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Bridged Di(alkyl- and 4,4,4-trifluorobutylimidazolium) Quaternary Salts Based on *p-tert*-Butylcalix[4]arene

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Di(alkyl- and 4,4,4-trifluorobutylimidazolium) quaternary halides of *p-tert*-butylcalix[4]arene, **5a**–**8a** and **11a**, were prepared and characterized. Metathetical reactions of these compounds with $LiN(SO_2CF_3)_2$ and KPF_6 in methanol and water gave the corresponding new quaternary salts **5b**–**8b** and **11b** and **5c**–**8c** and **11c,** respectively, with high thermal stabilities. Compounds **5a**–**d**, **6b**, and **11a**–**c** exhibit melting points <100 °C. On the basis of ^{1}H NMR and ^{13}C NMR spectral measurements, all of the new quaternary calix[4]arene salts were found to exist in a cone conformation. ^{1}H NMR titration experiments and electrospray MS spectra support the encapsulation of K^+ in the ionophoric cavity of **11c**.

In recent years, ionic liquids have attracted considerable interest as substitutes for volatile organic solvents in synthetic chemistry,[1] metal ion extraction,[2] capture of acidic gases, etc.[3] Ionic liquids often consist of an organic cation such as alkylpyridinium, dialkylimidazolium, or dialkyltriazolium, with an appropriate anion, such as halide- or fluorine-containing inorganic anions. By definition, ionic liquids melt <100 °C,[4] are thermally stable liquids over a wide temperature range, have negligible vapor pressure, are nonflammable, and have high loading capacity. These properties make them potentially useful in a large variety of industrial processes.[4]

Bis(imidazolium) and triimidazolium quaternary salts have received considerable attention in N-heterocyclic carbene chemistry,[5] anion recognition,[6] and catalytic synthesis.[7] For example, the synthesis and full characterization of some novel tris(carbene) ligand systems based on imidazolium salts and their corresponding dinuclear metal complexes were described.[8] A series of new bridging, chelating, and pincer N-heterocyclic carbene complexes of Rh^I, Rh^{III}, and Pd^{II} based on bis(imidazolium) salts which used pyridinyl and benzyl as linking units, and their effective applications for the Heck reaction, were reported.[9] The preparation of new polyimidazolium quaternary salts with special characteristics is still a challenging field.

Calix[4]arenes are a class of phenol−formaldehyde cyclic oligomers which can be functionalized in various ways at the phenolic hydroxyl groups or at the *para* position of the phenolic rings forming unique three-dimensional structures.[10] They are good building blocks or molecular scaffolds for the construction of some large supramolecular systems with defined structure or functional groups. Their derivatives have been widely used for recognition of metal ions, neutral molecules, and anions.[11] Calix[4]arene-crown derivatives also have good extraction ability and selectivity for different alkali metal ions.[12] They can be used as chromoionophoric systems for some metal ions.[13]

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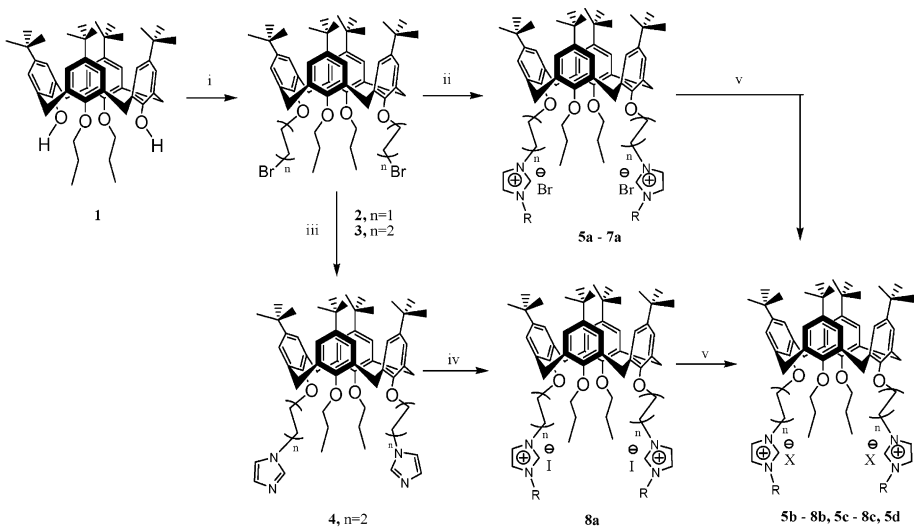
Scheme 1 [a]



Compound	n	R	X
5a	1	C_4H_9	-
5b	1	C_4H_9	$N(SO_2CF_3)_2$
5c	1	C_4H_9	PF_6
5d	1	C_4H_9	BF_4
6a	2	C_4H_9	-
6b	2	C_4H_9	$N(SO_2CF_3)_2$
6c	2	C_4H_9	PF_6
7a	2	CH_3	-
7b	2	CH_3	$N(SO_2CF_3)_2$
7c	2	CH_3	PF_6
8a	2	$C_3H_6CF_3$	-
8b	2	$C_3H_6CF_3$	$N(SO_2CF_3)_2$
8c	2	$C_3H_6CF_3$	PF_6

[a] Reagents and conditions: (i) $Br(CH_2CH_2)_nBr$ ($n = 1, 2$), NaH/DMF, 80 °C; (ii) *N*-alkylimidazolium; (iii) imidazole, NaH/THF, reflux; (iv) $CF_3CH_2CH_2CH_2I$, CH_3CN, 65 °C; (v) $CH_3OH + H_2O$ (10:1), $LiN(CF_3SO_2)_2$ or KPF_6 or $NaBF_4$.

On the basis of our earlier work,[14] we now describe a series of di(alkyl- and 4,4,4-trifluorobutyl)imidazolium-substituted *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[4]arene-crown-5 quaternary salts. Their thermal properties and coordination with potassium ion were also examined. To the best of our knowledge, there are no earlier studies of di(alkyl- or polyfluoroalkylimidazolium) derivatives of *p-tert*-butylcalix[4]arene.

