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Influence of the Number and Geometry of Binding Sites on Host–Guest Affinity: Imidazolium-Substituted Receptor Molecules for Small Inorganic Anions

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The influence of the number and relative geometry of the binding sites on the binding of spherical and tetragonal inorganic anions (Cl^-, Br^-, $H_2PO_4^-$, and HSO_4^-) has been studied by using imidazolium salts based on benzene and calix[4]arenes. Binding constants in DMSO were found to be in the range of 200–2000 $L\,mol^{-1}$. Three or four binding sites (**2b**–**4b**) lead to the nonselective binding of all anions indicating the decisive influence of the number of possible binding positions; binding constants of approximately 2000 for $H_2PO_4^-$, 1000 for HSO_4^-, 900 for Cl^-, and 800 $L\,mol^{-1}$ for Br^- were obtained. Benzene- (**1b**) and calixarene-based (**5b**) bis(imidazolium) salts exhibited a high selectivity towards $H_2PO_4^-$/HSO_4^- and Cl^-/Br^- indicating that for the complexation of $H_2PO_4^-$ and Cl^- two binding sites are necessary, and for Br^- and HSO_4^- at least three. In this case, selectivity could be obtained by simple variation of the number of identical binding positions.

Introduction

Anions play an important role in biological systems, for example, fluoride[1] and chloride channels, the phosphate backbone in DNA, and ATP. This has created a flurry of interest in artificial molecules that can recognize, selectively bind and/or sense anions mimicking natural systems.[2] Intermolecular forces such as ionic, dipolar, cation–π interactions and hydrogen bonds are involved in the recognition and binding process. Whereas, the binding of cations by a wide variety of host molecules is well established − in particular, crown ethers and cryptands[3] are very successful in this area − the selective and efficient binding of anions is still a challenge.[4–8]

The use of imidazolium salts as a recognition element for anions has already been demonstrated through the observed template effect of chloride anions in the formation of [1_4]imidazoliophanes.[9,10] Hence such moieties have been used in tripodal benzene receptors[11,12] for small inorganic anions,[13–15] phosphate,[16] inositol trisphosphate,[17] and ammonia[18] as well as for self-assembled molecular capsules.[19] Parallel to our own investigations reported here, Lee and co-workers have reported the use of a resorcinarene as the basic skeleton of an anion receptor.[20] Attaching four imidazolium cations to the upper rim of a resorcinarene using flexible linker groups gave rise to a receptor which showed good affinity towards dicarboxylic acids (K_{ass} = 200–16200 M^{-1}; DMSO), but only weak binding to spherical anions (Cl^- 210, Br^- 100 M^{-1}; DMSO).

During our own work with polar, water-soluble calixarenes as inverse phase-transfer catalysts[21] and imidazole-substituted calixarenes as simple enzyme mimics,[22] we developed methods for the synthesis of calix[4]arenes bearing 2–4 imidazolium salt moieties on the upper rim. Such macrocycles could be used as precursors for N-heterocyclic carbene ligands in the Suzuki cross-coupling reactions of aryl chlorides.[23]

Results and Discussion

With the aforementioned use of imidazolium salts in tripodal receptors in mind we decided to test whether the C_2- and C_4-symmetrically substituted calix[4]arene can be used in the recognition of anions. Therefore, we have synthesized C_2-, C_3- and C_4-symmetrical hosts **1**–**5** (see Scheme 1) by alkylation of 1-methylimidazole with the corresponding bromo- or chloromethyl compounds in chloroform. The syntheses of the calixarene receptors **4a** and **5a**[23] and the tripodal benzene **2**[11] have been reported previously. The derivatives **3a** and **1a** were obtained from a similar reaction of 1,3,5-tris(bromomethyl)benzene[24] and 1,3-bis(bromomethyl)-2,4,6-triethylbenzene[25] with 1-methylimidazoles in 89 and 72% yields, respectively. Compounds **1a**–**5a** were subsequently subjected to anion exchange with a saturated solution of NH_4PF_6 to afford anion receptors **1b**–**4b** in 81–85% yields and **5b** in 93% yield.

