



1,2-Bis[*N*-(*N'*-alkylimidazolium)]ethane salts as new guests for crown ethers and cryptands

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ABSTRACT

1,2-Bis[*N*-(*N'*-alkylimidazolium)]ethane salts form complexes presumed to be pseudorotaxanes with crown ether and cryptand hosts. The association constants of 1,2-bis[*N*-(*N'*-butylimidazolium)]ethane bis(hexafluorophosphate) with dibenzo-24-crown-8 and a dibenzo-24-crown-8-based pyridyl cryptand were estimated as $24 (\pm 1)$ and $348 (\pm 30) \text{ M}^{-1}$, respectively, in acetonitrile at 25 °C. The pseudorotaxane-like structure of the 1:2 complex of the *N'*-methyl analog with the cryptand was observed by X-ray crystallography. Replacement of the ethylene spacer with propylene and butylene spacers resulted in K_a values an order of magnitude smaller.

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1. Introduction

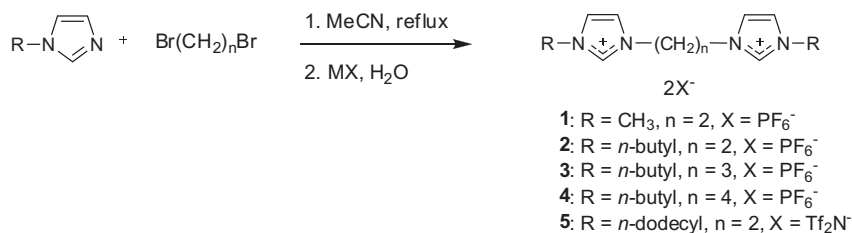
Imidazolium salts have been and are going to be significant not only in organometallic chemistry as precursors of *N*-heterocyclic carbenes,¹ but also in organic chemistry and material science areas as ionic liquids due to their unique chemical, physical, and electrical properties.² For 1,3-disubstituted imidazolium ionic liquid salts, all of the protons on the imidazolium ring are quite acidic; for example, the $\text{p}K_a$ of the C2 proton is 16–24, depending on the nature of the substituents on the two imidazolium nitrogens.³ The acidic protons are attractive in supramolecular chemistry, since more acidic protons provide stronger hydrogen bonds in the formation of supramolecular complexes, such as pseudorotaxanes.⁴ 1-Alkyl-3-methylimidazolium bromides bind with cucurbit[6]uril; the binding constant depends on the number of carbons in the alkyl chain.⁵ Schmitzer et al. reported that *N,N'*-disubstituted (benzyl or phenyl) methylene diimidazolium salts also act as guest molecules for various macrocycles with high association constants ($K_a=4200\text{--}7500 \text{ M}^{-1}$) in water: β -cyclodextrin, cucurbit[7]uril, and tetrapropoxycalix[4]arene.⁶ However, they reported lower K_a values (56 and 120 M^{-1}) for methylene bis[*N*-(*N'*-benzylimidazolium)] and methylene bis[*N*-(*N'*-phenylimidazolium)] bis(hexafluorophosphate)s with dibenzo-24-crown-8 (DB24C8) in CD_3CN .

There is a need for structural diversity in supramolecular building blocks; discovery of new pseudorotaxane systems drives new supramolecular structures and applications. On another front, for application of imidazolium salts and other ionic liquids in electroactive actuators, ion conductivity is a key parameter.⁷ In earlier work we demonstrated that pseudorotaxane complexes of dibenzylammonium salts with DB24C8^{8,9} and its derivatives¹⁰ are not ion paired. Similarly, we reported that the pseudorotaxane complex of *N,N'*-dimethyl-4,4'-bipyridinium ('paraquat' or 'dimethyl viologen') 2PF_6^- with DB24C8 likewise is not ion paired;^{9,11} this was subsequently corroborated by other workers.¹² It therefore appeared to us that pseudorotaxanes derived from DB24C8 and imidazolium ionic liquids would possess a larger fraction of 'free' ions than the ionic liquids themselves and thus possess enhanced performance in electroactive bending actuators. Driven by these two separate but related goals, here we report new ionic guests, alkylene 1,2-bis[*N*-(*N'*-alkylimidazolium)] salts with different alkyl substituents, and their complexation with crown-type host molecules. We also investigated the effect of C_2 , C_3 , and C_4 spacers on their complexation with DB24C8.

2. Results and discussion

The preparations of the imidazolium dicationic salts **1–5** were done in two steps (Scheme 1): the coupling reaction of the 1-alkylimidazole (2 M equiv) with a dibromoalkane (1 M equiv) and anion exchange in water. Non-commercial 1-hexylimidazole and 1-dodecylimidazole were prepared before quaternization.¹³ Most of the

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Scheme 1.

intermediate alkylene bis[*N*-(*N'*-alkylimidazolium)] bromide salts were very hygroscopic; however, the imidazolium salts of PF₆⁻ and Tf₂N⁻ salts were non-hygroscopic due to their hydrophobic anions.