Results and Discussion

All quaternary salts were prepared from **1** and **9** via the synthetic routes displayed in Schemes 1 and 2.[15] To obtain compounds **2** or **3**, an excess of 1,2-dibromoethane or 1,4-dibromobutane was used with **1** in the presence of NaH and DMF. Following flash column chromatography, **2** or **3** was found in 43 or 52% yield, respectively. Each was subse-

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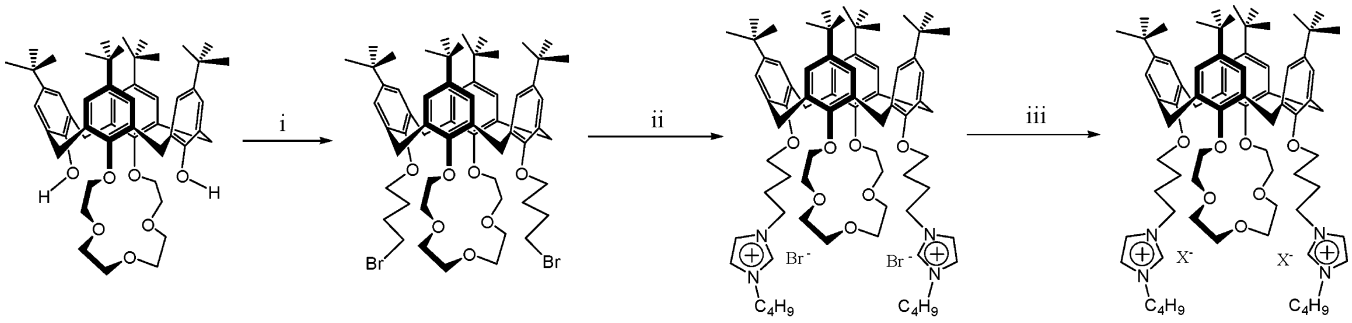
Scheme 2 [a]



9 **10** **11a** **11b,** X= $N(SO_2CF_3)_2$ **11c,** X= PF_6

[a] Reagents and conditions: (i) $Br(CH_2)_4Br$, NaH/DMF, 80 °C; (ii) *N*-butylimidazolium; (iii) $CH_3OH + H_2O$ (10:1), $LiN(CF_3SO_2)_2$ or KPF_6.

quently quaternized with *N*-methyl- or *N*-butylimidazole under neat conditions in sealed tubes. After 24 h at 60 °C, **3** and *N*-alkylimidazole reacted smoothly to form the quaternary salt essentially quantitatively. However, when **2** and *N*-butylimidazole were used, a higher temperature (~110 °C) and a longer reaction time (~48 h) were required to prepare **5a**. The ^{1}H NMR and ^{13}C NMR spectra of **5a** showed doublets at ~δ 4.30 and 3.10 ppm with a coupling constant, $J = 12.6$ Hz, in the former spectra. In the latter spectra, there is a singlet at ~δ 31 ppm which is assigned to the bridging methylene group in *p-tert*-butylcalix[4]arene.[16]

To take advantage of the interesting properties and potential applications that polyfluoroalkyl quaternary salts bring to the field of ionic liquids,[17] the 4,4,4-trifluorobutyl-quaternized salt of **4** was also prepared. Compound **4** was obtained by reaction of **3** and imidazole in the presence of sodium hydride with THF as solvent at reflux for 36 h. The isolated yield of the **4** is 62%. Then **4** was quaternized with 4,4,4-trifluorobutyl iodide in acetonitrile in a sealed tube for 20 h at 65 °C to form **8a.** A typical AB pattern was observed for the methylene bridge ArCH_2Ar protons as doublets with chemical shifts centered at δ 4.36 and 3.15 ppm ($J = 12.6$ Hz) in the ^{1}H NMR spectrum assigned to the axial and equatorial protons, respectively.

Calix[4]arene-crown-5 derivatives have been shown to have high extraction abilities and selectivities for different alkali metal cations, when dissolved in chloroform. Recently, ionic liquids as a new medium for extraction studies have attracted a lot of attention.[18] To obtain calix[4]arene-crown-5 derivatives that would be miscible with some known ionic liquids, **11a** was prepared by the reaction of **10** and *N*-butylimidazole under neat conditions at 80 °C for 48 h (Scheme 2). Compound **10** was prepared via a method similar to that used for **2** and **3**.

Metathesis of **5a**, **6a**, **7a**, **8a**, and **11a** with two metal salts ($LiN(SO_2CF_3)_2$ or KPF_6) led to the formation of some new quaternary salts in excellent isolated yields in methanol and water (10:1) at 25 °C. Compound **5a** also was reacted with $NaBF_4$ to form **5d**. All of the compounds (**5b**−**8b**, **11b**, **5c**−**8c**, **11c**, and **5d**) exist in a cone conformation as determined from their ^{1}H NMR and ^{13}C NMR spectra. The characteristic signal corresponding to a quaternary halide with a chemical shift between δ 10.69 and 10.20 ppm for the proton in the imidazolium ring has shifted upfield to δ 8.46−9.08 ppm. The melting points and decomposition temperatures for all quaternary salts as determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are given in Table 1. All quaternary salts were found to be thermally stable and to have high decomposition temperatures (T_d > 290 °C). The hexafluorophosphate salts were more stable thermally than the bis(trifluoromethanesulfonyl)amide salts or halides. Compounds **5a**−**d**, **6b**, and **11a**−**c** have melting points below 100 °C and, therefore, can be regarded as ionic liquids. While the different R groups influence the melting points to some extent, this does not occur in a regular fashion. As is to be expected, in general the melting points of the quaternary salts decrease when the halide anions are exchanged with NTf_2^- and PF_6^- anions.[19] The 4,4,4-trifluorobutyl group was introduced into **4** to form the quaternary iodide, **8a**, which was metathesized with $LiN(SO_2CF_3)_2$ and KPF_6 to give **8b** and **8c**, respectively. The melting points increased vis-à-vis the nonfluorinated butyl compounds.

Table 1. Phase Transition and Thermal Decomposition Temperatures of Quaternary Salts

compd	T_m[a]	T_d[b]	compd	T_m[a]	T_d[b]
5a	85	298	**5b**	52	343
5c	80	355	**5d**	87	358
6a	159	295	**6b**	51	385
6c	107	405	**7a**	243	295
7b	199	357	**7c**	291	370
8a	203	290	**8b**	130	357
8c	274	382	**11a**	72	294
11b	38	361	**11c**	56	372

[a] Phase transition temperature, °C. [b] Thermal degradation, °C.

While **7a**, **8a**, and **11a** were only partially miscible in methylene chloride, chloroform, and acetone at 25 °C, all other quaternary salts exhibited good solubility in methylene chloride, chloroform, acetone, ether, ethyl acetate, acetonitrile, and methanol.