By using compounds **1b**–**5b** we were able to monitor the influence of (a) the number of recognition sites (2–4) and

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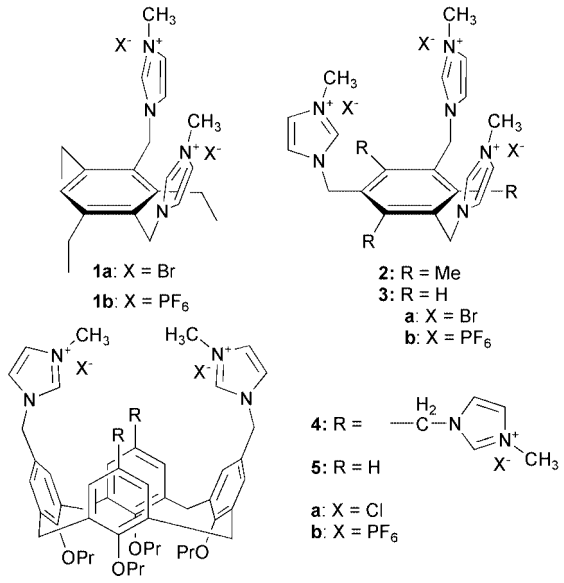

Scheme 1. C_2-, C_3- and C_4-symmetrical receptor molecules for spherical and nonspherical anions.

(b) the geometry of the recognition sites relative to each other (**1b**–**3b**, 120°; **4b**, 90°; **5b**, 180°) on the binding strength and selectivity towards spherical and tetragonal monoanions.

Therefore we studied the changes in the ^{1}H NMR spectra of hosts **1b**–**5b** caused by the addition of the anion as tetrabutylammonium salts in [D$_6$]DMSO at 298 K. All hosts exhibited downfield shifts of the 2-H signal of the imidazolium moieties upon addition of the anions (0.02–0.72 ppm). No significant shifts of the other proton signals of the receptor molecules could be observed indicating that the anions were bound by C-2–H···X$^-$ hydrogen bonding. Association constants were determined from the titration curves by using standard nonlinear curve-fitting techniques and are collected in Table 1 and visualized in Figure 1.

Table 1. Association constants (K_{ass}) for the complexation of anions[a] with the PF_6^- receptor salts **1b**–**5b** in [D$_6$]DMSO at 298 K.

	K_{ass} [M^{-1}]			
Host	$H_2PO_4^-$	HSO_4^-	Cl^-	Br^-
1b	1520	<10	740	<10
2b	2080	1100	1100	180
3b	1950	1210	1020	760
4b	1910	1110	950	850
5b	1980	200	900	200

[a] Anions used in this assay were in the form of their tetrabutylammonium salts. Estimated errors ca. 10%.

The observed data could only be fitted by a 1:1 binding model; no other host–guest stoichiometry gave useful fits of the experimental data proving the 1:1 complexation mode. Owing to the foreseen high tendency of both calixarene receptors **4b** and **5b** to self-aggregate no Job-plot analysis was performed to avoid any interference with micelle formation. The critical concentrations for self-aggregation were estimated by NMR dilution experiments to be around 5 mM in aqueous solution because in this medium maximum self-association effects could be expected. Additionally, all NMR titration experiments in DMSO using constant concentrations of host were performed well below the concentration necessary for association identified in aqueous solution. Thus, the effect of self-association on the anion-recognition processes was excluded.

The binding strength of the spherical chloride anion is in the same range for all receptors ($K_{ass} \approx 1000$ M^{-1}). Surprisingly, small changes in the number and relative geometries of the binding sites created selectivity: Flexible recep-