The complexation of **2** and DB24C8 was qualitatively observed by ¹H NMR in CD₃CN. After adding excess DB24C8 to a solution of **2** in CD₃CN at 25 °C, the imidazolium protons moved upfield. This system undergoes fast-exchange; only time-averaged signals appear in the ¹H NMR spectrum (Fig. 1). The fast-exchange in this complexation (Fig. 2) is reasonable due to the rod-like geometry of **2**, which in solution probably has a trans-conformation predominantly, consistent with the solid-state structure of **1** (Fig. 3). The fast exchange behavior exhibited by these systems is in contrast to the slow exchange reported for the methylene bridged bis(imidazolium) salts.⁶

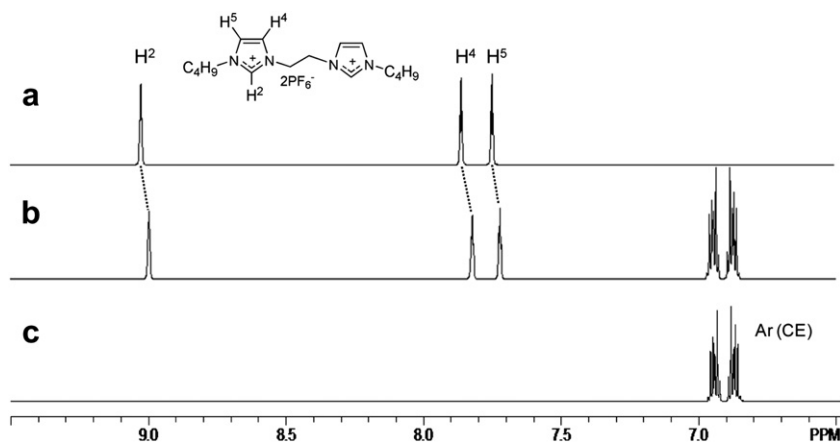


Figure 1. Partial 400 MHz ¹H NMR spectra of (a) **2** (2 mM), (b) **2**+DB24C8 (1:5 M ratio, 2 mM of **2**), and (c) DB24C8 (10 mM) in CD₃CN at 25 °C.

Isothermal microcalorimetric titration (ITC) was used to quantify the complexations of the host and guest compounds in solution. The results are summarized in Table 1.¹⁴ All experiments were performed under ambient conditions at 25 °C. The association constants and enthalpies of *N,N'*-dimethyl ethylene linked **1** and *N,N'*-dibutyl ethylene linked **2** with DB24C8 in MeCN are similar to each other and slightly lower than the *K*_a (56 M⁻¹) of bis[*N*-(*N'*-benzylimidazolium)]methane 2PF₆⁻ with DB24C8 determined by Schmitzer et al.

Table 1
ITC results: complexation of imidazolium salts by DB24C8 and Cryptand **6**

Imidazolium Salt	Macrocycle	Solvent	<i>K</i> _a (M ⁻¹)	Δ <i>H</i> (kcal/mol)	–Δ <i>S</i> (cal/mol deg)
1	DB24C8	MeCN ^a	27±3	–2.7±0.3	2.3±1.1
2	DB24C8	MeCN ^a	24±1	–2.5±0.1	2.0±0.3
3	DB24C8	MeCN ^a	4.3±0.8	–2.4±0.3	5.2±1.4
4	DB24C8	MeCN ^a	2.2±0.7	–2.5±0.4	6.8±2.0
5	DB24C8	CHCl ₃ ^a	30±1	–6.7±0.1	16±1
2	6	MeCN	348±30 ^b	–8.0±0.2	15±1

^a All of the complexes are of 1:1 stoichiometry; other assumed stoichiometries resulted in poorer fits.

^b For 1:1 assumed stoichiometry. 2:1H:G stoichiometry yielded: *K*_a=166±8; Δ*H*=18.1 kcal/mol; Δ*S*=–50 cal/mol deg.

using a single point NMR integration,⁶ which could be subject to significant error.^{8–11} The two imidazolium rings of methylene bis(imidazolium) salts cannot be parallel due to the tetrahedral geometry of the methylene spacer. In the case of the two-carbon spacer the trans-conformation of the ethylene unit is preferred (at room temperature, Fig. 3). The previously reported interactions of dicationic guests, bis(pyridinium)ethane¹⁵ and bis(benzimidazolium) ethane salts,¹⁶ with DB24C8, are also good examples to support this hypothesis. We predicted that the two imidazolium rings of **2** would be parallel and individually interact with the π-electron rich aromatic rings of DB24C8, leading to π-stacking interactions and higher *K*_a values. Contrary to our expectations based on these conformational, i.e., entropic arguments, the observed higher *K*_a values for the methylene⁶ versus the ethylene spacer can be attributed to the

higher acidity of the methylene protons as a result of the two neighboring positively charged nitrogen atoms (Fig. 2).