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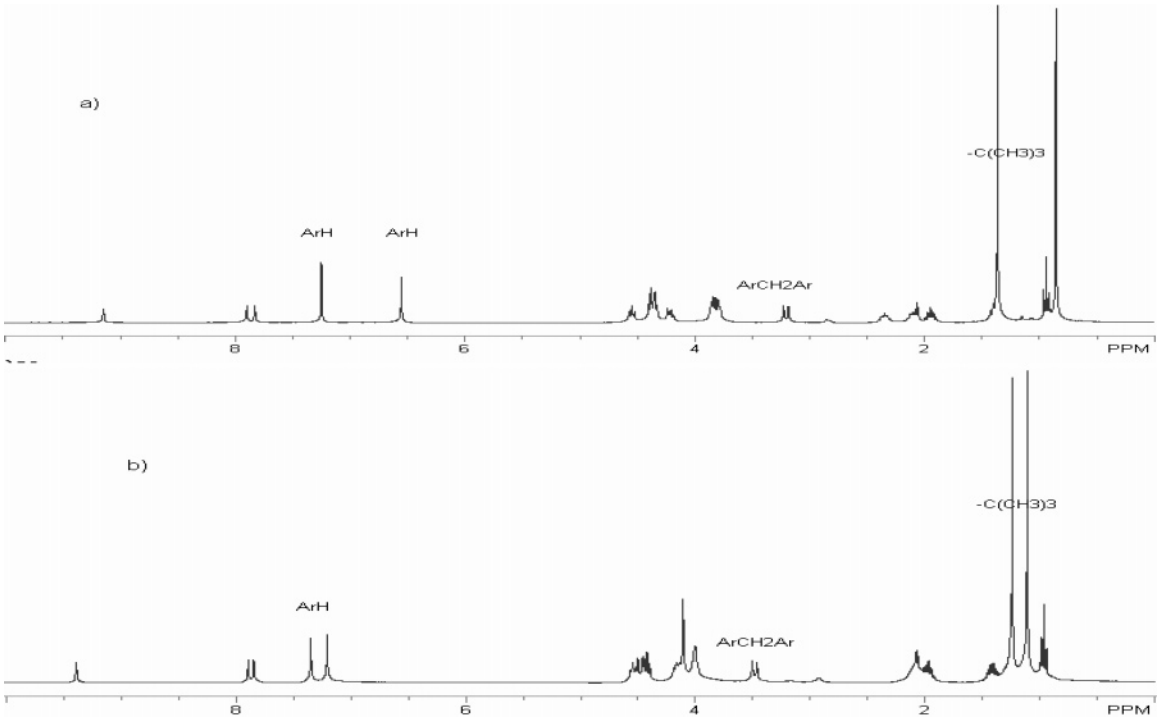

Figure 1. ^{1}H NMR spectra (300 MHz, CD_3COCD_3) of (a) **11c** and (b) **11c** and 1 equiv of KSCN.

The quaternary salts **11a**−**11c** also show good solubility in [BMIM]PF_6.

To learn about the extractive interactions of **11c** with alkali metal salts, ^{1}H NMR titration experiments were carried out. In Figure 1 are shown the ^{1}H NMR spectra of pure **11c** (a) and **11c** in the presence of an equivalent amount of KSCN (b) in acetone-d_6. The signals assigned to ArH in the calixarene have shifted downfield from δ 7.25 and 6.55 ppm to δ 7.34 and 7.20 ppm with the distance between these two peaks decreasing markedly suggesting additional deshielding arising from the presence of an electron-withdrawing species, such as a metal ion. The signals for $-C(CH_3)_3$ have shifted from δ 1.37 and 0.86 ppm to δ 1.22 and 1.09 The axial methylene protons in $ArCH_2Ar$ at δ 3.20 ppm ($J = 12.6$ Hz) have shifted downfield to δ 3.48 ppm which supports greater deshielding arising from an electron-withdrawing species. The signals of the equatorial methylene protons are overlapped with other methylene protons in the polyether chain or *N*-alkyl chain. This supports the presence of an ionic species such as K^+.

^{1}H NMR titration experiments using **11c** and 1 equiv of NaSCN caused no change in the proton spectra, which clearly indicated that **11c** has a higher selectivity and stronger binding ability with K^+ than with Na^+. To exclude the possibility of anion exchange between PF_6^- and SCN^-, a metathesis reaction of **11c** with KSCN in methanol was also carried out. Results indicated that anion exchange did not occur. It was concluded that the change in the ^{1}H NMR spectrum was derived from **11c** encapsulated with K^+ in the polyether ionophoric cavity.[20]

The results obtained by ESI-MS (positive ion mode) confirmed this conclusion. The spectrum of **11c** shows the cation base peak at *m*/*z* 582.1 belonging to the [**11c** − $2PF_6^-$]$^{2+}$ species, together with another peak with a much lower intensity at *m*/*z* 1310.1 for the [**11c** − PF_6^-]$^+$ species. The spectrum of an equimolar solution of **11c** and KSCN shows the base peak at *m*/*z* 630.9 which confirmed the presence of the [**11c** + KSCN − $2PF_6^-$]$^{2+}$ species. There with two other major peaks, one at *m*/*z* 1406.7 and the other one at *m*/*z* 401.6, corresponding to [**11c** + KSCN − PF_6^-]$^+$ and [**11c** + K^+ − $2PF_6^-$]$^{3+}$ species, respectively.

Conclusion

Quaternary salts containing di(alkyl- and 4,4,4-trifluorobutyl imidazolium)-substituted *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[4]arene-crown-5 as the cationic nuclei were prepared and characterized. These new salts have high thermal stabilities and good solubilities in many solvents. Some of them, based on melting point, can be classified as ionic liquids. It is anticipated they will have further applications in *N*-carbene chemistry and extraction separation chemistry.

Experimental Section

All anhydrous solvents were treated by standard methods. The chemicals were obtained commercially from Aldrich, Acros, Lancaster, or Synquest. Silica gel (0.060−0.200 mm, pore diameter ~ 4 nm) was used for column chromatography, and a standard Schlenk line system was used for some reactions. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AMX spectrometer at 300, 75, and 282 MHz, respectively. Chemical shifts are reported in ppm relative to the appropriate standard, $CFCl_3$ for ^{19}F and TMS for ^{1}H and ^{13}C NMR spectra. For reasons of clarity and to reduce

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space, the name calix[4]arene was used throughout instead of the IUPAC name:

Pentacyclo[19.3.1.1.^{3,7}1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13-(27),15,17,19(26),21,23-dodecane. DSC data were recorded by heating from 20 to 450 °C at 10 °C/min using a TA Instrument TA10 differential scanning calorimeter equipped with autocool and calibrated using indium. Thermogravimetric analysis (TGA) measurements were made using a TA instrument TA50. Samples were heated at 10 °C/min from 25 to 500 °C in a dynamic nitrogen atmosphere. Elemental analyses were performed at SIOC, Shanghai, China.

