Imidazolium receptors for the recognition of anions

Juyoung Yoon,*[a] Sook Kyung Kim,[a] N. Jiten Singh[b] and Kwang S. Kim*[b]

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This *tutorial review* covers imidazolium receptors for anion recognition according to their topological and structural classification, and includes benzene tripodal, cyclophane and calix-imidazolium, fluorescent imidazolium, ferrocenyl imidazolium, cavitand and calixarene, and polymeric imidazolium systems.

Introduction

Neutral anion receptors having amide, pyrrole, urea groups as binding sites form N–H···anion hydrogen bonds.[1] Most positively charged anion receptors have dealt with ammonium and guanidinium groups as binding sites interacting with the anions by either electrostatic forces or with N^+–H···anion hydrogen bonds.[1] In contrast, various positively charged


Juyoung Yoon

Juyoung Yoon was born in Busan in 1964. He was graduated with a BS from Seoul National University (1987) and received his PhD (1994) from The Ohio State University. After completing postdoctoral research at the University of California, Los Angeles (1994–1996) and at The Scripps Research Institute (1996–1998), he joined the faculty at Silla University in 1998. In 2002, he moved to Ewha Womans University, where he is currently an Associate Professor of the Department of Chemistry and Division of Nano Sciences. His research interests include investigations of fluorescent chemosensors, molecular recognition, organo EL materials and organic synthesis of biologically active compounds.


Sook Kyung Kim

Sook Kyung Kim was born in Busan in 1977. In 2000 and 2003, respectively, she has received her BS and Master degrees from Silla University. Currently she is working with Professor Juyoung Yoon at Ewha Womans University for her PhD degree investigating various fluorescent chemosensor for ions.


N. Jiten Singh

N. Jiten Singh was born in Kakching (India) in 1971. In 1994 and 1997, he received his MSc and MTech degrees from IIT Kanpur and IIT Delhi, respectively. During 1997–2002, he worked in the R&D center of Torrent Pharmaceutical Ltd. as a computer-aided-drug-designer. Currently he is working with Professor Kwang S. Kim at Pohang University of Science and Technology for his PhD degree. For his thesis, he is working on investigating the non-bonding interactions in anion receptors, molecular clusters and protein–drug complexes.


Kwang S. Kim

Kwang S. Kim was born in Seoul in 1950. He received his PhD degree in chemistry from the University of California, Berkeley. After spending a few years as an IBM postdoctoral fellow and as a Research Assistant Professor at Rutgers University, he joined Pohang University of Science and Technology. He is currently a Professor and the Director of the National Creative Research Initiative Center for Superfunctional Materials. His research interests include investigations of molecular recognition, receptors, drugs, biomolecules, nanomaterials, and molecular devices.

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[a] *Department of Chemistry and Division of Nano Sciences, Ewha Womans University, 11-1 Daehyon-Dong, Sodaemun-Ku, Seoul 120-750, Korea. E-mail: jyoon@ewha.ac.kr; Fax: 82-2-3277-2384; Tel: 82-2-3277-2400*
[b] *National Creative Research Initiative Center for Superfunctional Materials, Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea. E-mail: kim@postech.ac.kr; Fax: 82-54-279-8137; Tel: 82-54-279-2110*

imidazolium derivatives have been synthesized and studied as selective anion-receptors. Imidazolium group can make a strong interaction with anions through $(C–H)^{+}\cdots X^{-}$ type ionic hydrogen bond because the charge–charge electrostatic interaction dominates.[2] This type of interaction could also be envisaged in the crystal structure of imidazolium based ionic liquids[3a,b] and calix-[4]-pyrrole complexing with imidazolium salts.[3c]

The first examples of dicationic heterophanes based on imidazolium units as molecular recognition motifs for anions were reported by Alcalde *et al.* a few years ago.[4] In the same year, Sato *et al.* reported benzene based tripodal imidazolium receptor for anion recognition.[5] Various types of receptors containing imidazolium moieties, such as the benzene-based tripodal imidazolium receptors, imidazolium cyclophanes and calix-imidazoliums, imidazolium anthracenes, imidazolium calix[4]arene, imidazolium cavitand and imidazolium polythiophene have been reported. All these examples utilized the imidazolium moieties as the binding sites for anions. However, the different templates may provide different binding properties towards anions due to various binding pockets generated from these templates. Furthermore, introduction of fluorogenic and chromogenic moieties to the receptors enabled easy detection compared to the conventional ^{1}H NMR titration methods. Kim and coworkers have demonstrated various theoretical calculations for these imidazolium systems.