The *K*_a values for complexations of **3** (C₃ spacer) and **4** (C₄ spacer) with DB24C8 are an order of magnitude smaller than those of the analogous compound with a C₂ spacer (**2**). From a molecular structural viewpoint, three and four carbons between the imidazolium moieties make it less likely that both can interact with the aromatic rings of DB24C8. The spatial requirements for formation of hydrogen bonds are also less likely to be met when the two imidazolium rings are far from each other. Furthermore, only the protons of the methylene units attached to the positively charged nitrogen atoms are acidic enough to form hydrogen bonds with the crown ether oxygens; additional carbons in the spacer only increase the number of unfavorable binding conformations. Indeed the results support this analysis. The enthalpic changes for complexes of DB24C8 with **2**, **3**, and **4** are identical within experimental error; the order of magnitude decreases in *K*_a from the two carbon spacer to the four carbon spacer are entirely due to the increased entropic penalty for complexation, –2.0 to –5.2 to –6.8 eu, respectively.

The imidazolium salt **5** with *n*-dodecyl arms was synthesized to observe the complexation in a less polar solvent. However, the *K*_a of

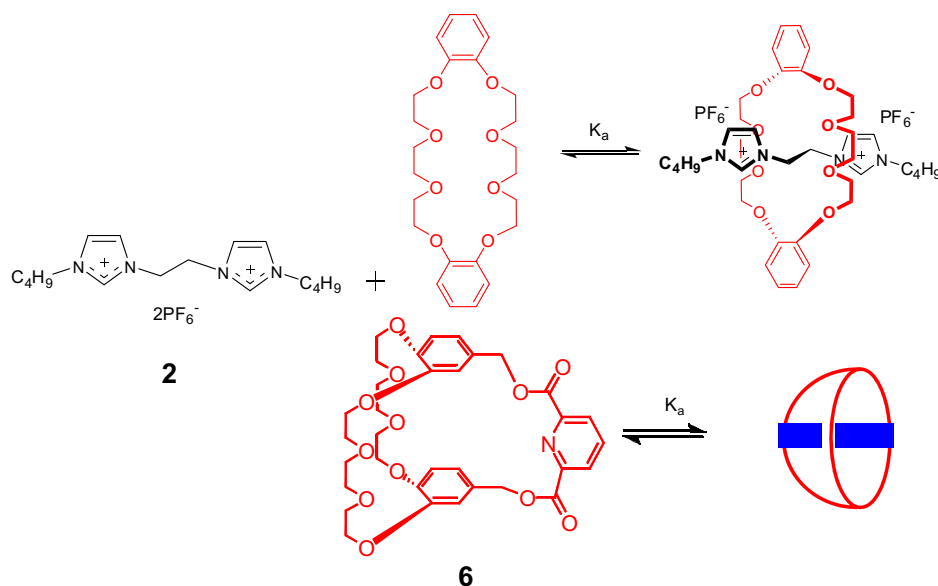


Figure 2. Schematic diagram of complexation of **2** with DB24C8 and DB24C8-based pyridyl cryptand **6**.¹¹

5 and DB24C8 in CHCl_3 at room temperature was almost the same as the K_a of the analogous methyl analog **1** in acetonitrile. Apparently the longer terminal chains are detrimental and offset the lower polarity of the solvent. This is reflected by the fact that the enthalpy of complexation of **5** with DB24C8 is actually 2.5 times more exothermic than that of **1**, as a result of the lower polarity solvent, but **5** suffers a seven-fold larger entropic penalty, apparently due to the long alkyl side chains.

