: C 39.66%, H 4.81%, N 5.77%, S 13.66%. MS (MALDI TOF): calcd for [M –

N[–](SO₂CF₃)₂]⁺ m/z = 2478.7, found m/z = 2480.0. IR ν_{max}: 1669, 1747 (C=O), 2965, 3328 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dime-thyl-3'-((pentoxycarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 43). Yield: 0.12 g (94%), mp 35 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 0.87 (t, ³J_{HH} = 6.7 Hz, 12H, O(CH₂)₄CH₃), 1.08 (s, 36H, (CH₃)₃C), 1.24–1.36 (m, 16H, O(CH₂)₃CH₂CH₃, O(CH₂)₂CH₂C₂H₅), 1.57 (m, 8H, OCH₂CH₂C₃H₇), 1.94 (m, 8H, –NCH₂CH₂CH₂NH), 3.16 (s, 24H, (CH₃)₂N⁺), 3.49 (m, 8H, –NCH₂CH₂CH₂NH), 3.54 (m, 8H, NCH₂CH₂CH₂–NH), 4.14 (t, ³J_{HH} = 6.5 Hz, 8H, OCH₂C₄H₉), 4.42 (s, 8H, N⁺CH₂CO), 4.79 (s, 8H, OCH₂CO), 7.39 (s, 8H, ArH), 8.47 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 168.26, 164.71, 158.00, 146.79, 134.42, 127.99, 119.66 (q), 74.21, 65.76, 62.35, 60.58, 51.11, 35.22, 33.89, 30.64, 27.43, 27.34, 22.49, 21.66, 13.77. El. anal. calcd for C₁₀₄H₁₅₆F₂₄N₁₂O₃₂S₁₂: C 42.67%, H 5.37%, N 5.74%, S 13.15%. Found: C 42.58%, H 5.36%, N 5.55%, S 13.00%. MS (ESI): calcd for [M – 2N[–](SO₂CF₃)₂]²⁺ m/z = 1183.4, [M – 3N[–](SO₂CF₃)₂]³⁺ m/z = 695.0, [M – 4N[–](SO₂CF₃)₂]⁴⁺ m/z = 451.6, found m/z = 1183.0, 695.3, 451.5. IR ν_{max}: 1669, 1747 (C=O), 2962, 3329 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((ethoxycarbonylmethyl)amidocarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 44). Yield: 0.13 g (97%), mp 63 °C. ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 1.11 (s, 36H, (CH₃)₃C), 1.26 (t, ³J_{HH} = 7.1 Hz, 12H, CH₃CH₂O–), 2.17 (m, 8H, NHCH₂CH₂CH₂N⁺), 3.31 (s, 12H, (CH₃)₂N⁺), 3.47 (m, 8H, NHCH₂CH₂CH₂N⁺), 3.62 (m, 8H, NHCH₂CH₂CH₂N⁺), 3.97 (d, ³J_{HH} = 5.5 Hz, 8H, NHCH₂CO), 4.10 (s, 8H, N⁺CH₂CO), 4.15 (q, ³J_{HH} = 7.1 Hz, 8H, CH₃CH₂O–), 4.89 (s, 8H, OCH₂CO), 7.35 (s, 8H, ArH), 7.77 (t, ³J_{HH} = 5.8 Hz, 4H, NHCH₂CH₂CH₂N⁺), 8.23 (br. s, 4H, NHCH₂CO). ¹³C NMR (100 MHz, 298 K, CDCl₃) δ: 169.35, 168.48, 162.93, 157.12, 147.89, 135.02, 127.69, 119.75 (q), 74.26, 64.84, 62.56, 61.60, 51.98, 41.34, 35.99, 34.34, 31.04, 22.96, 14.03. El. anal. calcd for C₁₀₀H₁₄₄F₂₄N₁₆O₃₆S₁₂: C 40.21%, H 4.86%, N 7.50%, S 12.88%. Found: C 40.12%, H 5.12%, N 7.53%, S 12.47%. MS (ESI): calcd for [M – 3N[–](SO₂CF₃)₂]³⁺ m/z = 715.5, [M – 4N[–](SO₂CF₃)₂]⁴⁺ m/z = 466.6, found m/z = 715.3, 466.6. IR ν_{max}: 1670, 1743 (C=O), 2966, 3354 (N–H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((ethoxycarbonylmethyl)amidocarbonylmethyl)amidocarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 45). Yield: 0.14 g (96%), mp 69 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.08 (s, 36H, (CH₃)₃C), 1.19 (t, ³J_{HH} = 7.1 Hz, 12H, CH₃CH₂O–), 1.93 (m, 8H, NHCH₂CH₂CH₂N⁺), 3.16 (s, 12H, (CH₃)₂N⁺), 3.24 (m, 8H, NHCH₂CH₂CH₂N⁺), 3.47 (m, 8H, NHCH₂CH₂CH₂N⁺), 3.86 (d, ³J_{HH} = 5.7 Hz, 8H, NHCH₂CO), 3.87 (d, ³J_{HH} = 6.1 Hz, 8H, NHCH₂CO), 4.06 (s, 8H, N⁺CH₂CO), 4.09 (q, ³J_{HH} = 7.1 Hz, 8H, CH₃CH₂O–), 4.80 (s, 8H, OCH₂CO), 7.40 (s, 8H, ArH), 8.50 (br. s, 16H, NHCH₂CH₂CH₂N⁺, NHCH₂CO), 8.82 (t, ³J_{HH} = 5.9 Hz, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 169.75, 168.51, 163.04, 157.72, 146.88, 134.43, 127.82, 119.48 (q), 73.34, 62.73, 62.02, 60.50, 54.78, 51.23, 41.53, 40.59, 35.36, 33.85, 30.68, 22.52, 13.97. El. anal. calcd for