25,27-Bis(bromobutoxy)-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene (3). A suspension of 60% NaH (240 mg, 10 mmol) and **1** (732 mg, 1.0 mmol) was stirred for 30 min at 25 °C in dry DMF (30 mL). Then 1,4-dibromobutane (4.32 g, 20 mmol) was added slowly and the mixture was stirred at 80 °C for 2 days. After cooling, it was filtered and the solvent removed in vacuo. The residue was acidified with 1 N HCl and extracted with methylene chloride (30 mL). The organic layer was washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was subjected to flash column chromatography (silica gel, CH_2Cl_2) to give a white solid: 520 mg (51.8% yield); mp 170 °C; ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 4H, ArH), 6.77 (s, 4H, ArH), 4.42 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 3.94 (t, J = 7.2 Hz, 4H, $-OCH_2CH_2-$), 3.84 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 3.54 (t, J = 6.7 Hz, 4H, $-CH_2CH_2Br$), 3.16 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.16 (m, 4H, $-CH_2CH_2CH_3$), 2.05 (m, 8H, $-CH_2CH_2CH_2Br$), 1.14 (s, 18H, $-CH_3$), 1.06 (s, 18H, $-CH_3$), 1.03 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$); ^{13}C NMR δ 153.5, 153.4, 144.5, 144.2, 133.9, 133.5, 125.0, 124.9, 76.9, 74.0, 33.8, 33.7, 33.6, 31.5, 31.4, 31.0, 29.7, 29.0, 23.5, 10.4. Anal. Calcd for $C_{58}H_{82}Br_2O_4$: C, 69.85; H, 8.24. Found: C, 70.14; H, 8.25.

25,27-Bis(bromoethoxy)-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene (2). This compound was prepared according to the same procedure as for **3**, except the reaction time is 4 days: 42.6% yield; mp 214 °C; ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 4H, ArH), 6.49 (s, 4H, ArH), 4.36 (d, J = 12.7 Hz, 4H, $ArCH_2Ar$), 4.31 (t, J = 7.2 Hz, 4H, $-OCH_2CH_2-$), 4.03 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 3.70 (t, J = 6.7 Hz, 4H, $-CH_2CH_2Br$), 3.20 (d, J = 12.7 Hz, 4H, $ArCH_2Ar$), 1.98 (m, 4H, $-CH_2CH_2CH_3$), 1.36 (s, 18H, $-CH_3$), 1.11 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$), 0.85 (s, 18H, $-CH_3$); ^{13}C NMR δ 153.5, 152.1, 145.7, 144.3, 135.3, 131.7, 125.6, 124.6, 77.8, 73.7, 34.1, 33.6, 31.7, 31.1, 31.0, 29.6, 23.6, 10.7. Anal. Calcd for $C_{54}H_{74}Br_2O_4$: C, 68.49; H, 7.88. Found: C, 68.35; H, 7.87.

25,27-Bis(bromobutoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]-arene-crown-5 (10). A suspension of 60% of NaH (170 mg, 4 mmol) and **9** (500 mg, 0.62 mmol) was stirred for 30 min at 25 °C in dry DMF (30 mL). Then 1,4-dibromobutane (2.16 g, 0.1 mol) was added slowly and the mixture stirred at 80 °C for 3 days. After cooling, it was filtered and the solvent was removed in vacuo. The residue was acidified with 1 N HCl and extracted with methylene chloride. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After the solvent was removed, the residue was subjected to flash column chromatography (silica gel, CH_2Cl_2 + $CH_3COOC_2H_5$ = 4:1) to obtain the product: 300 mg (yield 44.1%); mp 214 °C; ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 4H, ArH), 6.46 (s, 4H, ArH), 4.35 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 4.30 (m, 4H, $-OCH_2CH_2-$), 4.23 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 3.85 (bs, 4H, $-CH_2CH_2$), 3.78 (bs, 8H, $-OCH_2CH_2O-$), 3.53 (bs, 4H, $-CH_2CH_2Br$), 3.17 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.13 (bs, 8H, $-CH_2CH_2CH_2Br$), 1.36 (s, 18H, $-CH_3$), 0.83 (s, 18H, $-CH_3$); ^{13}C NMR δ 154.8, 152.2, 145.1, 144.2, 135.3, 131.6, 125.6, 124.5, 74.8, 72.6, 71.2, 70.4, 34.1, 33.7, 33.6, 31.7, 31.1, 30.9, 29.6, 29.2. Anal. Calcd for $C_{60}H_{84}Br_2O_7$: C, 66.90; H, 7.86. Found: C, 67.13; H, 7.72.

General Procedure for the Preparation of Compounds 5a, 6a, 7a, and 11a. The corresponding *p*-*tert*-butylcalix[4]arene bromide derivatives (**2**, **3**, or **10**) (0.1 mmol) and *N*-alkylimidazole (2.0 mmol) were mixed in a Pyrex tube and cooled to −196 °C. Dinitrogen was introduced, the tube was sealed, and the reaction mixture was heated at 60 or 110 °C depending on the reactants for 24 or 48 h. The reaction mixture was subjected to flash column chromatography to obtain a white solid.

25,27-Bis[4-(3-butylimidazolium-1-yl)ethoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene dibromide (5a): CH_2Cl_2 + CH_3OH = 10:1; yield 74%; mp 85 °C; ^{1}H NMR ($CDCl_3$) δ 10.20 (s, 2H, $-NCHN-$), 7.71 (s, 2H, $-NCHCHN-$), 7.20 (s, 2H, $-NCHCHN-$), 7.04 (s, 4H, ArH), 6.34 (s, 4H, ArH), 4.86 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.57 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 4.33 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 4.08 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 3.68 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.08 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 1.83 (m, 4H, $-CH_2CH_2CH_2$), 1.74 (m, 4H, $-CH_2CH_2CH_2$), 1.33 (m, 4H, $-CH_2CH_2CH_2$), 1.28 (s, 18H, $-CH_3$), 0.88 (m, 12H, $-CH_2CH_3$), 0.71 (s, 18H, $-CH_3$); ^{13}C NMR δ 151.5, 151.4, 146.3, 144.2, 136.5, 135.1, 130.9, 125.6, 124.2, 122.6, 121.9, 77.5, 70.3, 49.5, 48.4, 33.8, 33.2, 31.8, 31.3, 30.9, 30.6, 23.2, 19.1, 13.2, 10.2. Anal. Calcd for $C_{68}H_{98}Br_2N_4O_4\cdot 3H_2O$: C, 65.37; H, 8.39; N, 4.48. Found: C, 64.93; H, 8.06; N, 4.56.