Complexation of *N*-butyl compound **2** with the DB24C8-based pyridyl cryptand **6**¹¹ was also observed by ITC. Its K_a is >10 times higher and the exothermic enthalpy change is 3.2-fold larger than the binding of **2** with DB24C8. In spite of the sizeable entropic penalty (–15 eu), the larger K_a and enthalpy change are due to the presence of more binding sites on the cryptand. We tried to investigate the stoichiometry of the complex of **2** and **6** by ¹H NMR in CD_3CN ; however, to our surprise the chemical shift changes were within experimental error across a range of ratios with a total concentration of 2.2 mM.¹⁷

The formation of these complexes was also confirmed by high resolution ESI TOF mass spectrometry (see Supplementary data). A solution of **1** and DB24C8 yielded m/z 785.3108, which corresponds to the 1:1 complex after loss of one PF_6^- ion ($[\mathbf{1}+\text{DB24C8}-\text{PF}_6]^+$, calcd for $\text{C}_{34}\text{H}_{48}\text{N}_4\text{O}_8\text{PF}_6$ 785.3114). A solution of **2** and DB24C8 yielded m/z 869.4050, after loss of one PF_6^-

ion from the 1:1 complex ($[\mathbf{2}+\text{DB24C8}-\text{PF}_6]^+$, calcd for $\text{C}_{40}\text{H}_{60}\text{N}_4\text{O}_8\text{PF}_6$ 869.4062). A solution of **5** and DB24C8 gave m/z 1228.5961, corresponding to the 1:1 complex after loss of one TF_2N^- anion ($[\mathbf{5}+\text{DB24C8}-\text{TF}_2\text{N}]^+$, calcd for $\text{C}_{58}\text{H}_{92}\text{F}_6\text{N}_5\text{O}_{12}\text{S}_2$

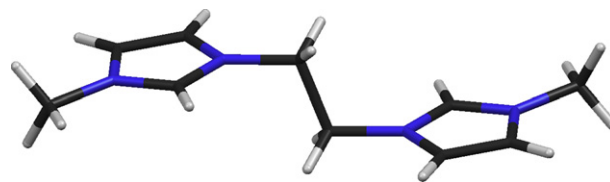


Figure 3. A capped-sticks view of the X-ray structure of **1**. PF_6^- anions are omitted for clarity. Ring plane/ring plane inclination of the two imidazolium rings: 0° .

1228.6082). Solutions of cryptand **6** and the imidazolium salts also gave mass numbers corresponding to the 1:1 complexes: m/z 976.3349 ($[\mathbf{1}+\mathbf{6}-\text{PF}_6]^+$, calcd for $\text{C}_{43}\text{H}_{53}\text{N}_5\text{O}_{12}\text{PF}_6$ 976.3333), and m/z 1060.4311 ($[\mathbf{2}+\mathbf{6}-\text{PF}_6]^+$, calcd for $\text{C}_{49}\text{H}_{65}\text{N}_5\text{O}_{12}\text{PF}_6$ 1060.4281). Every host-guest solution revealed only 1:1 host/guest complex peaks, even with an excess of the host.

A crystal structure of $\mathbf{1}\cdot(\mathbf{6})_2$ (Fig. 4) shows that the pseudo-rotaxane-like structure^{18–20} in the solid state was formed from one guest **1** and two hosts **6**. This observation of different

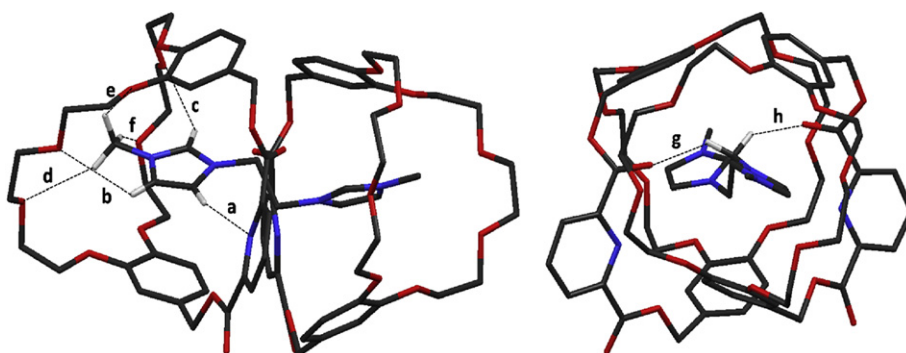
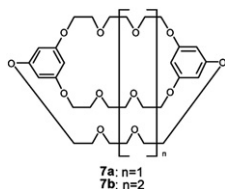


Figure 4. Two capped-sticks views of the X-ray structure of $\mathbf{1}\cdot(\mathbf{6})_2$: side view (left) and end view (right). There are two complexes in the unit cell and they are similar but not identical. These views are one of the complexes. PF_6^- anions, MeCN molecules and some hydrogens are omitted for clarity. One PF_6^- anion is disordered. H···O (or N) distances (Å), C–H···O (or N) angles (degrees) of: (a) 2.60, 165.4; (b) 2.89, 126; (c) 2.64, 138; d) 2.71, 155; (e) 2.68, 122; (f) 2.79, 166; (g) 2.30, 135; (h) 2.23, 145.