$C_{108}H_{156}F_{24}N_{20}O_{40}S_{12}$: C 40.34%, H 4.89%, N 8.71%, S 11.97%. Found: C 41.00%, H 4.71%, N 7.58%, S 12.41%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 523.7$, found $m/z = 523.6$. IR ν_{max} : 1663 (C=O), 2965, 3342 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((ethoxycarbonyl[*S*-methyl)methyl)amidocarbonylmethyl)ammoniumpropyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 46). Yield: 0.12 g (90%), mp 56 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.08 (s, 36H, $(CH_3)_3C$), 1.19 (t, $^3J_{HH} = 7.1$ Hz, 12H, CH_3CH_2O-), 1.31 (d, $^3J_{HH} = 7.3$ Hz, 12H, CH_3CH), 1.92 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.16 (s, 12H, $(CH_3)_2N^+$), 3.23 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.48 (m, 8H, $NHCH_2CH_2CH_2N^+$), 4.06 (s, 8H, N^+CH_2CO), 4.09 (m, 8H, CH_3CH_2O-), 4.26 (m, 4H, CH_3CH), 4.80 (s, 8H, OCH_2CO), 7.39 (s, 8H, ArH), 8.50 (t, $^3J_{HH} = 5.4$ Hz, 4H, $NHCH_2CH_2CH_2N^+$), 9.02 (d, $^3J_{HH} = 6.7$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 171.45, 167.98, 163.20, 158.28, 146.99, 134.03, 127.79, 119.49 (q), 74.03, 62.43, 61.69, 60.83, 51.16, 47.75, 35.12, 33.52, 30.36, 22.74, 16.63, 13.51. El. anal. calcd for $C_{104}H_{152}F_{24}N_{16}O_{36}S_{12}$: C 41.05%, H 5.03%, N 7.36%, S 12.64%. Found: C 40.51%, H 4.69%, N 6.16%, S 13.32%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 480.6$, found $m/z = 480.5$. IR ν_{max} : 1672 (C=O), 2966, 3353 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-((3''-propylphthalimide)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 47). Yield: 0.13 g (93%), mp 83 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.07 (s, 36H, $(CH_3)_3C$), 1.88 (m, 8H, $CH_2CH_2CH_2Pht$), 2.05 (m, 8H, $NHCH_2CH_2CH_2N^+$), 2.98 (s, 24H, $(CH_3)_3N^+$), 3.22–3.30 (m, 16H, $NHCH_2CH_2CH_2N$, $CH_2CH_2CH_2Pht$), 3.37 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.67 (t, $^3J_{HH} = 5.9$ Hz, 8H, $CH_2CH_2CH_2Pht$), 4.80 (s, 8H, OCH_2CO), 7.38 (s, 8H, ArH), 7.80–7.88 (m, 16H, Pht), 8.50 (t, $^3J_{HH} = 5.2$ Hz, 4H, $NHCH_2CH_2CH_2N^+$). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 168.22, 168.01, 158.00, 146.77, 134.42, 131.65, 128.03, 123.03, 119.52 (q), 74.24, 61.22, 60.96, 50.07, 35.37, 34.58, 33.91, 30.68, 22.44, 21.64. El. anal. calcd for $C_{120}H_{144}F_{24}N_{16}O_{32}S_{12}$: C 45.56%, H 4.59%, N 7.08%, S 12.16%. Found: C 46.16%, H 4.45%, N 6.61%, S 12.79%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 480.6$, found $m/z = 480.6$. IR ν_{max} : 1668, 1708, 1772 (C=O), 2963, 3334 (N-H).

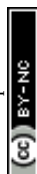
5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-methyl-2',2'-diethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 48). Yield: 0.12 g (90%), mp 72 °C. 1H NMR (400 MHz, 298 K, $CDCl_3$) δ : 1.11 (s, 36H, $(CH_3)_3C$), 1.32 (t, $^3J_{HH} = 7.2$ Hz, 24H, CH_3CH_2-), 3.03 (s, 12H, $(CH_3)_3N^+$), 3.38 (q, $^3J_{HH} = 7.2$ Hz, 16H, $-CH_2CH_3$), 3.48 (t, $^3J_{HH} = 6.3$ Hz, 8H, $-NCH_2CH_2NH$), 3.85 (m, 8H, NCH_2CH_2NH), 4.91 (s, 8H, OCH_2CO), 7.36 (s, 8H, ArH), 8.36 (br. s, 8H, CONH). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ : 169.70, 156.74, 148.21, 135.01, 127.79, 119.72 (q), 73.88, 59.11, 56.99, 47.52, 34.35, 32.94, 31.02, 7.62. El. anal. calcd for $C_{84}H_{124}F_{24}N_{12}O_{24}S_{12}$: C 39.93%, H 4.95%, N 6.65%, S 15.23%. Found: C 40.05%, H 5.06%, N 6.78%, S 15.02%. MS (ESI): calcd for $[M - 3N^-(SO_2CF_3)_2]^{3+}$ $m/z = 562.0$, found $m/z = 561.9$. IR ν_{max} : 1667 (C=O), 2965, 3315 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2',2'-triethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 49). Yield: 0.12 g (95%), mp 68 °C. 1H NMR (400 MHz, 298 K, $CDCl_3$) δ : 1.11 (s, 36H, $(CH_3)_3C$), 1.30 (t, $^3J_{HH} = 7.1$ Hz, 36H, CH_3CH_2-), 3.33 (q, $^3J_{HH} = 7.1$ Hz, 24H, $-CH_2CH_3$), 3.40 (m, 8H, $-NCH_2CH_2NH$), 3.77 (m, 8H, NCH_2CH_2NH), 4.91 (s, 8H, OCH_2CO), 7.36 (s, 8H, ArH), 8.40 (br. s, 8H, CONH). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ : 169.75, 156.70, 148.16, 135.01, 127.83, 119.75 (q), 73.85, 55.03, 53.51, 34.34, 32.66, 31.02, 7.28. El. anal. calcd for $C_{88}H_{132}F_{24}N_{12}O_{24}S_{12}$: C 40.92%, H 5.15%, N 6.51%, S 14.90%. Found: C 41.11%, H 5.13%, N 6.58%, S 14.67%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 365.6$, $[M - 3N^-(SO_2CF_3)_2]^{3+}$ $m/z = 580.7$, found $m/z = 365.7$, 580.5. IR ν_{max} : 1674 (C=O), 2963, 3314 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-benzyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 50). Yield: 0.12 g (94%), mp 60 °C. 1H NMR (400 MHz, 298 K, $CDCl_3$) δ : 1.10 (s, 36H, $(CH_3)_3C$), 1.39 (t, $^3J_{HH} = 7.1$ Hz, 24H, (CH_3CH_2-)), 3.24 (q, $^3J_{HH} = 6.9$ Hz, 16H, $-CH_2CH_3$), 3.39 (t, $^3J_{HH} = 7.1$ Hz, 8H, $-NCH_2CH_2NH$), 3.93 (m, 8H, NCH_2CH_2NH), 4.43 (s, 8H, N^+CH_2Ph), 4.95 (s, 8H, OCH_2CO), 7.35 (s, 8H, ArH), 7.41–7.46 (m, 20H, Ar'H), 8.51 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ : 169.90, 156.78, 148.04, 135.0, 132.36, 131.06, 129.62, 127.82, 126.19, 119.74 (q), 73.85, 61.76, 55.18, 53.70, 34.18, 32.78, 31.02, 7.83. El. anal. calcd for $C_{108}H_{140}F_{24}N_{12}O_{24}S_{12}$: C 45.82%, H 4.98%, N 5.94%, S 13.59%. Found: C 45.86%, H 5.23%, N 6.12%, S 13.44%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 427.6$, found $m/z = 427.4$. IR ν_{max} : 1672 (C=O), 2967, 3330 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(ethoxycarbonylmethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 51). Yield: 0.12 g (92%), mp 43 °C. 1H NMR (400 MHz, 298 K, $CDCl_3$) δ : 1.11 (s, 36H, $(CH_3)_3C$), 1.25 (m, 12H, OCH_2CH_3), 1.33 (t, $^3J_{HH} = 7.2$ Hz, 24H, CH_3CH_2-), 3.66 (m, 16H, $-CH_2CH_3$), 3.73 (m, 8H, $-NCH_2CH_2NH$), 3.83 (m, 8H, NCH_2CH_2NH), 4.14 (m, 8H, OCH_2CH_3), 4.19 (s, 8H, N^+CH_2CO), 4.90 (s, 8H, OCH_2CO), 7.36 (s, 8H, ArH), 8.36 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ : 169.90, 163.93, 156.72, 148.19, 142.94, 139.0, 135.06, 127.73, 119.89 (q), 73.89, 62.97, 56.99, 55.74, 34.40, 32.92, 31.02, 13.68, 7.60. El. anal. calcd for $C_{96}H_{140}F_{24}N_{12}O_{32}S_{12}$: C 40.96%, H 5.01%, N 5.97%, S 13.67%. Found: C 41.11%, H 4.89%, N 6.01%, S 13.45%. MS (ESI): calcd for $[M - 2N^-(SO_2CF_3)_2]^{2+}$ $m/z = 1127.3$, $[M - 3N^-(SO_2CF_3)_2]^{3+}$ $m/z = 657.6$, $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 423.6$, found $m/z = 1126.9$, 657.6, 423.5. IR ν_{max} : 1669, 1748 (C=O), 2962, 3328 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(pentoxycarbonylmethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 52). Yield: 0.13 g (93%), mp 39 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 0.86 (t, $^3J_{HH} = 6.8$ Hz, 12H, $O(CH_2)_4CH_3$), 1.08 (s, 36H, $(CH_3)_3C$), 1.21–1.32 (m, 16H, $O(CH_2)_3CH_2CH_3$, $O(CH_2)_2CH_2C_2H_5$), 1.26 (t, $^3J_{HH} = 7.1$ Hz, 24H,