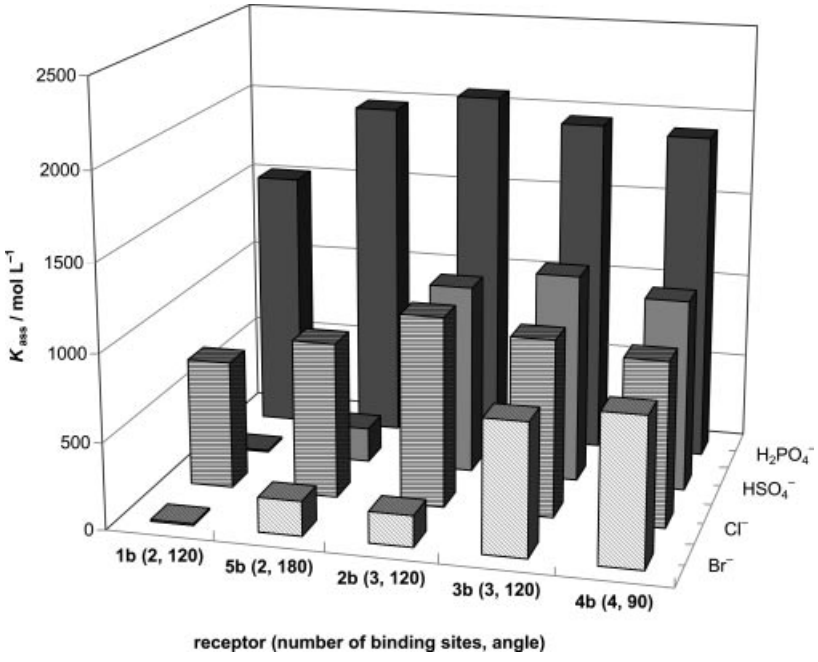

Figure 1. Association constants (K_{ass}/M^{-1}) for the complexation of anions with the PF_6^- receptor salts **1b**–**5b** in [D$_6$]DMSO at 298 K depending on the number and relative angle of binding sites.

tors **3b** and **4b** exhibited only small chloride/bromide selectivities of about 1.2. However, by using receptor **2b** or **1b**, selectivities of 6 and >70, respectively, were observed. Presumably, the cavity provided for the anion is not large enough to host the bromide anion. Additionally, no significant conformational change is possible to accommodate the bromide anion because of the reduced flexibility introduced by the alkyl substituents on the benzene skeleton. Although calixarene receptor **4b** has twice as many docking sites as **5b**, the latter has the same affinity for the chloride anion proving that only two imidazolium groups were used for binding. Clearly, the calixarene skeleton adopts a pinched-cone conformation upon complexation forcing two imidazolium groups away from the binding center so that only two could contribute to productive binding in both **4b** and **5b**. However, calixarene **5b** exhibited better chloride/bromide selectivity (4.5) than **4b**. The proposed binding modes are in agreement with models recently proposed by ab initio calculations.[11,12,26]

Dihydrogen phosphate always binds with similar binding affinity ($K_{ass} \approx 2000$ M^{-1}) and therefore one can assume that in all cases again only two imidazolium groups take part in the binding. In contrast, hydrogen sulfate was significantly better bound by receptors with three (**2b**, **3b**) or four (**4b**) binding sites. In this case, at least three imidazolium salts are necessary for efficient binding. Furthermore, subtle changes in the geometry strongly influence the binding strength. Two imidazolium sites attached at an angle of 120° (**1b**) proved to be less effective than two imidazolium sites in opposite positions, as in the calixarene-based receptor **5b**.

Because the pincer-type receptor **5b** shows reasonable selectivity for phosphate anions, we were interested in whether such a receptor can interact with the phosphate backbone of DNA. Therefore, we added calixarene **5b** to an aqueous solution of calf thymus DNA used as a model system. Surprisingly, the CT-DNA precipitated instantly after addition of the calixarene derivative at any concentration tested; a calixarene derivative similar to **5b** but with only one attached imidazolium group also showed no binding affinity towards CT-DNA, as studied by UV/Vis spectroscopy. This strikingly different binding towards DNA is currently under investigation.

Conclusion

In summary, supramolecular imidazolium salts based on benzene and calix[4]arenes are easily accessible and efficient receptor molecules for small inorganic anions ($H_2PO_4^-$, HSO_4^-, Cl^- and Br^-); their receptor abilities could be fine-tuned by changing the number and relative geometry of the necessary binding sites.