stoichiometries in solution and the solid state is consistent with several other crown ether and cryptand complexes: both cryptands **7a** and **7b** with paraquat,²⁰ DB24C8 with paraquat,¹¹ bis(*p*-xylyl)-26-crown-8 with paraquat,²¹ DB24C8 with *N,N'*-dialkyl paraquats,²² and DB24C8 with 'diquat' (*N,N'*-ethylene-2,2'-bipyridinium 2PF₆).²³



The structure of guest **1** in the present complex (Fig. 4) is somewhat different from the crystal structure of **1** itself (Fig. 3); the imidazolium planes are twisted at a 44° angle, to accommodate the π - π stacking with the aromatic rings of **6**. Centroid to centroid distances of the phenylene and imidazolium rings are 3.6–3.9 Å and dihedral angles of the phenylene and imidazolium planes are 12–23°. The catechol rings of different host molecules in the 1:2 complex are significantly tilted, which causes the twisted imidazolium rings. All of the hydrogens of **1** are hydrogen-bonded with oxygen atoms (or the nitrogen atom) of **6**. One of the imidazolium hydrogens interacts with the nitrogen atom and the other two bind with oxygens in the ethyleneoxy arms. Interestingly ester carbonyl oxygens seem to strongly interact with the ethylene protons of **1**; the H...O distances are 2.23 and 2.30 Å (g and h in Fig. 4).

In summary, the complexation of alkylene 1,2-bis[*N*-(*N'*-alkylimidazolium)] salts with DB24C8 was confirmed by ¹H NMR spectroscopy, mass spectrometry and ITC titrations. The association constants for pseudorotaxane (or pseudorotaxane-like complex) formation from the 1,2-bis[*N*-(*N'*-alkylimidazolium)]ethanes with DB24C8 in solution are $K_a=24$ to 30 M^{-1} in MeCN or CHCl₃ and $K_a=348\text{ M}^{-1}$ in MeCN for **2** with cryptand **6**. However, alkylene bis[*N*-(*N'*-alkylimidazolium)] salts with a C₃ or C₄ spacer show weaker binding with DB24C8. The host/guest threaded structure was confirmed by the X-ray crystal structure of the 1:2 complex of **1** and **6**; every proton of the guest molecule participates in hydrogen bonding with oxygen or nitrogen atoms of the cryptand **6**. These readily accessible imidazolium salts are expected to be valuable in the construction of larger supramolecular systems, such as polypseudorotaxanes,²⁴ and in construction of pseudorotaxane or rotaxane actuators based on ionic liquids and polyelectrolytes. Our results in these areas will be published in due course.

3. Experimental section

3.1. General comments

3.1.1. Materials. Dibenzo-24-crown-8 was purchased from Aldrich Chem. Co., Inc. and used as received. Acetone for the quaternization reactions was dried with anhydrous CaSO₄ and then distilled. Acetonitrile was dried with anhydrous K₂CO₃ and then distilled. All other chemicals and solvents were used as received.

Instruments. ¹H and ¹³C NMR spectra were obtained on Varian Inova 400 MHz and Unity 400 MHz spectrometers. High resolution electrospray ionization time-of-flight mass spectrometry (HR ESI TOF MS) was carried out on an Agilent 6220 Accurate Mass TOF LC/MS Spectrometer in positive ion mode. Melting points were observed on a Büchi B-540 apparatus at a 2 °C/min heating rate. ITC titrations were run on a Microcal MCS ITC. Raw isotherm data were collected using the Microcal Observer software. Integration and fitting of the isothermal data (K_a and ΔH) were accomplished using Origin software with a one set of sites algorithm.

3.2. General anion exchange procedure

Into a solution of bromide salt (1 equiv) in deionized water, KPF₆ (or LiTf₂N, 2–4 equiv) was added with stirring, which continued for 1–2 h at room temperature. The precipitate was filtered and washed with deionized water twice. Drying in a vacuum oven gave the pure imidazolium PF₆⁻ (or Tf₂N⁻) salt.