CH₃CH₂N⁺), 1.57 (m, 8H, OCH₂CH₂C₃H₇), 3.52–3.60 (m, 32H, –N⁺CH₂CH₃, –NCH₂CH₂NH, –NCH₂CH₂NH), 4.10 (t, ³J_{HH} = 6.8 Hz, 8H, OCH₂C₄H₉), 4.44 (s, 8H, N⁺CH₂CO), 4.85 (s, 8H, OCH₂CO), 7.40 (s, 8H, ArH), 8.78 (t, ³J_{HH} = 5.1 Hz, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 168.96, 164.72, 157.65, 147.04, 134.59, 127.87, 119.26 (q), 74.22, 65.87, 55.90, 55.42, 55.98, 33.91, 32.14, 30.61, 27.40, 27.31, 21.66, 13.77, 7.36. El. anal. calcd for C₁₀₈H₁₆₄F₂₄N₁₂O₃₂S₁₂: C 43.48%, H 5.54%, N 5.63%, S 12.90%. Found: C 43.52%, H 5.63%, N 5.55%, S 12.72%. MS (ESI): calcd for [M – 4N[–](SO₂CF₃)₂]⁴⁺ m/z = 465.6, found m/z = 465.8. IR ν_{max}: 1672, 1746 (C=O), 2962, 3313 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-((ethoxycarbonylmethyl)amidocarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 53). Yield: 0.13 g (95%), mp 66 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.07 (s, 36H, (CH₃)₃C), 1.28 (t, ³J_{HH} = 7.1 Hz, 12H, CH₃CH₂O–), 1.28 (t, ³J_{HH} = 7.0 Hz, 24H, CH₃CH₂N⁺), 3.52 (q, ³J_{HH} = 7.0 Hz, 8H, CH₃CH₂N⁺), 3.55 (m, 8H, NHCH₂CH₂N⁺), 3.62 (m, 8H, NHCH₂CH₂N⁺), 3.93 (d, ³J_{HH} = 5.6 Hz, 8H, NHCH₂CO), 4.10 (q, ³J_{HH} = 7.1 Hz, 8H, CH₃CH₂O–), 4.11 (s, 8H, N⁺CH₂CO), 4.83 (s, 8H, OCH₂CO), 7.39 (s, 8H, ArH), 8.76 (t, ³J_{HH} = 5.7 Hz, 4H, NHCH₂CH₂N⁺), 9.06 (t, ³J_{HH} = 5.6 Hz, 4H, NHCH₂CO). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 169.06, 168.99, 163.58, 157.58, 146.81, 134.56, 127.96, 119.43 (q), 74.14, 60.78, 56.34, 56.08, 55.09, 40.67, 34.04, 32.18, 30.55, 13.98, 7.35. El. anal. calcd for C₁₀₈H₁₆₀F₂₄N₁₆O₃₆S₁₂: C 41.85%, H 5.20%, N 7.23%, S 12.42%. Found: C 42.11%, H 4.92%, N 7.33%, S 12.12%. MS (ESI): calcd for [M – 4N[–](SO₂CF₃)₂]⁴⁺ m/z = 480.6, found m/z = 480.6. IR ν_{max}: 1180 (COC), 1676 (C=O), 2965, 3353 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-((ethoxycarbonylmethyl)amidocarbonylmethyl)amidocarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 54). Yield: 0.14 g (94%), mp 64 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.07 (s, 36H, (CH₃)₃C), 1.19 (t, ³J_{HH} = 7.1 Hz, 12H, CH₃CH₂O–), 1.28 (t, ³J_{HH} = 6.7 Hz, 24H, CH₃CH₂N⁺), 3.50–3.58 (m, 24H, CH₃CH₂N⁺, NHCH₂CH₂N⁺), 3.62 (m, 8H, NHCH₂CH₂N⁺), 3.84 (d, ³J_{HH} = 5.9 Hz, 8H, NHCH₂CO), 3.87 (d, ³J_{HH} = 6.0 Hz, 8H, NHCH₂CO), 4.08 (s, 8H, N⁺CH₂CO), 4.10 (q, ³J_{HH} = 7.1 Hz, 8H, CH₃CH₂O), 4.83 (s, 8H, OCH₂CO), 7.45 (s, 8H, ArH), 8.50 (t, ³J_{HH} = 5.9 Hz, 4H, NHCH₂CH₂N⁺), 8.74 (br. s, 4H, CONH), 8.87 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 170.10, 169.34, 168.80, 163.67, 158.08, 147.57, 135.05, 128.46, 119.57 (q), 74.54, 60.93, 56.99, 56.49, 55.58, 41.87, 41.05, 34.41, 32.68, 31.14, 14.41, 7.89. El. anal. calcd for C₁₁₂H₁₆₄F₂₄N₂₀O₄₀S₁₂: C 41.12%, H 5.05%, N 8.56%, S 11.76%. Found: C 40.99%, H 5.07%, N 8.66%, S 11.54%. MS (ESI): calcd for [M – 3N[–](SO₂CF₃)₂]³⁺ m/z = 810.3, [M – 4N[–](SO₂CF₃)₂]⁴⁺ m/z = 537.6, found m/z = 810.3, 537.8. IR ν_{max}: 1182 (COC), 1665 (C=O), 2966, 3332 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-((ethoxycarbonyl[S-methyl]methyl)amidocarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (cone 55). Yield: 0.12 g (92%), mp 63 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.08 (s, 36H, (CH₃)₃C), 1.18 (t, ³J_{HH} = 7.1 Hz, 12H, CH₃CH₂O–),