Experimental Section

General Remarks: Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Infrared (IR) spectra were obtained with a Bruker Vector 22 instrument using KBr pellets unless otherwise stated. Absorptions ($\tilde{\nu}$) are given in wavenumbers (cm^{-1}). NMR spectra were recorded with a Bruker DRX 400 (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C NMR) or a Bruker AMX 500 (500.14 MHz for ^{1}H and 125.76 MHz for ^{13}C NMR) instrument. Tetramethylsilane was used as the internal standard (δ = 0.00 ppm) in the ^{1}H NMR spectra and solvent signals were used as reference [$\delta(CDCl_3)$ = 77.0 ppm, δ([D$_6$]DMSO) = 39.5 ppm, δ([D$_4$]methanol) = 49.3 ppm] in the ^{13}C NMR spectra. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Assignments of ^{13}C NMR chemical shifts were made based on proton-coupled ^{13}C, (C,H) correlation, and DEPT-135 spectra. Mass spectra were obtained with a Finnigan MAT TSQ7000 (FAB) or a Bruker Daltonics Reflex III (MALDI-TOF) spectrometer. Solvents were dried by standard procedures. All reaction mixtures were stirred magnetically unless otherwise noted. NMR titration experiments were performed as reported previously.[21]

General Procedure for the Alkylation of 1-Methylimidazole: A solution of the corresponding bromomethyl compound (5.60 mmol) and 1-methylimidazole (1.50 mL, 18.9 mmol) in $CHCl_3$ (80 mL) was refluxed for 2–4 d. The resulting precipitate was isolated by filtration; the mother liquor was concentrated and another precipitate was isolated. All solid material was digested with Et_2O to give a colorless solid.

1,3,5-Tris[(3-methylimidazol-3-iumyl)methyl]benzene Tribromide (3a): Yield: 3.00 g (4.97 mmol, 89%). M.p. 235–240 °C. ^{1}H NMR ([D$_4$]MeOH): δ = 4.01 (s, 9 H, N-CH$_3$), 5.57 (s, 6 H, Ar-CH$_2$-Im), 7.64 (s, 3 H, Im-H), 7.74 (s, 3 H, Ar-H), 7.76 (s, 3 H, Im-H), 9.23 (s, 3 H, N-CH-N) ppm. ^{13}C NMR ([D$_4$]MeOH): δ = 37.19 (N-CH$_3$), 53.47 (Ar-CH$_2$-Im), 124.14, 125.63 (Im-C), 138.67 (N-CH-N), 131.29, 137.85 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3470 (s), 3077 (s), 3055 (s), 3008 (s) (NR_4^+), 2856 (s) (C–H), 1573 (m), 1556 (m) (C=C), 1446 (m), 1373 (m) (C–H), 1157 (s), 621 (m) cm^{-1}. $C_{21}H_{27}Br_3N_6$ (603.13): calcd. C 41.82, H 4.51, N 13.93; found C 39.92, H 4.73, N 12.92.

1,3,5-Tris[(3-methylimidazol-3-iumyl)methyl]-2,4,6-trimethylbenzene Tribromide (2a): Yield: 2.63 g (4.08 mmol, 81%). M.p. 286 °C. ^{1}H NMR ([D$_4$]MeOH): δ = 2.43 (s, 9 H, Ar-CH$_3$), 4.01 (s, 9 H, N-CH$_3$), 5.66 (s, 6 H, Ar-CH$_2$-Im), 7.66 (t, J = 1.7 Hz, 3 H, Im-H), 7.77 (t, J = 1.8 Hz, 3 H, Im-H), 9.14 (s, 3 H, N-CH-N) ppm. ^{13}C NMR ([D$_4$]MeOH): δ = 17.27 (Ar-CH$_3$), 37.22 (N-CH$_3$), 49.87 (Ar-CH$_2$-Im), 124.04, 125.69 (Im-C), 137.91 (N-CH-N), 130.97, 143.54 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3449 (s), 3342 (s), 3100 (s), 3067 (s) (NR_4^+), 1573 (s) (C=C), 1453 (m), 1334 (m) (C–H), 1160 (s), 620 (s) cm^{-1}. MS (MALDI-TOF; DHB): calcd. for $C_{24}H_{33}N_6Br_2^+$ 563.1; found 563.3 [M – Br]$^+$. $C_{24}H_{33}Br_3N_6 \cdot 2H_2O$ (681.30): calcd. C 42.31, H 5.47, N 12.33; found C 42.25, H 5.36, N 12.33.