3.3. Synthetic procedures or alkylene bis-(*N*-alkylimidazolium) salts

3.3.1. 1,2-Bis[*N*-(*N'*-methylimidazolium)]ethane bis(hexafluorophosphate) (1**).** A solution of 1-methylimidazole (2.49 g, 30 mmol) and 1,2-dibromoethane (2.82 g, 15 mmol) in MeCN (20 mL) was refluxed for 3 days. The precipitate was filtered after cooling, and washed with tetrahydrofuran (THF) three times. Drying in a vacuum oven gave the colorless crystalline bromide salt (4.54 g, 86%), mp 231.1–233.8 °C (lit. mp 230–234 °C).²⁵ Compound **1** was obtained by following the general anion exchange procedure; from bromide salt (4.50 g), KPF₆ (5.52 g, 30 mmol), and deionized water (40 mL) colorless crystalline solid **1** (5.26 g, 73% based on 1,2-dibromoethane), mp 213.8–214.9 °C, was isolated. ¹H NMR (400 MHz, CD₃CN 23 °C): δ 3.85 (s, 6H), 4.62 (s, 4H), 7.33 (t, $J=2$, 2H), 7.42 (t, $J=2$, 2H), 8.40 (s, 2H). ¹³C NMR (100 MHz, CD₃CN, 23 °C): δ 37.2, 49.7, 123.5, 125.6, 137.6. HRMS (ESI): [M–PF₆]⁺, found 337.1022. C₁₀H₁₆N₄PF₆ requires 337.1017.

3.3.2. 1,2-Bis[*N*-(*N'*-butylimidazolium)]ethane bis(hexafluorophosphate) (2**).** The same procedure was used as for **1**. From 1-butylimidazole (6.21 g, 50 mmol) and 1,2-dibromoethane (4.69 g, 25 mmol) in MeCN (25 mL) colorless crystalline bromide salt (9.64 g, 88%), mp 166.5–168.2 °C, was produced. The general anion exchange procedure was used; from the bromide salt (1.30 g, 3.0 mmol) and KPF₆ (1.65 g, 9 mmol) in deionized water (10 mL) colorless crystalline **2** (1.54 g, 91%), mp 181.6–182.5 °C, was isolated. ¹H NMR (400 MHz, acetone-*d*₆ 23 °C): δ 0.94 (t, $J=7$, 6H), 1.33 (m, 4H), 1.78–1.85 (m, 4H), 4.14 (m, 4H), 5.04 (s, 4H), 7.39 (m, 4H), 8.42 (s, 2H). ¹³C NMR (100 MHz, acetone-*d*₆, 23 °C): δ 13.5, 19.8, 32.4, 49.9, 50.6, 123.6, 124.2, 137.5. HRMS (ESI): [M–PF₆]⁺, found 421.1966. C₁₆H₂₈N₄PF₆ requires 421.1950.

3.3.3. 1,3-Bis[*N*-(*N'*-butylimidazolium)]propane bis(hexafluorophosphate) (3**).** The same procedure was used as for **1**, except the bromide salt could not be filtered because it was a viscous oil. From 1-butylimidazole (3.73 g, 30 mmol) and 1,3-dibromopropane (3.03 g, 15 mmol) in MeCN (20 mL), a light brown viscous liquid (bromide salt, 5.81 g, 86%) was isolated. The general anion exchange procedure was used; from the oily bromide salt (5.00 g, 11.1 mmol) and KPF₆ (6.20 g, 33 mmol) in deionized water (40 mL) colorless crystalline solid **3** (6.25 g, 97% from the bromide salt), mp 96.4–97.7 °C, resulted. ¹H NMR (400 MHz, acetone-*d*₆, 23 °C): δ 0.94 (t, $J=7$, 6H), 1.38 (m, 4H), 1.94 (m, 4H), 2.74 (m, 2H), 4.36 (t, $J=7$, 4H), 4.55 (t, $J=7$, 2H), 7.81 (m, 4H), 9.12 (s, 2H). ¹³C NMR (100 MHz, acetone-*d*₆, 23 °C): δ 13.6, 20.0, 31.5, 32.6, 47.5, 50.4, 123.6, 123.9, 136.9. HRMS (ESI): [M–PF₆]⁺, found 435.2143. C₁₇H₃₀N₄PF₆ requires 435.2112.

3.3.4. 1,4-Bis[*N*-(*N'*-butylimidazolium)]butane bis(hexafluorophosphate) (4**).** The same procedure was used as for **3**; from 1-butylimidazole (3.73 g, 30 mmol) and 1,4-dibromobutane (3.24 g, 15 mmol) in MeCN (20 mL), a light brown viscous liquid (bromide salt, 5.71 g, 82%) resulted. The anion exchange procedure was used; from the oily bromide salt (5.70 g, 2.3 mmol) and KPF₆ (5.56 g, 30 mmol) in deionized water (40 mL) **4** was isolated as an off-white viscous liquid (7.05 g, 96% from the bromide salt), which solidified in a vacuum oven, mp 50.4–52.4 °C. ¹H NMR (400 MHz, CD₃CN, 23 °C): δ 0.94 (t, $J=7$, 6H), 1.34 (m, 4H), 1.78–1.85 (m, 8H), 2.74 (m, 4H), 4.14

(m, 8H), 7.38 (m, 4H), 8.42 (s, 2H). ^{13}C NMR (100 MHz, CD_3CN , 23 °C): δ 13.7, 20.0, 27.2, 32.5, 49.8, 50.4, 123.4, 123.6, 136.3. HRMS (ESI): $[\text{M}-\text{PF}_6]^+$, found 449.2304. $\text{C}_{18}\text{H}_{32}\text{N}_4\text{PF}_6$ requires 449.2269.