1.30 (d, ³J_{HH} = 7.3 Hz, 12H, CH₃CH), 1.31 (t, ³J_{HH} = 7.2 Hz, 24H, CH₃CH₂N⁺), 3.48–3.61 (m, 24H, NHCH₂CH₂N⁺, N⁺CH₂CH₃), 3.63 (m, 8H, NHCH₂CH₂N⁺), 4.09 (s, 8H, N⁺CH₂CO), 4.11 (m, 8H, CH₃CH₂O–), 4.27 (m, 4H, CH₃CH), 4.84 (s, 8H, OCH₂CO), 7.40 (s, 8H, ArH), 8.81 (br. s, 4H, NHCH₂CH₂N⁺), 9.23 (d, ³J_{HH} = 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, 32.19, 30.55, 16.56, 13.96, 7.35. El. anal. calcd for C₁₀₈H₁₆₀F₂₄N₁₆O₃₆S₁₂: C 41.85%, H 5.20%, N 7.23%, S 12.42%. Found: C 42.01%, H 5.17%, N 7.43%, S 12.17%. MS (ESI): calcd for [M – 4N[–](SO₂CF₃)₂]⁴⁺ m/z = 494.6, found m/z = 494.3. IR ν_{max}: 1183 (COC), 1680 (C=O), 2966, 3347 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-trimethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 56). Yield: 0.11 g (95%), mp 106 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.21 (s, 36H, (CH₃)₃C), 1.90 (m, 8H, –NCH₂CH₂CH₂NH), 3.06 (s, 36H, (CH₃)₃N⁺), 3.18 (m, 8H, –NCH₂CH₂CH₂NH), 3.31 (m, 8H, NCH₂CH₂CH₂NH), 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: 167.09, 157.35, 145.86, 133.12, 127.57, 119.75 (q), 70.93, 63.31, 52.37, 35.76, 33.95, 30.58, 22.94. El. anal. calcd for C₈₀H₁₁₆F₂₄N₁₂O₂₄S₁₂: C 38.89%, H 4.73%, N 6.80%, S 15.57%. Found: C 39.03%, H 4.91%, N 6.73%, S 15.72%. MS (MALDI TOF): calcd for [M – N[–](SO₂CF₃)₂]⁺ m/z = 2190.4, found m/z = 2190.1. IR ν_{max}: 1669 (C=O), 2966, 3313 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-ethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 57). Yield: 0.12 g (96%), mp 96 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.21 (s, 36H, (CH₃)₃C), 1.24 (t, ³J_{HH} = 7.0 Hz, 12H, N⁺CH₂CH₃), 1.87 (m, 8H, –NCH₂CH₂CH₂NH), 2.99 (s, 24H, (CH₃)₂N⁺), 3.19 (m, 8H, –NCH₂CH₂CH₂NH), 3.24 (m, 8H, NCH₂CH₂CH₂NH), 3.33 (q, ³J_{HH} = 7.1 Hz, 8H, N⁺CH₂CH₃), 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, 49.44, 35.92, 33.85, 30.75, 22.43, 7.76. El. anal. calcd for C₈₄H₁₂₄F₂₄N₁₂O₂₄S₁₂: C 39.93%, H 4.95%, N 6.65%, S 15.23%. Found: C 39.74%, H 5.10%, N 6.78%, S 15.25%. MS (MALDI TOF): calcd for [M – N[–](SO₂CF₃)₂]⁺ m/z = 2244.6, found m/z = 2244.8. IR ν_{max}: 1669 (C=O), 2966, 3310 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(3',3'-dimethyl-3'-benzyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 58). Yield: 0.11 g (94%), mp 87 °C. ¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 1.20 (s, 36H, (CH₃)₃C), 2.04 (m, 8H, –NCH₂CH₂CH₂NH), 2.97 (s, 24H, (CH₃)₂N⁺), 3.22 (m, 8H, –NCH₂CH₂CH₂NH), 3.27 (m, 8H, NCH₂CH₂CH₂NH), 4.03 (s, 8H, OCH₂CO), 4.53 (s, 8H, N⁺CH₂CO), 7.51–7.57 (m, 20H, Ar'H), 7.60 (s, 8H, ArH), 8.07 (br. s, 4H, CONH). ¹³C NMR (100 MHz, 298 K, DMSO-d₆) δ: 167.62, 157.18, 145.98, 133.09, 132.91, 130.34, 128.93, 127.91, 127.49, 119.34 (q), 71.01, 66.16, 61.13, 49.32, 35.85, 33.85, 30.76, 22.63. El. anal. calcd for C₁₀₄H₁₃₂F₂₄N₁₂O₂₄S₁₂: C 45.01%, H 4.79%, N 6.06%, S 13.87%.



Found: C 44.96%, H 4.99%, N 5.90%, S 13.62%. MS (MALDI TOF): calcd for $[M - N^-(SO_2CF_3)_2]^+ m/z = 2495.8$, found $m/z = 2495.3$. IR $\nu_{\max}$: 1672 (C=O), 2965, 3374 (NH).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-(ethoxycarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 59). Yield: 0.11 g (94%), mp 53 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.20 (s, 36H, $(CH_3)_3C$), 1.25 (t, $^3J_{HH} = 7.1$ Hz, 12H, OCH_2CH_3), 1.92 (m, 8H, $-NCH_2CH_2CH_2NH$), 3.18 (m, 8H, $-NCH_2CH_2CH_2NH$), 3.20 (s, 24H, $(CH_3)_2N^+$), 3.51 (m, 8H, $NCH_2CH_2CH_2NH$), 4.00 (s, 8H, OCH_2CO), 4.23 (q, $^3J_{HH} = 7.2$ Hz, 8H, $N^+CH_2CH_3$), 4.42 (s, 8H, N^+CH_2CO), 7.59 (s, 8H, ArH), 8.02 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 167.40, 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. calcd for $C_{92}H_{132}F_{24}N_{12}O_{32}S_{12}$: 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): calcd for $[M - N^-(SO_2CF_3)_2]^+ m/z = 2476.6$, found $m/z = 2476.9$. IR $\nu_{\max}$: 1666, 1748 (C=O), 2969, 3316 (NH).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-(pentoxycarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 60). Yield: 0.13 g (92%), mp 47 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 0.88 (t, $^3J_{HH} = 6.9$ Hz, 12H, CH_2CH_3), 1.20 (s, 36H, $(CH_3)_3C$), 1.22–1.30 (m, 16H, $O(CH_2)_2CH_2C_2H_5$, $O(CH_2)_3CH_2CH_3$), 1.62 (m, 8H, $OCH_2CH_2C_3H_7$), 1.92 (m, 8H, $-NCH_2CH_2CH_2NH$), 3.19 (s, 24H, $(CH_3)_2N^+$), 3.30 (m, 8H, $NCH_2CH_2CH_2NH$), 3.53 (m, 8H, $-NCH_2CH_2CH_2NH$), 3.99 (s, 8H, OCH_2CO), 4.19 (t, $^3J_{HH} = 6.5$ Hz, 8H, $OCH_2C_4H_9$), 4.48 (s, 8H, N^+CH_2CO), 7.61 (s, 8H, ArH), 8.06 (br. s, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 167.36, 164.75, 157.12, 145.98, 133.05, 127.54, 119.58 (q), 70.94, 65.79, 62.31, 60.46, 51.20, 35.67, 33.82, 30.73, 27.42, 27.36, 22.53, 21.66, 13.78. El. anal. calcd for $C_{104}H_{156}F_{24}N_{12}O_{32}S_{12}$: C 42.67%, H 5.37%, N 5.74%, S 13.15%. Found: C 42.55%, H 5.44%, N 5.53%, S 12.89%. MS (ESI): calcd for $[M - 3N^-(SO_2CF_3)_2]^{3+} m/z = 695.0$, $[M - 4N^-(SO_2CF_3)_2]^{4+} m/z = 451.6$, found $m/z = 695.0$, 451.5. IR $\nu_{\max}$: 1667, 1747 (C=O), 2962, 3312 (NH).