This review covers recent development of imidazolium receptors for the recognition of various anions. We have grouped the receptors according to their topological and structural classification, which includes benzene tripodal, cyclophane and calix-[n]-imidazolium, fluorescent imidazolium, ferrocenyl imidazolium, cavitand and calixarene, and polymeric imidazolium systems.

Benzene tripodal systems

A benzene based tripodal receptor with three imidazolium groups **1** was reported by Sato *et al.* (Fig. 1).[5] The host **1** displayed a selective binding with Cl^{-} over Br^{-} and I^{-} in acetonitrile, which was confirmed *via* ^{1}H NMR titration experiments.[5] Kim and coworkers clarified that this tricationic heterocycle interacts strongly with anions through $(C–H)^{+}\cdots X^{-}$ type ionic hydrogen bond between the hydrogen on the electron-deficient C(2) carbon atom of the imidazolium ring and the guest anion, and shows a selective binding for F^{-} over other halide anions.[2] For better anion binding affinity, the benzene based tripodal receptor was theoretically modified and experimentally realized[2] as tripodal nitro-imidazolium receptor **2**, which showed strong affinity and high selectivity for Cl^{-}. The association constant for Cl^{-} in a 9 : 1 mixture of acetonitrile-d_3 and DMSO-d_6 was 1.1×10^{6} M^{-1}.

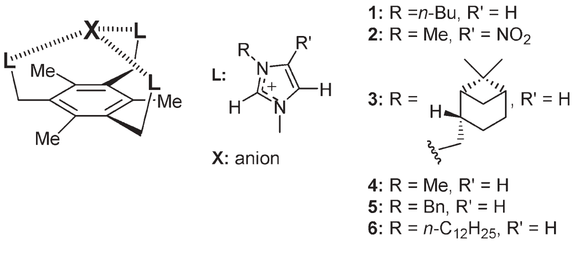

Fig. 1 Benzene tripodal systems.

Howarth *et al.* reported a homochiral tripodal imidazolium system (**3**) which could distinguish between sodium (*R*)-2-aminopropionate and sodium (*S*)-2-aminopropionate.[7] From the ^{1}H NMR experiments, it is reported that the imidazolium salt forms a complex with the (*R*) enantiomer but not with the (*S*) enantiomer.

Ru-Gang *et al.* recently reported similar benzene tripodal systems (**4**, **5** and **6**) (Fig. 1) and bis-imidazolium (**7**) (Fig. 2).[8] The binding properties of halide and hexafluorophosphate salts of these imidazoliums towards various anions, such as CO_3^{2-}, HCO_3^{-}, $H_2PO_4^{-}$, HPO_4^{2-}, PO_4^{3-} and halides, were examined in water *via* UV spectroscopic titration experiments. The association constant for **5** with PO_4^{3-} in water was observed to be as large as 5465 M^{-1}.

Cyclophane and calix-imidazolium systems

Alcalde *et al.* reported cyclophane type receptors as shown in Fig. 3 (**8a** and **8b**).[4] Interestingly, in the X-ray crystal structure of **8a·2Cl·2H$_2$O**, the dication **8a** adopts a chair-like conformation. On the other hand, the molecular shape of dication **8b** in **8b·2Cl·3.5H$_2$O** assumes a cone-like conformation, but both cations **8a** and **8b** have similar molecular cavity dimensions: a square of 5 Å side. The deshielding effects of C(2)–H (in imidazolium rings) were reported to be in the order of $H_2PO_4^{-} > F^{-} > CH_3CO_2^{-} > CN^{-} > Cl^{-}$.

Xie *et al.* reported cyclophanes based on the imidazolium (**9** and **10**) or benzimidazolium groups.[9] UV spectroscopic titration in acetonitrile showed 1 : 1 complexes between the cyclophanes and halide anions. The binding constant of **9** with

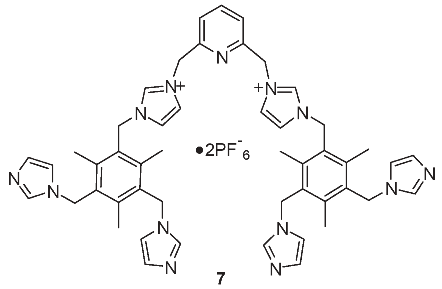

Fig. 2 Bis-imidazolium receptor **7**.