1,3-Bis[(3-methylimidazol-3-iumyl)methyl]-2,4,6-triethylbenzene Dibromide (1a): Yield: 3.20 g (6.25 mmol, 72%) from 1,3-bis(bromomethyl)-2,4,6-triethylbenzene (3.00 g, 8.63 mmol) and 1-methylimidazole (1.53 mL, 19.2 mmol) in $CHCl_3$ (80 mL). M.p. >70 °C (decomp.). ^{1}H NMR ([D$_4$]MeOH): δ = 1.08 (t, J = 7.5 Hz, 3 H, CH$_2$-CH$_3$), 1.24 (t, J = 7.5 Hz, 6 H, CH$_2$-CH$_3$), 2.73 (q, J = 7.5 Hz, 4 H, CH$_2$-CH$_3$), 2.80 (q, J = 7.6 Hz, 2 H, CH$_2$-CH$_3$), 3.98 (s, 6 H, N-CH$_3$), 5.59 (s, 4 H, Ar-CH$_2$), 7.36 (s, 1 H, Ar-H), 7.61 (t, J = 1.9 Hz, 2 H, Im-H), 7.65 (t, J = 1.8 Hz, 2 H, Im-H), 8.88 (s, 2 H, N-CH-N) ppm. ^{13}C NMR ([D$_4$]MeOH): δ = 15.90 (CH$_2$-CH$_3$), 16.57 (CH$_2$-CH$_3$), 24.58 (CH$_2$-CH$_3$), 27.42 (CH$_2$-CH$_3$), 37.12 (N-CH$_3$), 48.38 (Ar-CH$_2$-Im) 123.86, 125.62 (Im-C), 137.80 (N-CH-N), 128.11, 130.60, 146.84, 148.86 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3431 (s), 3070 (s), 2971 (s) (NR_4^+), 1570 (m) (C=C), 1465 (m), 1332 (m) (C–H), 1157 (s), 620 (m) cm^{-1}. MS (MALDI-TOF): calcd. for

$C_{22}H_{33}N_4Br_2^+$ 515.1; found 515 [M + H]$^+$. $C_{22}H_{32}Br_2N_4$ (512.32): calcd. C 51.58, H 6.30, N 10.94; found C 47.80, H 6.17, N 10.53.

5,11,17,23-Tetrakis[(3-methylimidazol-3-iumyl)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Tetrachloride (4a): Yield: 1.17 g (1.05 mmol, 83%). M.p. 194 °C. ^{1}H NMR ([D$_4$]MeOH): δ = 1.06 (t, J = 7.3 Hz, 12 H, CH$_2$-CH_3), 1.98 (m, 8 H, CH_2-CH$_3$), 3.31 (d, J = 12.9 Hz, 4 H, Ar-CH$_2^{eq.}$-Ar), 3.92 (t, J = 7.5 Hz, 8 H, O-CH$_2$), 3.99 (s, 12 H, N-CH$_3$), 4.52 (d, J = 12.9 Hz, 4 H, Ar-CH$_2^{ax.}$-Ar), 5.25 (s, 8 H, Ar-CH$_2$-Im), 6.94 (s, 8 H, Ar-H), 7.57 (s, 3 H, Im-H), 7.63 (s, 4 H, Im-H), 9.14 (s, 3 H, N-CH-N) ppm. ^{13}C NMR ([D$_4$]MeOH): δ = 11.00 (CH$_2$-CH$_3$), 24.69 (CH$_2$-CH$_3$), 31.92 (Ar-CH$_2$-Ar), 36.91 (N-CH$_3$), 54.22 (Ar-CH$_2$-Im), 78.53 (O-CH$_2$), 123.72, 125.33 (Im-C), 138.01 (N-CH-N), 129.23, 130.74, 137.43, 158.91 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3412 (s), 3142 (m), 3073 (m) (Ar-H), 2961 (s), 2929 (s), 2873 (s) (C–H), 1627 (m) (-C=N-), 1569 (m) (C=C), 1465 (m), 1384 (w), 1357 (w), 1288 (w) (C–H), 1225 (m), 1163 (s), 1067 (w), 1040 (w), 1008 (m) (Ar-O–C), 756 (m) (Ar-H) cm^{-1}. MS (pos. FAB): calcd. for $C_{60}H_{76}N_8O_4Cl_4 - Cl^+$ 1079.7; found 1079.6 [M – Cl]$^+$. $C_{60}H_{76}Cl_4N_8O_4{\cdot}4.5H_2O$ (1196.19): calcd. C 60.25, H 7.16, N 9.37; found C 60.39, H 7.52, N 9.22.