25,27-Bis[4-(3-butylimidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene dibromide (6a): CH_2Cl_2 + CH_3OH = 20:1; yield 78%; mp 159 °C; ^{1}H NMR ($CDCl_3$) δ 10.69 (s, 2H, $-NCHN-$), 7.56 (s, 2H, $-NCHCHN-$), 7.35 (s, 2H, $-NCHCHN-$), 7.09 (s, 4H, ArH), 6.49 (s, 4H, ArH), 4.56 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.38 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 4.36 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 4.06 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.72 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.14 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.12 (m, 4H, $-CH_2CH_2CH_2$), 2.07 (m, 4H, $-CH_2CH_2CH_2$), 1.94 (m, 12H, $-CH_2CH_2CH_2$), 1.33 (s, 18H, $-CH_3$), 1.10 (t, J = 3.5 Hz, 6H, $-CH_2CH_3$), 0.98 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$), 0.86 (s, 18H, $-CH_3$); ^{13}C NMR δ 153.8, 152.4, 145.1, 144.0, 137.1, 135.2, 131.9, 125.4, 124.4, 122.3, 121.8, 73.5, 49.9, 49.8, 33.9, 33.5, 32.0, 31.6, 31.3, 31.1, 31.0, 27.4, 26.6, 23.6, 19.5, 13.4, 10.9. Anal. Calcd for $C_{72}H_{106}Br_2N_4O_4\cdot 6H_2O$: C, 63.61; H, 8.75; N, 4.22. Found: C, 63.52; H, 8.37; N, 4.58.

25,27-Bis[4-(3-methylimidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene dibromide (7a): CH_2Cl_2 + CH_3OH = 2:1; yield 74%; mp 243 °C; ^{1}H NMR (CD_3COCD_3) δ 10.44 (s, 2H, $-NCHN-$), 8.17 (s, 2H, $-NCHCHN-$), 7.91 (s, 2H, $-NCHCHN-$), 7.13 (s, 4H, ArH), 6.65 (s, 4H, ArH), 4.68 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.44 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.14 (s, 6H, NCH_3), 4.07 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 3.76 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.17 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.06 (m, 8H, $-CH_2CH_2CH_2$), 1.96 (m, 4H, $-CH_2CH_2CH_2$), 1.30 (s, 18H, $-CH_3$), 1.08 (t, J = 3.5 Hz, 6H, $-CH_2CH_3$), 0.93 (s, 18H, $-CH_3$); ^{13}C NMR δ 155.1, 153.7, 145.4, 144.5, 138.6, 135.9, 133.3, 126.2, 125.4, 124.2, 123.4, 78.1, 74.9, 50.2, 36.7, 34.5, 34.2, 31.9, 31.6, 31.5, 28.2, 27.6, 24.3, 11.2. Anal. Calcd for $C_{66}H_{94}Br_2N_4O_4$: C, 58.27; H, 8.12; N, 4.60. Found: C, 58.61; H, 7.90; N, 4.29.

25,27-Bis[4-(3-butylimidazolium-1-yl)butoxy]-5,11,17,23-tetra-*tert*-butylcalix[4]arene dibromide(11a): CH_2Cl_2 + CH_3OH = 1:1; yield 72%; mp 72 °C; ^{1}H NMR ($CDCl_3$) δ 10.66 (s, 2H, $-NCHN-$), 8.08 (s, 2H, $-NCHCHN-$), 7.40 (s, 2H,

−NCHCHN−), 7.05 (s, 4H, ArH), 6.99 (s, 4H, ArH), 4.62 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 4.37−4.03 (m, 28H), 3.33 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.03 (m, 8H, $-CH_2CH_2CH_2$), 1.90 (m, 4H, $-CH_2CH_2CH_2$), 1.37 (m, 4H, $-CH_2CH_2CH_2$), 1.15 (s, 18H, $-CH_3$), 1.09 (s, 18H, $-CH_3$), 0.96 (t, J = 7.4 Hz, 6H, $-CH_2CH_3$); ^{13}C NMR δ 150.7, 149.0, 147.7, 147.5, 137.0, 134.2, 125.8, 123.3, 121.8, 121.5, 116.5, 77.3, 71.4, 69.9, 69.7, 49.7, 49.3, 34.1, 34.0, 32.2, 31.3, 31.2, 30.7, 26.9, 25.9, 25.6, 19.5, 13.5. Anal. Calcd for $C_{74}H_{108}Br_2N_4O_7 + 4H_2O$: C, 63.60; H, 8.37; N, 4.01. Found: C, 63.58; H, 8.35; N, 3.84.

25,27-Bis[4-(1-imidazolium)butoxy]-26, 28-dipropoxy-5,11,-17,23-tetra-*tert*-butylcalix[4]arene (4). To a solution of NaH (50 mg, 1.2 mmol) in THF (10 mL), the solution of imidazolium (23 mg, 0.33 mmol) in THF was added slowly (10 mL) at 0 °C. The mixture was stirred at 25 °C for 1 h, a solution of **3** (300 mg, 0.3 mmol) in THF (10 mL) was added, and the mixture was refluxed for 36 h. It was filtered to remove the solvent. The residue was acidified with 1 N HCl (10 mL), washed with water, and subjected to flash column chromatography (CH_2Cl_2 + CH_3OH = 20:1) to obtain a white solid: 180 mg (yield 61.6%); mp 88 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (s, 2H, −NCHN−), 7.10 (s, 2H, −NCHCHN−), 6.93 (s, 2H, −NCHCHN−), 6.85 (s, 4H, ArH), 6.74 (s, 4H, ArH), 4.36 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.01 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 3.86 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 3.82 (t, J = 7.9 Hz, 4H, $-CH_2CH_2N-$), 3.14 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 1.98 (m, 12H, $-CH_2CH_2CH_2$), 1.14 (s, 18H, $-CH_3$), 1.06 (s, 18H, $-CH_3$), 0.99 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$); ^{13}C NMR δ 153.6, 152.9, 144.5, 144.4, 136.9, 133.8, 133.2, 129.6, 125.0, 124.9, 118.6, 76.7, 46.9, 33.8, 33.7, 31.4, 31.3, 31.0, 28.1, 27.3, 10.3. Anal. Calcd for $C_{64}H_{88}N_4O_4 \cdot H_2O$: C, 77.22; H, 9.11, N, 5.63. Found: C, 77.66; H, 9.00, N, 5.61.