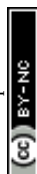
5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-((ethoxycarbonylmethyl)amidocarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 61). Yield: 0.13 g (98%), mp 73 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.19 (t, $^3J_{HH} = 7.1$ Hz, 12H, CH_3CH_2O-), 1.20 (s, 36H, $(CH_3)_3C$), 1.93 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.18 (s, 12H, $(CH_3)_2N^+$), 3.22 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.50 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.96 (d, $^3J_{HH} = 5.7$ Hz, 8H, $NHCH_2CO$), 3.99 (s, 8H, OCH_2CO), 4.10 (q, $^3J_{HH} = 7.1$ Hz, 8H, CH_3CH_2O-), 4.12 (s, 8H, N^+CH_2CO), 7.59 (s, 8H, ArH), 8.03 (t, $^3J_{HH} = 5.4$ Hz, 4H, $NHCH_2CH_2CH_2N^+$), 9.04 (t, $^3J_{HH} = 5.7$ Hz, 4H, $NHCH_2CO$). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 170.79, 169.34, 167.78, 163.90, 157.56, 147.15, 131.57, 128.09, 119.34 (q), 71.56, 62.25, 61.13, 60.21, 51.80, 43.30, 40.99, 31.01, 22.80, 14.39. El. anal. calcd for $C_{100}H_{144}F_{24}N_{16}O_{36}S_{12}$: C 40.21%, H 4.86%, N 7.50%, S 12.88%. Found: C 40.43%, H 4.97%, N 7.34%, S 12.56%. MS (ESI): calcd

for $[M - 4N^-(SO_2CF_3)_2]^{4+} m/z = 466.6$, found $m/z = 466.6$. IR $\nu_{\max}$: 1180 (COC), 1673 (C=O), 2968, 3374 (N-H).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-((ethoxycarbonylmethyl)amidocarbonylmethyl)amidocarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 62). Yield: 0.14 g (97%), mp 76 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.18 (t, $^3J_{HH} = 7.1$ Hz, 12H, CH_3CH_2O-), 1.20 (s, 36H, $(CH_3)_3C$), 1.93 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.18 (s, 12H, $(CH_3)_2N^+$), 3.19 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.49 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.86 (br. s, 8H, $NHCH_2CO$), 3.87 (br. s, 8H, $NHCH_2CO$), 3.97 (s, 8H, OCH_2CO), 4.08 (s, 8H, N^+CH_2CO), 4.09 (q, $^3J_{HH} = 7.1$ Hz, 8H, CH_3CH_2O-), 7.59 (s, 8H, ArH), 8.02 (t, $^3J_{HH} = 4.9$ Hz, 4H, $NHCH_2CH_2CH_2N^+$), 8.50 (t, $^3J_{HH} = 5.7$ Hz, 4H, CONH), 8.86 (t, $^3J_{HH} = 5.4$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 170.14, 168.82, 167.93, 157.53, 146.55, 133.46, 128.09, 119.32 (q), 71.39, 63.14, 62.53, 60.97, 51.76, 42.03, 41.12, 36.29, 34.34, 31.22, 22.96, 14.52. El. anal. calcd for $C_{108}H_{156}F_{24}N_{20}O_{40}S_{12}$: C 40.34%, H 4.89%, N 8.71%, S 11.97%. Found: C 40.70%, H 5.05%, N 8.92%, S 11.66%. MS (ESI): calcd for $[M - 3N^-(SO_2CF_3)_2]^{3+} m/z = 791.3$, $[M - 4N^-(SO_2CF_3)_2]^{4+} m/z = 523.5$, found $m/z = 791.3$, 523.6. IR $\nu_{\max}$: 1182 (COC), 1663 (C=O), 2966, 3313 (N-H).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-((ethoxycarbonyl[S-methyl]methyl)amidocarbonylmethyl)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 63). Yield: 0.13 g (97%), mp 60 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.18 (t, $^3J_{HH} = 7.1$ Hz, 12H, CH_3CH_2O-), 1.20 (s, 36H, $(CH_3)_3C$), 1.33 (d, $^3J_{HH} = 7.3$ Hz, 12H, CH_3CH), 1.93 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.18 (s, 12H, $(CH_3)_2N^+$), 3.19 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.51 (m, 8H, $NHCH_2CH_2CH_2N^+$), 4.01 (s, 8H, OCH_2CO), 4.09 (s, 8H, N^+CH_2CO), 4.10 (q, $^3J_{HH} = 7.1$ Hz, 8H, CH_3CH_2O-), 4.30 (m, 4H, CH_3CH), 7.59 (s, 8H, ArH), 8.03 (t, $^3J_{HH} = 4.9$ Hz, 4H, $NHCH_2CH_2CH_2N^+$), 9.04 (d, $^3J_{HH} = 6.5$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 172.05, 166.94, 162.72, 157.53, 145.93, 133.83, 127.27, 119.53 (q), 70.65, 62.43, 61.15, 60.62, 51.16, 47.99, 35.62, 33.55, 30.37, 23.09, 16.65, 13.81. El. anal. calcd for $C_{104}H_{152}F_{24}N_{16}O_{36}S_{12}$: C 41.05%, H 5.03%, N 7.36%, S 12.64%. Found: C 39.86%, H 4.66%, N 6.96%, S 13.50%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+} m/z = 480.6$, found $m/z = 480.4$. IR $\nu_{\max}$: 1181 (COC), 1679 (C=O), 2965, 3357 (N-H).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(3',3'-dimethyl-3'-3''-propylphthalimide)ammoniumpropyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 64). Yield: 0.13 g (91%), mp 87 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.21 (s, 36H, $(CH_3)_3C$), 1.88 (m, 8H, $CH_2CH_2CH_2Pht$), 2.05 (m, 8H, $NHCH_2CH_2CH_2N^+$), 2.99 (s, 24H, $(CH_3)_2N^+$), 3.17 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.29 (m, 8H, $CH_2CH_2CH_2Pht$), 3.39 (m, 8H, $NHCH_2CH_2CH_2N^+$), 3.67 (t, $^3J_{HH} = 6.2$ Hz, 8H, $CH_2CH_2CH_2Pht$), 3.99 (s, 8H, OCH_2CO), 7.60 (s, 8H, ArH), 7.84–7.89 (m, 16H, Pht), 8.04 (t, $^3J_{HH} = 5.3$ Hz, 4H, $NHCH_2CH_2CH_2N^+$). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 167.98, 167.32, 157.15, 146.11, 134.41, 133.07, 131.70, 127.54, 123.06, 119.32 (q), 71.01, 61.35, 61.12, 49.86, 35.79, 34.56, 33.84, 30.74, 22.48, 21.65. El. anal. calcd for $C_{120}H_{144}F_{24}N_{16}O_{32}S_{12}$: C