5,17-Bis[(3-methylimidazol-3-iumyl)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Dichloride (5a): Yield: 530 mg (0.62 mmol, 40%). M.p. >280 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, J = 7.6 Hz, 6 H, CH$_2$-CH_3), 1.09 (t, J = 7.3 Hz, 6 H, CH$_2$-CH_3), 1.93 (m, 8 H, CH_2-CH$_3$), 3.17 (d, J = 13.4 Hz, 4 H, Ar-CH$_2^{eq.}$-Ar), 3.69 (t, J = 6.8 Hz, 4 H, O-CH$_2$), 4.00 (m, 10 H, O-CH$_2$ and N-CH$_3$), 4.45 (d, J = 13.1 Hz, 4 H, Ar-CH$_2^{ax.}$-Ar), 4.95 (s, 4 H, Ar-CH$_2$-Im), 6.29 (s, 4 H, Ar-H), 6.71 (s, 2 H, Im-H), 6.91 (t, J = 7.5 Hz, 2 H, Ar-H), 7.10 (d, J = 7.3 Hz, 4 H, Ar-H), 7.84 (s, 2 H, Im-H), 10.27 (s, 2 H, N-CH-N) ppm. ^{13}C NMR ($CDCl_3$): δ = 9.65, 10.54 (CH$_2$-CH$_3$), 22.74, 23.29 (CH$_2$-CH$_3$), 30.68 (Ar-CH$_2$-Ar), 36.35 (N-CH$_3$), 52.75 (Ar-CH$_2$-Im), 76.39, 77.23 (O-CH$_2$), 120.84, 123.79 (Im-C), 136.81 (N-CH-N), 122.61, 125.30, 128.33, 129.05, 134.96, 135.98, 156.49, 157.09 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3410 (s) (NR$_4^+$), 3071 (m) (Ar-H), 2961 (s), 2933 (s), 2873 (s) (C–H), 1606 (m), 1572 (m) (C=C), 1464 (s), 1434 (m), 1384 (m), 1354 (m), 1304 (m), 1281 (m) (C–H), 1257 (m), 1217 (s), 1162 (s), 1129 (m), 1082 (m), 1039 (m) (Ar-O–C), 890 (m), 836 (w), 777 (m), 755 (m) (Ar-H) cm^{-1}. MS: (MALDI-TOF, DHB): calcd. for $C_{50}H_{62}O_4N_4Cl^+$ 817.4; found 817.4 [M – Cl]$^+$. $C_{50}H_{62}Cl_2N_4O_4{\cdot}2.2H_2O$ (893.60): C 67.21, H 7.49, N 6.27; found C 67.21, H 7.55, N 6.13.

General Procedure for Anion Exchange: A saturated solution of NH_4PF_6 (3 mL) was added dropwise to a solution of the chloride or bromide salts **1a**–**5a** (1.00 mmol) in water (3 mL). A light-brown solid precipitated which was separated by filtration and dried in vacuo.