25,27-Bis[4-(3-(4,4,4-trifluorobutyl)imidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene Diiodide (8a). To a solution of 4 (200 mg, 0.2 mmol) in acetonitrile (1.5 mL) in a Pyrex tube was added 4,4,4-trifluorobutyl iodide (238 mg, 10 mmol). It was sealed and heated to 65 °C for 20 h. After cooling, the solvent was removed, and the residue was washed with a dilute solution of $Na_2S_2O_3$ (160 mg, 1 mmol), which was extracted with CH_2Cl_2. It was subjected to flash column chromatography (CH_2Cl_2 + CH_3OH = 20:1) to get a white solid: 245 mg (yield 82.3%); mp 203 °C; ^{1}HNMR ($CDCl_3$) δ 10.44 (s, 2H, −NCHN−), 7.48 (s, 2H, −NCHCHN−), 7.39 (s, 2H, −NCHCHN−), 7.11 (s, 4H, ArH), 6.48 (s, 4H, ArH), 4.54 (m, 8H, $-OCH_2CH_2-$), 4.36 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 4.05 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.71 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.15 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.32 (m, 12H, $-CH_2CH_2CH_2$), 2.15 (m, 4H, $-CH_2CH_2CH_2$), 1.92 (m, 4H, $-CH_2CH_2CH_2$), 1.33 (s, 18H, $-CH_3$), 1.08 (t, J = 3.5 Hz, 6H, $-CH_2CH_3$); 0.85 (s, 18H, $-CH_3$); ^{13}C NMR δ 154.6, 152.9, 145.8, 144.7, 138.0, 136.1, 132.5, 126.2, 125.1, 122.7, 122.4, 127.2 (q, J = 274.8 Hz, CH_2CF_3), 78.2, 74.2, 51.1, 49.1, 34.7, 34.2, 32.3, 31.8, 31.7, 31.3 (q, J = 29.3 Hz, CH_2CF_3), 27.6, 27.3, 24.5, 23.7, 11.7; ^{19}F NMR δ −65.6 (t, J = 10.2 Hz, CH_2CF_3). Anal. Calcd for $C_{72}H_{100}I_2F_6N_4O_4$: C, 59.50; H, 6.94; N, 3.85. Found: C, 59.18; H, 6.97; N, 3.70.

General Procedure for Anion Metathesis. Compounds **5a**, **6a**, **7a**, **8a**, and **11a** (0.1 mmol) were taken in a 50 mL round-bottomed flask and dissolved in CH_3OH (30 mL). An aqueous solution (3 mL) of $LiN(CF_3SO_2)_2$, KPF_6, or $NaBF_4$ (0.12 mmol) was added, and the reaction mixture was stirred for 3 h at room temperature. The solvent was removed and the residue washed with water and extracted with methylene chloride or ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$. The solvent was removed in vacuo to obtain desired products.

25,27-Bis[4-(3-butylimidazolium-1-yl)ethoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(trifluoromethanesulfonyl)amide (5b): yield 85%; mp 52 °C; ^{1}H NMR ($CDCl_3$) δ 8.46 (s, 2H, −NCHN−), 7.35 (s, 2H, −NCHCHN−), 7.25 (s, 2H, −NCHCHN−), 7.15 (s, 4H, ArH), 6.46 (s, 4H, ArH), 4.81 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.64 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 4.20 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.14 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.76 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.20 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 1.86 (m, 8H, $-CH_2CH_2CH_2$), 1.42 (m, 4H, $-CH_2CH_2CH_2$), 1.36 (s, 18H, $-CH_3$), 0.99 (m, 12H, $-CH_2CH_3$), 0.84 (s, 18H, $-CH_3$); ^{13}C NMR δ 151.7, 146.8, 144.8, 135.4, 135.3, 131.3, 125.9, 124.7, 122.6, 122.5, 119.7 [q, J = 319.2 Hz, $N(SO_2CF_3)_2$], 77.8, 70.3, 49.9, 49.5, 34.2, 33.6, 31.8, 31.6, 31.2, 31.0, 23.3, 19.3, 13.2, 10.1; ^{19}F NMR δ −78.9 ($N(SO_2CF_3)_2$). Anal. Calcd for $C_{72}H_{98}F_{12}N_6O_{14}S_4$: C, 53.12; H, 6.07; N, 5.16. Found: C, 53.45; H, 6.09; N, 5.14.

25,27-Bis[4-(3-butylimidazolium-1-yl)ethoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(hexafluorophosphate) (5c): yield 82%; mp 80 °C; ^{1}H NMR ($CDCl_3$) δ 8.54 (s, 2H, −NCHN−), 7.30 (s, 2H, −NCHCHN−), 7.29 (s, 2H, −NCHCHN−), 7.18 (s, 4H, ArH), 6.47 (s, 4H, ArH), 4.84 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.45 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 4.30 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.21 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.87 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.23 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 1.88 (m, 4H, $-CH_2CH_2CH_2$), 1.80 (m, 4H, $-CH_2CH_2CH_2$), 1.38 (s, 18H, $-CH_3$), 0.96 (m, 12H, $-CH_2CH_3$); 0.84 (s, 18H, $-CH_3$); ^{13}C NMR δ 152.4, 151.7, 146.6, 144.4, 135.9, 135.4, 131.5, 125.9, 124.5, 122.4, 121.9, 77.8, 70.8, 49.9, 48.5, 34.2, 33.6, 31.6, 31.2, 31.0, 29.2, 22.9, 19.4, 13.3, 9.9; ^{19}F NMR δ −72.0 (d, J = 711.5 Hz, PF_6); ^{31}P NMR δ −144.3 (sep, J = 711.5 Hz, PF_6). Anal. Calcd for $C_{68}H_{98}F_{12}N_4O_4P_2$: C, 61.62; H, 7.45; N, 4.23. Found: C, 61.60; H, 7.49; N, 4.04.

25,27-Bis[4-(3-butylimidazolium-1-yl)ethoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(tetrafluoroborate) (5d): yield 87%; mp 87 °C; ^{1}H NMR ($CDCl_3$) δ 8.87 (s, 2H, −NCHN−), 7.30 (s, 2H, −NCHCHN−), 7.29 (s, 2H, −NCHCHN−), 7.18 (s, 4H, ArH), 6.48 (s, 4H, ArH), 4.89 (t, J = 7.4 Hz, 4H, $-OCH_2CH_2-$), 4.45 (t, J = 8.3 Hz, 4H, $-OCH_2CH_2-$), 4.31 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 4.27 (t, J = 7.6 Hz, 4H, $-NCH_2CH_2-$), 3.88 (t, J = 7.6 Hz, 4H, $-CH_2CH_2N-$), 3.22 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 1.81−1.93 (m, 8H, $-CH_2CH_2CH_2$), 1.41 (s, 18H, $-CH_3$), 0.97 (m, 12H, $-CH_2CH_3$), 0.84 (s, 18H, $-CH_3$); ^{13}C NMR δ 152.6, 151.8, 146.6, 144.4, 136.7, 135.5, 131.5, 125.9, 124.6, 122.1, 121.9, 77.9, 71.0, 49.9, 48.3, 34.2, 33.6, 31.7, 31.6, 31.1, 31.0, 23.1, 19.5, 13.4, 10.1; ^{19}F NMR δ −151.5 (BF_4). Anal. Calcd for $C_{68}H_{98}B_2F_8N_4O_4$: C, 67.55; H, 8.17; N, 4.63. Found: C, 67.64; H, 8.26; N, 4.51.