45.56%, H 4.59%, N 7.08%, S 12.16%. Found: C 45.45%, H 4.26%, N 7.01%, S 12.45%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 480.6$, found $m/z = 480.5$. IR ν_{max} : 1668, 1708, 1771 (C=O), 2967, 3314 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2'-methyl-2',2'-diethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 65). Yield: 0.12 g (90%), mp 83 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.22 (s, 36H, $(CH_3)_3C$), 1.26 (t, $^3J_{HH} = 7.1$ Hz, 24H, (CH_3CH_2-)), 3.02 (s, 12H, $(CH_3)_3N^+$), 3.21 (m, 8H, $-NCH_2CH_2NH$), 3.37 (q, $^3J_{HH} = 7.1$ Hz, 16H, $-CH_2CH_3$), 3.48 (m, 8H, NCH_2CH_2NH), 4.05 (s, 8H, OCH_2CO), 7.60 (s, 8H, ArH), 8.17 (t, $^3J_{HH} = 5.6$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) 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. calcd for $C_{84}H_{124}F_{24}N_{12}O_{24}S_{12}$: C 39.93%, H 4.95%, N 6.65%, S 15.23%. Found: C 40.02%, H 4.99%, N 6.48%, S 15.03%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 351.5$, found $m/z = 351.3$. IR ν_{max} : 1671 (C=O), 2969, 3375 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2',2'-triethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 66). Yield: 0.11 g (92%), mp 79 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.21 (s, 36H, $(CH_3)_3C$), 1.23 (t, $^3J_{HH} = 7.0$ Hz, 36H, CH_3CH_2-), 3.14 (m, 8H, $-NCH_2CH_2NH$), 3.31 (m, 24H, $-CH_2CH_3$), 3.45 (m, 8H, NCH_2CH_2NH), 4.04 (s, 8H, OCH_2CO), 7.60 (s, 8H, ArH), 8.14 (t, $^3J_{HH} = 5.7$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 168.05, 154.01, 145.92, 133.26, 127.55, 119.67 (q), 70.51, 53.57, 52.46, 33.88, 31.83, 30.84, 7.04. El. anal. calcd for $C_{88}H_{132}F_{24}N_{12}O_{24}S_{12}$: C 40.92%, H 5.15%, N 6.51%, S 14.90%. Found: C 41.23%, H 5.13%, N 6.71%, S 15.07%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 365.5$, found $m/z = 365.4$. IR ν_{max} : 1670 (C=O), 2964, 3374 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-benzyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 67). Yield: 0.12 g (93%), mp 76 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.19 (s, 36H, $(CH_3)_3C$), 1.39 (t, $^3J_{HH} = 7.0$ Hz, 24H, (CH_3CH_2-)), 3.15 (m, 8H, $-NCH_2CH_2NH$), 3.25 (q, $^3J_{HH} = 7.0$ Hz, 16H, $-CH_2CH_3$), 3.61 (m, 8H, NCH_2CH_2NH), 4.20 (s, 8H, OCH_2CO), 4.58 (s, 8H, N^+CH_2Ph), 7.50–7.56 (m, 20H, Ar'H), 7.61 (s, 8H, ArH), 8.34 (t, $^3J_{HH} = 5.8$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 168.05, 153.77, 145.78, 133.41, 132.68, 130.43, 129.12, 119.49 (q), 70.82, 60.56, 54.12, 53.17, 33.84, 32.04, 30.85, 11.11, 7.51. El. anal. calcd for $C_{108}H_{140}F_{24}N_{12}O_{24}S_{12}$: C 45.82%, H 4.98%, N 5.94%, S 13.59%. Found: C 46.07%, H 5.28%, N 5.99%, S 13.35%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 427.2$, found $m/z = 427.4$. IR ν_{max} : 1671 (C=O), 2966, 3393 (NH).

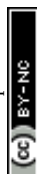
5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(ethoxycarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 68). Yield: 0.12 g (93%), mp 58 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.21 (s, 36H, $(CH_3)_3C$), 1.26 (t, $^3J_{HH} = 7.1$ Hz, 12H, OCH_2CH_3), 1.28 (t, $^3J_{HH} = 7.0$ Hz, 24H, CH_3CH_2-), 3.45–3.60 (m, 32H, $-CH_2CH_3$, $-NCH_2CH_2NH$, $-NCH_2CH_2NH$), 4.08 (s, 8H, OCH_2CO), 4.24 (q, $^3J_{HH} = 7.1$ Hz,