1,3,5-Tris[(3-methylimidazol-3-iumyl)methyl]benzene Tris(hexafluorophosphate) (1b): Yield: 670 mg (0.84 mmol, 84%). M.p. 165 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 3.85 (s, 9 H, N-CH$_3$), 5.39 (s, 6 H, Ar-CH$_2$-Im), 7.41, (s, 3 H, Ar-H), 7.64 (s, 3 H, Im-H), 7.67 (s, 3 H, Im-H), 9.08 (s, 3 H, N-CH-N) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 36.09 (N-CH$_3$), 51.58 (Ar-CH$_2$-Im), 122.48, 124.27 (Im-C), 136.91 (N-CH-N), 128.76, 136.38 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3182 (w) (NR$_4^+$), 2923 (w), 2853 (w) (C–H), 1585 (m) (C=C), 1448 (m), 1429 (m) (C–H), 1159 (m), 828 (s), 556 (s) cm^{-1}. MS (MALDI-TOF; DHB): calcd. for $C_{21}H_{27}N_6F_{12}P_2^+$ 653.2; found 653.1 [M – PF$_6$]$^+$.

1,3,5-Tris[(3-methylimidazol-3-iumyl)methyl]-2,4,6-trimethylbenzene Tris(hexafluorophosphate) (2b): Yield: 970 mg (1.15 mmol, 74%). M.p. 280 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.31 (s, 9 H, CH$_3$), 3.82 (s, 9 H, N-CH$_3$), 5.54 (s, 6 H, Ar-CH$_2$-Im), 7.61, (s, 3 H, Im-H), 7.72 (s, 3 H, Im-H), 8.76 (s, 3 H, N-CH-N) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 16.33 (CH$_3$), 36.05 (N-CH$_3$), 47.79 (Ar-CH$_2$-Im), 122.28, 124.00 (Im-C), 136.91 (N-CH-N), 129.55, 141.25 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3165 (w) (NR$_4^+$), 1575 (w) (C=C), 1486 (w), 1333 (w), 1159 (m), 833 (s), 558 (s) cm^{-1}. MS (MALDI-TOF; DHB): calcd. for $C_{24}H_{33}N_6F_{12}P_2^+$ 695.2; found 695.2 [M – PF$_6$]$^+$.

1,3-Bis[(3-methylimidazol-3-iumyl)methyl]-2,4,6-triethylbenzene Bis(hexafluorophosphate) (3b): Yield: 510 mg (0.79 mmol, 81%). M.p. >193 °C (decomp.). ^{1}H NMR ([D$_6$]DMSO): δ = 0.91 (t, J = 7.2 Hz, 3 H, CH$_2$-CH$_3$) 1.10 (t, J = 7.2 Hz, 6 H, CH$_2$-CH$_3$), 2.61 (q, J = 7.3 Hz, 6 H, CH$_2$-CH$_3$), 3.82 (s, 6 H, N-CH$_3$), 5.43 (s, 4 H, Ar-CH$_2$), 7.24 (s, 1 H, Ar-H), 7.61 (t, J = 1.9 Hz, 2 H, Im-H), 7.69 (t, J = 1.8 Hz, 2 H, Im-H), 8.79 (s, 2 H, N-CH-N) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 15.17 (CH$_2$-CH$_3$), 16.08 (CH$_2$-CH$_3$), 22.82 (CH$_2$-CH$_3$), 25.58 (CH$_2$-CH$_3$), 36.07 (N-CH$_3$), 122.46, 123.99 (Im-C), 136.21 (N-CH-N), 126.99, 128.43, 145.05, 146.36 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3396 (m), 3177 (m), 2976 (m) (NR$_4^+$), 1576 (m) (C=C), 1428 (m) (C–H), 1160 (m), 834 (s) (Ar-H), 558 (s) cm^{-1}. MS (MALDI-TOF; DHB): calcd. for $C_{22}H_{32}N_4F_6P^+$ 499.2; found 499.5 [M – PF$_6$]$^+$.