25,27-Bis[4-(3-butylimidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(trifluoromethanesulfonyl)amide (6b): yield 81%; mp 51 °C; ^{1}H NMR ($CDCl_3$) δ 8.84 (s, 2H, −NCHN−), 7.37 (s, 2H, −NCHCHN−), 7.35 (s, 2H, −NCHCHN−), 6.99 (s, 4H, ArH), 6.64 (s, 4H, ArH), 4.39 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.28 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.20 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 4.02 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.76 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.17 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.16 (m, 4H, $-CH_2CH_2CH_2$), 2.04 (m, 4H, $-CH_2CH_2CH_2$), 1.91 (m, 12H, $-CH_2CH_2CH_2$), 1.25 (s, 18H, $-CH_3$), 1.10 (t, J = 3.5 Hz, 6H, $-CH_2CH_3$); 0.98 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$), 0.85(s, 18H, $-CH_3$); ^{13}C NMR δ 153.3, 152.7, 144.9, 144.2, 135.2, 134.7, 132.6, 125.3, 124.6, 122.3, 122.9, 126.1,

121.9, 117.6, 113.4 [q, J = 315.0 Hz, $N(SO_2CF_3)_2$], 77.1, 73.3, 50.0, 49.8, 33.9, 33.6, 31.8, 31.5, 31.2, 31.0, 27.1, 26.6, 23.3, 19.3, 13.1, 10.3; ^{19}F NMR δ −78.9 [$N(SO_2CF_3)_2$]. Anal. Calcd for $C_{76}H_{106}F_{12}N_6O_{12}S_4$: C, 55.26; H, 6.47; N, 5.09. Found: C, 55.47; H, 6.42; N, 4.97.

25,27-Bis[4-(3-butylimidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(hexafluorophosphate) (6c): yield 78%; mp 107 °C; ^{1}H NMR ($CDCl_3$) δ 8.77 (s, 2H, −NCHN−), 7.22 (s, 2H, −NCHCHN−), 7.16 (s, 2H, −NCHCHN−), 7.15 (s, 4H, ArH), 6.47 (s, 4H, ArH), 4.39 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.31 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.18 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 4.07 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.70 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.15 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.32 (m, 4H, $-CH_2CH_2CH_2$), 2.05 (m, 4H, $-CH_2CH_2CH_2$), 1.90 (m, 12H, $-CH_2CH_2CH_2$), 1.37 (s, 18H, $-CH_3$), 1.10 (t, J = 3.5 Hz, 6H, $-CH_2CH_3$), 0.98 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$), 0.84 (s, 18H, $-CH_3$); ^{13}C NMR δ 153.8, 152.2, 144.9, 143.7, 135.5, 135.3, 131.7, 125.3, 124.2, 121.8, 121.5, 77.6, 73.5, 49.8, 49.5, 33.8, 33.4, 31.5, 31.4, 30.9, 30.8, 26.5, 26.4, 23.4, 19.1, 13.1, 10.2; ^{19}F NMR δ −72.1 (d, J = 711.5 Hz, PF_6); ^{31}P NMR δ −144.2 (sep, J = 711.5 Hz, PF_6). Anal. Calcd for $C_{72}H_{106}F_{12}N_4O_4P_2$: C, 62.59; H, 7.73; N, 4.06. Found: C, 62.79; H, 7.63; N, 3.90.

25,27-Bis[4-(3-methylimidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(trifluoromethanesulfonyl)amide (7b): yield 88%; mp 199 °C; ^{1}H NMR ($CDCl_3$) δ 9.08 (s, 2H, −NCHN−), 7.80 (s, 2H, −NCHCHN−), 7.75 (s, 2H, −NCHCHN−), 7.00 (s, 4H, ArH), 6.77 (s, 4H, ArH), 4.52 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.42 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.08 (s, 6H, $-NCH_3$), 3.89 (m, 8H, $-CH_2CH_2N(O)-$), 3.18 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.20 (m, 4H, $-CH_2CH_2CH_2$), 2.05 (m, 8H, $-CH_2CH_2CH_2$), 1.21 (s, 18H, $-CH_3$), 1.04 (s, 18H, $-CH_3$), 0.99 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$); ^{13}C NMR δ 154.8, 153.8, 145.1, 144.9, 137.3, 135.1, 133.9, 126.0, 125.7, 124.9, 123.4, 121.4 [q, J = 319.4 Hz, $N(SO_2CF_3)_2$], 77.4, 74.9, 50.3, 36.7, 34.4, 34.3, 31.9, 31.8, 31.6, 27.8, 27.6, 24.0, 10.6; ^{19}F NMR δ −79.8 [$N(SO_2CF_3)_2$]. Anal. Calcd for $C_{70}H_{94}F_{12}N_6O_{12}S_4$: C, 53.63; H, 6.04; N, 5.36. Found: C, 53.40; H, 6.02; N, 5.30.

25,27-Bis[4-(3-methylimidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(hexafluorophosphate) (7c): yield 83%; mp 291 °C; ^{1}H NMR ($CDCl_3$) δ 9.01 (s, 2H, −NCHN−), 7.79 (s, 2H, −NCHCHN−), 7.73 (s, 2H, −NCHCHN−), 6.90 (s, 4H, ArH), 6.88 (s, 4H, ArH), 4.51 (t, J = 7.6 Hz, 4H, $-OCH_2CH_2-$), 4.42 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.07 (s, 6H, $-NCH_3$), 3.90 (t, J = 6.7 Hz, 4H, $-OCH_2CH_2-$), 3.84 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.18 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.18 (m, 8H, $-CH_2CH_2CH_2$), 2.05 (m, 4H, $-CH_2CH_2CH_2$), 1.12 (s, 18H, $-CH_3$), 1.10 (s, 18H, $-CH_3$), 0.99 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$); ^{13}C NMR δ 154.4, 154.2, 145.1, 144.9, 137.4, 134.6, 134.5, 125.9, 124.9, 124.7, 123.4, 77.6, 74.9, 50.3, 36.6, 34.4, 31.8, 31.7, 31.6, 31.4, 27.8, 27.6, 24.1, 10.6; ^{19}F NMR δ −72.8 (d, J = 706.9 Hz, PF_6); ^{31}P NMR δ −144.1 (sep, J = 706.9 Hz, PF_6). Anal. Calcd for $C_{66}H_{94}F_{12}N_4O_4P_2$: C, 61.10; H, 7.30; N, 4.32. Found: C, 61.17; H, 7.20; N, 4.21.