8H, OCH_2CH_3), 4.46 (s, 8H, N^+CH_2CO), 7.61 (s, 8H, ArH), 8.22 (t, $^3J_{HH} = 4.7$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 168.04, 164.63, 157.00, 145.99, 133.07, 127.40, 119.46 (q), 70.60, 62.13, 55.83, 55.53, 55.08, 33.85, 31.98, 30.85, 13.73, 7.36. El. anal. calcd for $C_{96}H_{140}F_{24}N_{12}O_{32}S_{12}$: C 40.96%, H 5.01%, N 5.97%, S 13.67%. Found: C 41.12%, H 4.95%, N 5.99%, S 13.55%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 423.6$, found $m/z = 423.5$. IR ν_{max} : 1670, 1747 (C=O), 2967, 3374 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-(pentoxycarbonylmethyl)ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 69). Yield: 0.11 g (91%), mp 49 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 0.87 (t, $^3J_{HH} = 6.6$ Hz, 12H, $-O(CH_2)_4CH_3$), 1.21 (s, 36H, $(CH_3)_3C$), 1.27–1.35 (m, 16H, $O(CH_2)_3CH_2CH_3$, $OCH_2CH_2C_3H_7$), 1.28 (t, $^3J_{HH} = 7.0$ Hz, 24H, $(CH_3CH_2N^+)$), 1.65 (m, 8H, $O(CH_2)_2CH_2C_2H_5$), 3.44–3.65 (m, 32H, $-N^+CH_2CH_3$, $-NCH_2CH_2NH$, $-NCH_2CH_2NH$), 4.07 (s, 8H, OCH_2CO), 4.19 (q, $^3J_{HH} = 6.5$ Hz, 8H, $OCH_2C_4H_9$), 4.48 (s, 8H, N^+CH_2CO), 7.69 (s, 8H, ArH), 8.22 (t, $^3J_{HH} = 5.1$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 168.01, 164.77, 156.91, 146.00, 133.00, 127.45, 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. calcd for $C_{108}H_{164}F_{24}N_{12}O_{32}S_{12}$: 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): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 465.6$, found $m/z = 465.5$. IR ν_{max} : 1671, 1746 (C=O), 2961, 3373 (NH).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-((ethoxycarbonylmethyl)amidocarbonylmethyl)ammonium-ethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 70). Yield: 0.13 g (93%), mp 62 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.20 (t, $^3J_{HH} = 7.1$ Hz, 12H, CH_3CH_2O-), 1.21 (s, 36H, $(CH_3)_3C$), 1.31 (t, $^3J_{HH} = 7.0$ Hz, 24H, $CH_3CH_2N^+$), 3.48 (m, 8H, $NHCH_2CH_2N^+$), 3.53–3.59 (m, 16H, $CH_3CH_2N^+$, $NHCH_2CH_2N^+$), 3.96 (d, $^3J_{HH} = 5.7$ Hz, 8H, $NHCH_2CO$), 4.05 (s, 8H, OCH_2CO), 4.12 (q, $^3J_{HH} = 7.0$ Hz, 8H, CH_3CH_2O-), 4.11 (s, 8H, N^+CH_2CO), 7.60 (s, 8H, ArH), 8.22 (t, $^3J_{HH} = 5.4$ Hz, 4H, $NHCH_2CH_2N^+$), 9.10 (t, $^3J_{HH} = 5.7$ Hz, 4H, $NHCH_2CO$). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) 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. calcd for $C_{108}H_{160}F_{24}N_{16}O_{36}S_{12}$: C 41.85%, H 5.20%, N 7.23%, S 12.42%. Found: C 41.99%, H 5.31%, N 7.24%, S 12.05%. MS (ESI): calcd for $[M - 4N^-(SO_2CF_3)_2]^{4+}$ $m/z = 480.6$, found $m/z = 481.0$. IR ν_{max} : 1180 (COC), 1685 (C=O), 2967, 3364 (N-H).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[*N*-(2',2'-diethyl-2'-((ethoxycarbonylmethyl)amidocarbonylmethyl)amidocarbonylmethyl)ammoniummethyl]carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4]arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 71). Yield: 0.14 g (94%), mp 64 °C. 1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.19 (t, $^3J_{HH} = 7.1$ Hz, 12H, CH_3CH_2O-), 1.21 (s, 36H, $(CH_3)_3C$), 1.30 (t, $^3J_{HH} = 7.1$ Hz, 24H, $CH_3CH_2N^+$), 3.44 (m, 8H, $NHCH_2CH_2N^+$), 3.51–3.58 (m, 24H, $CH_3CH_2N^+$, $NHCH_2CH_2N^+$), 3.87 (br. s, 8H, $NHCH_2CO$), 3.88 (br. s, 8H, $NHCH_2CO$), 4.04 (s, 8H, OCH_2CO), 4.08 (q, $^3J_{HH} = 7.1$ Hz, 8H, CH_3CH_2O-), 4.09 (s, 8H, N^+CH_2CO), 7.59 (s, 8H, ArH), 8.21 (br. t, 4H, $NHCH_2CH_2N^+$), 8.51 (t, $^3J_{HH} = 5.7$ Hz, 4H, CONH), 8.90



(t, $^3J_{\text{HH}} = 5.4$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 170.14, 168.84, 168.43, 163.49, 157.59, 146.49, 131.42, 127.97, 119.60 (q), 72.17, 60.98, 57.08, 56.37, 55.59, 41.92, 41.13, 34.35, 32.47, 31.21, 14.47, 7.90. El. anal. calcd for $\text{C}_{112}\text{H}_{164}\text{F}_{24}\text{N}_{20}\text{O}_{40}\text{S}_{12}$: C 41.12%, H 5.05%, N 8.56%, S 11.76%. Found: C 41.07%, H 5.15%, N 8.49%, S 11.92%. MS (ESI): calcd for $[\text{M} - 3\text{N}^-(\text{SO}_2\text{CF}_3)_2]^{3+}$ $m/z = 810.3$, $[\text{M} - 4\text{N}^-(\text{SO}_2\text{CF}_3)_2]^{4+}$ $m/z = 537.6$, found $m/z = 810.0$, 537.7. IR ν_{max} : 1181 (COC), 1666 (C=O), 2968, 3363 (N-H).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[N-(2',2'-diethyl-2'-((ethoxycarbonyl[S-methyl]methyl)amidocarbonylmethyl) ammoniummethyl)carbomoylmethoxy]-2,8,14,20-tetrathiacalix[4] arene tetra[bis(trifluoromethylsulfonyl)imide] (1,3-alternate 72). Yield: 0.13 g (96%), mp 62 °C. ^1H NMR (400 MHz, 298 K, DMSO- d_6) δ : 1.19 (t, $^3J_{\text{HH}} = 7.1$ Hz, 12H, $\text{CH}_3\text{CH}_2\text{O}-$), 1.21 (s, 36H, $(\text{CH}_3)_3\text{C}$), 1.32 (d, $^3J_{\text{HH}} = 7.3$ Hz, 12H, CH_3CH), 1.34 (t, $^3J_{\text{HH}} = 7.2$ Hz, 24H, $\text{CH}_3\text{CH}_2\text{N}^+$), 3.49 (m, 8H, $\text{NHCH}_2\text{CH}_2\text{N}^+$), 3.51–3.58 (m, 24H, $\text{N}^+\text{CH}_2\text{CH}_3$, $\text{NHCH}_2\text{CH}_2\text{N}^+$), 4.07 (s, 8H, OCH_2CO), 4.09–4.11 (m, 16H, $\text{N}^+\text{CH}_2\text{CO}$, $\text{CH}_3\text{CH}_2\text{O}-$), 4.30 (m, 4H, CH_3CH), 7.60 (s, 8H, ArH), 8.23 (t, $^3J_{\text{HH}} = 6.7$ Hz, 4H, $\text{NHCH}_2\text{CH}_2\text{N}^+$), 9.11 (d, $^3J_{\text{HH}} = 6.7$ Hz, 4H, CONH). ^{13}C NMR (100 MHz, 298 K, DMSO- d_6) δ : 171.63, 167.99, 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, 30.83, 16.56, 13.97, 7.34. El. anal. calcd for $\text{C}_{108}\text{H}_{160}\text{F}_{24}\text{N}_{16}\text{O}_{36}\text{S}_{12}$: C 41.85%, H 5.20%, N 7.23%, S 12.42%. Found: C 42.08%, H 5.38%, N 6.97%, S 12.09%. MS (ESI): calcd for $[\text{M} - 4\text{N}^-(\text{SO}_2\text{CF}_3)_2]^{4+}$ $m/z = 494.6$, found $m/z = 494.6$. IR ν_{max} : 1181 (COC), 1680 (C=O), 2969, 3361 (N-H).