5,11,17,23-Tetrakis[(3-methylimidazol-3-iumyl)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Tetrakis(hexafluorophosphate) (4b): Yield: 640 mg (0.41 mmol, 82%). M.p. >200 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 0.96 (t, J = 7.5 Hz, 12 H, CH$_2$-CH$_3$), 1.87 (m, 8 H, CH$_2$-CH$_3$), 3.22 (d, J = 13.4 Hz, 4 H, Ar-CH$_2^{eq.}$-Ar), 3.81 (t, J = 7.3 Hz, 8 H, O-CH$_2$), 3.86 (s, 12 H, N-CH$_3$), 4.41 (d, J = 13.3 Hz, 4 H, Ar-CH$_2^{ax.}$-Ar), 5.03 (s, 8 H, Ar-CH$_2$-Im), 6.80 (s, 8 H, Ar-H), 7.47 (s, 4 H, Im-H), 7.69 (s, 4 H, Im-H), 9.03 (s, 4 H, N-CH-N) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 10.24 (CH$_2$-CH$_3$), 22.90 (CH$_2$-CH$_3$), 30.31 (Ar-CH$_2$-Ar), 36.06 (N-CH$_3$), 52.12 (Ar-CH$_2$-Im), 76.74 (O-CH$_2$), 122.00, 124.15 (Im-C), 136.35 (N-CH-N), 127.89, 128.93, 135.30, 156.86 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3334 (m), 3172 (m) (NR$_4^+$), 2966 (m), 2934 (m), 2878 (m) (C–H), 1577 (m) (C=C), 1462 (m), 1389 (w), 1358 (w), 1290 (m) (C–H), 1228 (m), 1166 (m), 1109 (w), 1067 (w), 1039 (w) (Ar-O–C), 834 (s) (Ar-H), 558 (s) cm^{-1}. MS (MALDI-TOF; DHB): calcd. for $C_{60}H_{76}O_4N_8P_3F_{18}^+$ 1407.5; found 1407.4 [M – PF$_6$]$^+$.

5,17-Bis[(3-methylimidazol-3-iumyl)methyl]-25,26,27,28-tetrapropoxycalix[4]arene Bis(hexafluorophosphate) (5b): Yield: 420 mg (0.39 mmol, 93%). M.p. 210 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 0.89 (t, J = 7.5 Hz, 6 H, CH$_2$-CH$_3$), 1.03 (t, J = 7.5 Hz, 6 H, CH$_2$-CH$_3$), 1.86 (m, 8 H, CH$_2$-CH$_3$), 3.17 (d, J = 13.4 Hz, 4 H, Ar-CH$_2^{eq.}$-Ar), 3.66 (t, J = 6.8 Hz, 4 H, O-CH$_2$), 3.86 (s, 6 H, N-CH$_3$), 3.91 (t, J = 7.7 Hz, 4 H, O-CH$_2$), 4.34 (d, J = 13.1 Hz, 4 H, Ar-CH$_2^{ax.}$-Ar), 5.25 (s, 4 H, Ar-CH$_2$-Im), 6.33 (m, 6 H, Ar-H and Im-H), 7.06 (m, 6 H, Ar-H), 7.71 (s, 2 H, Im-H), 9.16 (s, 2 H, N-CH-N) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 10.07, 10.73 (CH$_2$-CH$_3$), 22.93, 23.17 (CH$_2$-CH$_3$), 30.40 (Ar-CH$_2$-Ar), 36.11 (N-CH$_3$), 52.08 (Ar-CH$_2$-Im), 76.45, 76.93 (O-CH$_2$), 122.36, 124.19 (Im-C), 136.62 (N-CH-N), 122.19, 127.90, 128.19, 128.93, 133.40, 136.57, 155.55, 157.54 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3336 (m), 3169 (m) (NR$_4^+$), 2966 (m), 2935 (m), 2877 (m) (C–H), 1579 (m) (C=C), 1462 (m), 1388 (w), 1284 (w) (C–H), 1224 (m), 1166 (m), 1134 (w), 1108 (w), 1084 (w), 1040 (w) (Ar-O–C), 834 (s) (Ar-H), 558 (s) cm^{-1}. MS (MALDI-TOF; DHB): calcd. for $C_{50}H_{62}O_4N_4PF_6^+$ 927.4; found 927.4 [M – PF$_6$]$^+$.

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