3.3.5. 1-Dodecylimidazole. To a solution of imidazole (6.81 g, 100 mmol) in NaOH (50%) solution (8.80 g, 110 mmol), 1-bromododecane (24.92 g, 100 mmol) and THF (30 mL) were added. The mixture was refluxed for 3 days. After the mixture had cooled, THF was removed by a rotoevaporator. The residue was extracted with dichloromethane/water three times. The combined organic layer was washed with water and dried over Na_2SO_4 . The drying agent was filtered and the filtrate was concentrated. Column chromatography through a short silica-gel column with THF gave a clear yellow oil 20.51 g (87%). ^1H NMR (CDCl_3 , 22 °C): δ 0.88 (t, $J=7$, 3H), 1.29 (m, 18H), 1.76 (m, $J=7$, 2H), 3.91 (t, $J=7$, 4H), 6.90 (s, 1H), 7.05 (s, 1H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ 14.0, 22.6, 26.4, 29.0, 29.2, 29.3, 29.4, 29.5, 31.0, 31.8, 46.9, 118.6, 129.2, 136.9. The ^1H NMR spectrum was exactly identical to the literature report.²⁶

3.3.6. 1,2-Bis[*N*-(*N*'-dodecylimidazolium)]ethane di[bis(trifluoromethanesulfonyl)imide] (5). A solution of 1-dodecylimidazole (3.78 g, 16 mmol) and 1,2-dibromoethane (1.50 g, 8 mmol) in MeCN (15 mL) was refluxed for 3 days. After the mixture had cooled, the volatile materials were removed under vacuum. The residue was dispersed in THF (30 mL) and the insoluble bromide salt was filtered. The filter cake was washed with THF three times. Drying in a vacuum oven gave colorless a crystalline solid (bromide salt, 4.54 g, 86%), mp 249.3–252.9 °C (dec). The general anion exchange procedure was used, except the mixture was stirred at 50 °C for 24 h; from the bromide salt (2.70 g, 6.4 mmol), LiTf_2N (4.32 g, 15 mmol), and deionized water (60 mL), crystalline **5** (3.89 g, 97% from the bromide salt), mp 45.5–47.7 °C, was isolated. ^1H NMR (400 MHz, CDCl_3 , 23 °C): δ 0.87 (t, $J=7$, 6H), 1.25–1.31 (m (br), 36H), 1.86 (t, $J=7$, 4H), 4.15 (t, $J=7$, 4H), 4.74 (s, 4H), 7.33 (t, $J=2$, 2H), 7.60 (t, $J=2$, 2H), 8.84 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C): δ 14.2, 22.8, 26.3, 29.0, 29.4, 29.5, 29.6, 29.7, 32.0, 48.5, 50.7, 123.0, 123.3, 136.0. HRMS (ESI): $[\text{M}-\text{Tf}_2\text{N}]^+$, found 780.3997. $\text{C}_{34}\text{H}_{60}\text{F}_6\text{N}_5\text{O}_4\text{S}_2$ requires 780.3985.

3.4. Example of ITC titration methods

Stock solutions of titrant **1** (175 mM) and **6** (6.11 mM) in MeCN were prepared using volumetric flasks. All titrations were run at 25 °C. The high gain (high sensitivity) system was used, and the reference offset was set at 50% of the maximum. During each titration, 10 injections of 2.0 μL , 20 injections of 2.5 μL , 25 injections of 3.0 μL , and 26 injections of 4.0 μL of **1** were made consecutively into the cell containing **6**. Injections were made every 180 s with a primary filter period of 2 s, and a secondary filter period of 4 s. The switch time for the filter periods was at 120 s. After the titration isotherm was recorded, the raw data were reduced using commercial software and the supplied algorithms from the manufacturer. A control titration was also completed so that the heat of dilution from the titrant could be subtracted from the original titration isotherm. The parameters of the control titration were the same as those used in the original titration with the exception that the cell solution was replaced with pure MeCN. The control isotherm was integrated using the same method as the original titration and the energy values obtained were subtracted from the integrated point plot of the original titration. The integration data from the titrations were fit using the 'One Set of Sites' model; other stoichiometries yielded unsatisfactory fits of the data.