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Notes and references

- 1 K. Shimojo and M. Goto, *Chem. Lett.*, 2004, **33**, 320–321.
- 2 K. Shimojo and M. Goto, *Anal. Chem.*, 2004, **76**, 5039–5044.
- 3 N. Sieffert and G. Wipff, *J. Phys. Chem. A*, 2006, **110**, 1106–1117.
- 4 N. Sieffert and G. Wipff, *J. Phys. Chem. B*, 2006, **110**, 19497–19506.
- 5 T. Sun, Z. Wang and X. Shen, *Inorg. Chim. Acta*, 2012, **390**, 8–11.
- 6 P. K. Mohapatra, P. Kandwal, M. Iqbal, J. Huskens, M. S. Murali and W. Verboom, *Dalton Trans.*, 2013, **42**, 4343–4347.
- 7 F. Yang, F. Guo, Z. Jiao, C. Li and J. Ye, *J. Iran. Chem. Soc.*, 2012, **9**, 327–332.
- 8 B. Aitken, M. Lee, M. Hunley, H. Gibson and K. Wagener, *Macromolecules*, 2010, **43**, 1699–1701.
- 9 J. Weng, C. Wang, H. Li and Y. Wang, *Green Chem.*, 2006, **8**, 96–99.
- 10 J. Pernak, M. Smiglak, S. T. Griffin, W. L. Hough, T. B. Wilson, A. Pernak, J. Zabielska-Matejuk, A. Fojutowski, K. Kita and R. D. Rogers, *Green Chem.*, 2006, **8**, 798–806.
- 11 X. L. Yuan, S. J. Zhang and X. M. Lu, *J. Chem. Eng. Data*, 2007, **52**, 596–599.
- 12 S. Werner, M. Haumann and P. Wasserscheid, *Annu. Rev. Chem. Biomol. Eng.*, 2010, **1**, 203–230.
- 13 Y. A. Gao, Z. H. Li, J. M. Du, B. X. Han, G. Z. Li, W. G. Hou, D. Shen, L. Q. Zheng and G. Y. Zhang, *Chem.-Eur. J.*, 2005, **11**, 5875–5880.
- 14 P. Montes-Navajas, A. Corma and H. J. Garcia, *J. Mol. Catal. A: Chem.*, 2008, **279**, 165–169.
- 15 N. Inazumi, S. Yamamoto and Y. Sueishi, *J. Inclusion Phenom. Macrocyclic Chem.*, 2007, **59**, 33–39.
- 16 D. N. Shurpik, L. S. Yakimova, I. K. Rizvanov, V. V. Plemenkov and I. I. Stoikov, *Macroheterocycles*, 2015, **8**, 128–134.
- 17 L. S. Yakimova, D. N. Shurpik, L. H. Gilmanova, A. R. Makhmutova, A. Rakhimbekova and I. I. Stoikov, *Org. Biomol. Chem.*, 2016, **14**, 4233–4238.
- 18 R. V. Nosov and I. I. Stoikov, *Macroheterocycles*, 2014, **7**, 345–350.
- 19 I. Spendlikova, J. John, V. Cuba, J. Jirasek and P. Lhotak, *J. Radioanal. Nucl. Chem.*, 2015, **304**, 257–262.
- 20 M. MacKova, M. Himl, J. Budka, M. Pojarova, I. Cisarova, V. Eigner, P. Curinova, H. Dvorakova and P. Lhotak, *Tetrahedron*, 2013, **69**, 1397–1402.
- 21 D.-D. Zheng, D.-Y. Fu, Y. Wu, Y.-L. Sun, L.-L. Tan, T. Zhou, S.-Q. Ma, X. Zha and Y.-W. Yang, *Chem. Commun.*, 2014, **50**, 3201–3203.
- 22 Y. Zhou, H. Li and Y.-W. Yang, *Chin. Chem. Lett.*, 2015, **26**, 825–828.
- 23 M. Yamada, Y. Ootashiro, Y. Kondo and F. Hamada, *Tetrahedron Lett.*, 2013, **54**, 1510–1514.
- 24 M. Yamada, M. Rajiv Gandhi, U. M. R. Kunda and F. Hamada, *J. Inclusion Phenom. Macrocyclic Chem.*, 2016, **85**, 1–18.
- 25 A. D. Iampolska, S. G. Kharchenko, Z. V. Voitenko, S. V. Shishkina, A. B. Ryabitskii and V. I. Kalchenko, *Phosphorus Sulfur Relat. Elem.*, 2016, **191**, 174–179.
- 26 T. Ogoshi, N. Ueshima, T. Yamagishi, Y. Toyota and N. Matsumi, *Chem. Commun.*, 2012, **48**, 3536–3538.
- 27 A. Kokorin, *Ionic liquids: theory, properties, new approaches*, InTech, 2011.
- 28 F. Hurley and T. Wler, *J. Electrochem. Soc.*, 1951, **98**, 203–206.
- 29 J. Hallet and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.
- 30 P. Wasserscheid and T. Welton, *Ionic liquids in synthesis: second edition*, John Wiley & Sons, Inc., 2009.
- 31 S. L. Craig, *Angew. Chem., Int. Ed.*, 2009, **48**, 2645–2647.
- 32 J. Lopes and A. Padua, *J. Phys. Chem. B*, 2006, **110**, 3330–3335.
- 33 J. H. Davis, K. J. Forrester and T. Merrigan, *Tetrahedron Lett.*, 1988, **39**, 8955–8958.
- 34 K. Singh, D. G. Marangoni, J. G. Quinn and R. D. Singer, *J. Colloid Interface Sci.*, 2009, **335**, 105–111.
- 35 E. A. Andreyko, P. L. Padnya and I. I. Stoikov, *J. Phys. Org. Chem.*, 2015, **28**, 527–535.
- 36 Y. Huo, S. Xia, Y. Zhang and M. Peisheng, *Ind. Eng. Chem. Res.*, 2009, **48**, 2212–2217.



- 37 M. K. Rauf, R. Mushtaq, A. Badshah, R. Kingsford-Adaboh, J. J. E. K. Harrison and H. Ishida, *J. Chem. Crystallogr.*, 2013, **43**, 144–150.
- 38 P. L. Padnya, E. A. Andreyko, O. A. Mostovaya, I. Kh. Rizvanov and I. I. Stoikov, *Org. Biomol. Chem.*, 2015, **13**, 5894–5904.
- 39 S. Zhang, N. Sun, X. He, X. Lu and X. Zhang, *J. Phys. Chem. Ref. Data*, 2006, **35**, 1475–1517.
- 40 E. A. Andreyko, P. L. Padnya, R. R. Daminova and I. I. Stoikov, *RSC Adv.*, 2014, **4**, 3556–3565.
- 41 E. A. Andreyko, P. L. Padnya and I. I. Stoikov, *Colloids Surf., A*, 2014, **454**, 74–83.
- 42 F. Gutmann and L. E. Lyons, *Organic Semiconductors*, Wiley, New York, 1967.