25,27-Bis[4-(3-(4,4,4-trifluorobutyl)imidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(trifluoromethanesulfonyl)amide (8b): yield 86%; mp 130 °C; ^{1}H NMR ($CDCl_3$) δ 8.88 (s, 2H, −NCHN−), 7.42 (s, 2H, −NCHCHN−), 7.33 (s, 2H, −NCHCHN−), 7.03 (s, 4H, ArH), 6.61 (s, 4H, ArH), 4.37 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.33 (m, 8H, $-OCH_2CH_2-$), 4.03 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.74 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.17 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.20 (m, 12H, $-CH_2CH_2CH_2$), 2.03 (m, 4H, $-CH_2CH_2CH_2$), 1.90 (m, 4H, $-CH_2CH_2CH_2$), 1.27 (s, 18H, $-CH_3$), 1.02 (t, J = 7.3 Hz, 6H, $-CH_2CH_3$), 0.96 (s, 18H, $-CH_3$); ^{13}C NMR δ 154.1, 153.3, 145.8, 144.9, 136.2, 135.6, 133.1, 127.8 (q, J = 159.5 Hz, CH_2CF_3), 126.1, 125.3, 123.2, 123.0, 120.4 [q, J = 319.1 Hz, $N(SO_2CF_3)_2$], 77.9, 73.9, 50.9, 49.1, 34.7, 34.3, 32.3, 32.0 (q, J = 2.3 Hz, $CH_2CH_2CF_3$), 31.9, 31.0 (q, J = 29.6 Hz, CH_2CF_3), 27.7, 27.3, 24.1, 23.6, 11.0; ^{19}F NMR δ −66.2 (t, J = 9.6 Hz, CH_2CF_3), −79.1 [$N(SO_2CF_3)_2$]. Anal. Calcd for $C_{76}H_{100}F_{18}N_6O_{12}S_4$: C, 52.87; H, 5.73; N, 4.78. Found: C, 52.86; H, 5.84; N, 4.64.

25,27-Bis[4-(3-(4,4,4-trifluorobutyl)imidazolium-1-yl)butoxy]-26,28-dipropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene bis(hexafluorophosphate) (8c): yield 84%; mp 274 °C; ^{1}H NMR ($CDCl_3$) δ 8.74 (s, 2H, −NCHN−), 7.33 (s, 2H, −NCHCHN−), 7.24 (s, 2H, −NCHCHN−), 7.14 (s, 4H, ArH), 6.54 (s, 4H, ArH), 4.42 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 4.28 (m, 8H, $-OCH_2CH_2-$), 4.08 (t, J = 6.7 Hz, 4H, $-NCH_2CH_2-$), 3.72 (t, J = 7.2 Hz, 4H, $-CH_2CH_2N-$), 3.19 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 2.32−1.92 (m, 20H, $-CH_2CH_2CH_2$), 1.36 (s, 18H, $-CH_3$), 1.11 (t, J = 3.5 Hz, 6H, $-CH_2CH_3$), 0.90 (s, 18H, $-CH_3$); ^{13}C NMR δ 154.7, 153.1, 145.8, 144.7, 136.5, 136.2, 132.6, 126.2, 125.2, 122.9, 122.5, 126.9 (q, J = 274.4 Hz, CH_2CF_3), 78.3, 74.3, 50.7, 49.0, 34.7, 34.2, 32.4, 32.1 (q, J = 3.3 Hz, $CH_2CH_2CF_3$), 31.8, 30.8 (q, J = 29.5 Hz, CH_2CF_3), 27.3, 27.0, 24.3, 23.3, 11.1; ^{19}F NMR δ −66.1 (t, J = 10.2 Hz, CH_2CF_3), −71.8 (d, J = 710.9 Hz, PF_6); ^{31}P NMR δ −144.2 (sep, J = 711.2 Hz, PF_6). Anal. Calcd for $C_{72}H_{100}F_{18}N_4O_4P_2$: C, 58.06; H, 6.77; N, 3.76. Found: C, 58.43; H, 6.82; N, 3.65.

25,27-Bis[4-(3-butylimidazolium-1-yl)butoxy]-5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown-5 bis(trifluoromethanesulfonyl)-amide (11b): yield 80%; mp 38 °C; ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 2H, −NCHN−), 7.60 (s, 2H, −NCHCHN−), 7.36 (s, 2H, −NCHCHN−), 7.15 (s, 4H, ArH), 6.45 (s, 4H, ArH), 4.31−4.16 (m, 20H), 3.80 (bs, 12H), 3.17 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.21 (m, 4H, $-CH_2CH_2CH_2$), 2.00 (m, 4H, $-CH_2CH_2CH_2$), 1.86 (m, 4H, $-CH_2CH_2CH_2$), 1.41 (m, 4H, $-CH_2CH_2CH_2$), 1.36 (s, 18H, $-CH_3$), 0.96 (t, J = 7.5 Hz, 6H, $-CH_2CH_3$), 0.83 (s, 18H, $-CH_3$); ^{13}C NMR δ 154.6, 151.8, 145.4, 144.5, 135.4, 135.1, 131.4, 125.7, 124.7, 122.8, 122.5, 115.6 [q, J = 318.8, $N(SO_2CF_3)_2$], 74.6, 72.5, 71.2, 70.8, 70.0, 49.9, 34.1, 33.6, 31.9, 31.7, 31.1, 30.8, 27.9, 27.2, 19.4, 13.2; ^{19}F NMR δ −78.9 ($N(SO_2CF_3)_2$). Anal. Calcd for $C_{78}H_{108}F_{12}N_6O_{15}S_4$: C, 55.28; H, 6.31; N, 4.87. Found: C, 55.29; H, 6.44; N, 4.66.

25,27-Bis[4-(3-butylimidazolium-1-yl)butoxy]-5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown-5 bis(hexafluorophosphate) (11c): yield 82%; mp 56 °C; ^{1}H NMR ($CDCl_3$) δ 8.71 (s, 2H, −NCHN−), 7.55 (s, 2H, −NCHCHN−), 7.32 (s, 2H, −NCHCHN−), 7.14 (s, 4H, ArH), 6.44 (s, 4H, ArH), 4.29−4.14 (m, 20H), 3.79 (m, 12H) 3.16 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.19 (bs, 4H, $-CH_2CH_2CH_2$), 1.99 (bs, 4H, $-CH_2CH_2CH_2$), 1.86 (m, 4H, $-CH_2CH_2CH_2$), 1.35 (s, 18H, $-CH_3$), 1.28 (m, 4H, $-CH_2CH_2CH_2$), 0.93 (t, J = 7.6 Hz, 6H, $-CH_2CH_3$), 0.82 (s, 18H, $-CH_3$); ^{13}C NMR δ 154.6, 151.9, 145.3, 144.4, 135.1, 135.0, 131.4, 125.7, 124.6, 122.7, 122.4, 74.6, 72.5, 71.1, 70.8, 70.2, 69.9, 49.8, 34.1, 33.5, 31.8, 31.6, 31.0, 30.8, 27.7, 27.2, 19.3, 13.2; ^{19}F NMR δ −72.0 (d, J = 711.5 Hz, PF_6); ^{31}P NMR δ −144.1 (sep, J = 711.5 Hz, PF_6). Anal. Calcd for $C_{74}H_{108}F_{12}N_4O_7P_2$: C, 61.06; H, 7.48; N, 3.85. Found: C, 61.45; H, 7.49; N, 3.65.

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