3.5. X-ray crystallography

3.5.1. Crystal growing and crystallography of 1. Colorless prisms crystallized from acetone/pentane at room temperature. The

chosen crystal was centered on the goniometer of an Oxford Diffraction Gemini A Ultra diffractometer operating with Mo $K\alpha$ radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.²⁷ The Laue symmetry and systematic absences were consistent with the monoclinic space groups $C2/c$ and Cc . The centric space group $C2/c$ was chosen based on the E-statistics. The structure was solved by direct methods and refined using SHELXTL NT.²⁸ The asymmetric unit of the structure comprises 0.5 crystallographically independent molecules. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms.

Crystal data: prism, colorless, crystal size=0.21×0.21×0.09 mm³, $\text{C}_{10}\text{H}_{16}\text{N}_4 \cdot 2\text{PF}_6$, $M=482.21$, wavelength=0.71073 Å, monoclinic, space group $C2/c$, $a=22.186$ (3) Å, $b=6.4852$ (3) Å, $c=14.4065$ (13) Å, $\alpha=90^\circ$, $\beta=122.621$ (15)°, $\gamma=90^\circ$, $V=1745.8$ (3) Å³, $Z=4$, $D_c=1.835$ Mg/m³, $T=100$ (2) K, $\mu=0.376$ mm⁻¹, 11,193 reflections collected, 2562 [R(int)=0.0300] independent reflections, 2562/0/128 data/restraints/parameters, $F(000)=968$, $R_1=0.0358$, $wR_2=0.0780$ (all data), $R_1=0.0288$, $wR_2=0.0759$ [$I>2\sigma(I)$], and goodness-of-fit on $F^2=1.051$. This file corresponds to CCDC 768151.

3.5.2. Crystal growing and crystallography of 1·(6)₂. A colorless plate of **1·(6)₂** was obtained in two steps. First, a 1:2 mixture of **1** and **6** was dissolved in MeCN and then the solvent was removed by evaporation in an open vial at room temperature. Then, the residue was re-dissolved in acetone and the crystal was grown by vapor diffusion of pentane into the acetone solution at room temperature. The colorless plate was centered on the goniometer of an Oxford Diffraction SuperNova diffractometer operating with Cu $K\alpha$ radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.²⁷ The Laue symmetry and systematic absences were consistent with the monoclinic space group $P2_1/n$. The structure was solved by direct methods and refined using SHELXTL NT.²⁸ In the final refinement model, the asymmetric unit included four host molecules, two guest salts, seven CH_3CN and one partially occupied H_2O . A 2 position disorder model was used for one PF_6^- , two C-atoms in the arm of a host molecule, and one CH_3CN molecule. The CH_3CN is disordered across an inversion center and relative occupancies were constrained to 0.5. The relative occupancies of the remaining disordered atoms refined to 0.59 and 0.41. For steric reasons, the water molecule could only be present at the same time as the disordered PF_6^- with occupancy 0.59; consequently, the water occupancy was tied to the PF_6^- occupancy of 0.59. Anisotropic displacement parameters suggest additional PF_6^- and CH_3CN disorder, but attempts to model this disorder did not improve the model and were abandoned. All non-hydrogen atoms were refined anisotropically except for two CH_3CN molecules and the partially occupied water molecule. A riding model was used for all hydrogen atoms. The H-atoms of the water molecule were not included in the refinement.

Crystal data: plate, colorless, crystal size=0.4460×0.1156×0.0205 mm³, $2\{[(\text{C}_{33}\text{H}_{37}\text{NO}_{12})_2 \cdot \text{C}_{10}\text{H}_{16}\text{N}_4][\text{PF}_6]_2\} \cdot 7\text{C}_2\text{H}_3\text{N} \cdot 0.59\text{H}_2\text{O}$, $M=3820.97$, wavelength=1.54178 Å, monoclinic, space group $P2_1/n$, $a=30.5666$ (14) Å, $b=14.1326$ (5) Å, $c=42.0175$ (18) Å, $\alpha=90^\circ$, $\beta=99.972$ (4)°, $\gamma=90^\circ$, $V=17876.7$ (13) Å³, $Z=4$, $D_c=1.420$ Mg/m³, $T=100$ (2) K, $\mu=1.356$ mm⁻¹, 89614 reflections collected, 34633 [R(int)=0.0563] independent reflections, 34633/66/2413 data/restraints/parameters, $F(000)=7984$, $R_1=0.1248$, $wR_2=0.2297$ (all data), $R_1=0.0820$, $wR_2=0.2095$ [$I>2\sigma(I)$], and goodness-of-fit on $F^2=1.030$. This file corresponds to CCDC 768150.

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Supplementary data

NMR spectra for all synthesized compounds, ITC titration data, mass spectrometric results and X-ray crystal structures. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.07.010. These data include MOL files and InChIKeys of the most important compounds described in this article.

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