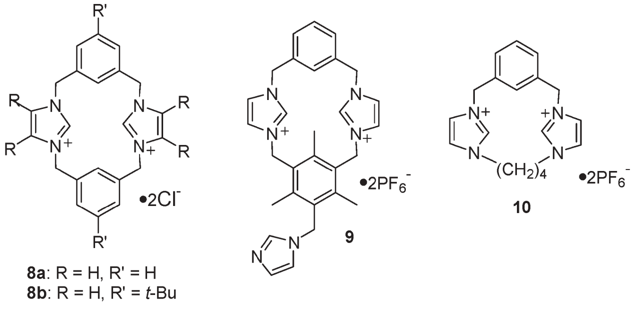

Fig. 3 Structures of cyclophane-type imidazolium receptors **8**, **9** and **10**.

Cl^- is reported as 4.06×10^4 M^{-1}, which is 2, 5 and 2000 times those of **9** with Br^-, F^- and I^-, respectively. In view of the relative H-bonding ability and basicity, the interaction between simple imidazolium cations and halide anions should be in the order $F^- > Cl^- > Br^- > I^-$.

Sato *et al.* reported a tetracationic heterophane (**11**) (Fig. 4), which forms a 1 : 1 inclusion complex with halides and oxoanions in DMSO-d_6.[10] From the ^{1}H NMR titration experiments, the binding affinity of this receptor was reported to be in the order $HSO_4^- > Br^- > H_2PO_4^- > Cl^- > I^- > ClO_4^-$, which was explained based on the size of anions.

Kim and coworkers have recently synthesized a novel calix[4]imidazolium[2]pyridine (**12**) and reported its various X-ray crystal structures with different anions (Fig. 5).[11] For example, crystals of **12·F(PF$_6$)$_3$** complex were obtained by the addition of tetrabutylammonium fluoride (TBAF)·$3H_2O$ to a solution of **12·(PF$_6$)$_4$** in acetonitrile. On the other hand, crystallization of the host complex **12·(PF$_6$)$_4$** with TBACl from acetonitrile solution afforded crystals of **12·Cl$_2$(PF$_6$)$_4$**. Furthermore, the addition of one equivalent of TBABr to **12·(PF$_6$)$_4$** resulted in a crystal in which the unit cell contains two layers: one composed of **12·Br$_2$(PF$_6$)$_4$** and the other composed of the free receptor **12·(PF$_6$)$_4$**. The binding constant of the F^- binding with **12** in DMSO with ^{1}H–NMR was calculated to be 28,900 M^{-1}. The detailed conformation analysis using the density functional calculation predicted that the most stable conformer of the complex in DMSO and binding affinities were in good agreement with the experiments. Unlike the fluoride anion, the chloride and bromide anions of larger size do not fit in the center of the cavity of **12**, and furthermore these anions favor nonspherical or surface conformations in order to keep the extra electron in a large empty space.[12]

The template effect exerted by the chloride anion in the ring closure reaction was reported by Mencarelli *et al*. The rate of the ring closure of monocation **13** increased up to 10 times in the presence of 0.04 M Bu_4NCl (Scheme 1).[13]

Beer *at al.* reported acyclic and macrocyclic (**14** and **15**) transition metal dithiocarbamate complexes containing positively charged imidazolium moieties (Fig. 6).[14] A similar host compound using benzene tripodal system is also reported in the same paper. The UV-Vis spectroscopic binding studies revealed that $H_2PO_4^-$ is complexed selectively in preference to F^- and Cl^- for the acyclic hosts. Copper(II) dithiocarbamate imidazolium systems were reported to sense $H_2PO_4^-$ and Cl^-, which was monitored by cyclic voltammetry.

Temperature dependent conformational studies of *o*- and *m*-cyclophane type imidazolium receptors were reported[15,16] while Rajakumar *et al.*[17]published syntheses for benzimidazolophanes and imidazolophanes. However, no anion binding studies were reported.

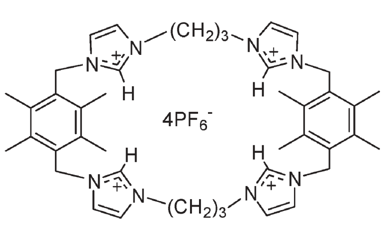

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Fig. 4 Structures of cyclophane-type imidazolium receptor **11**.

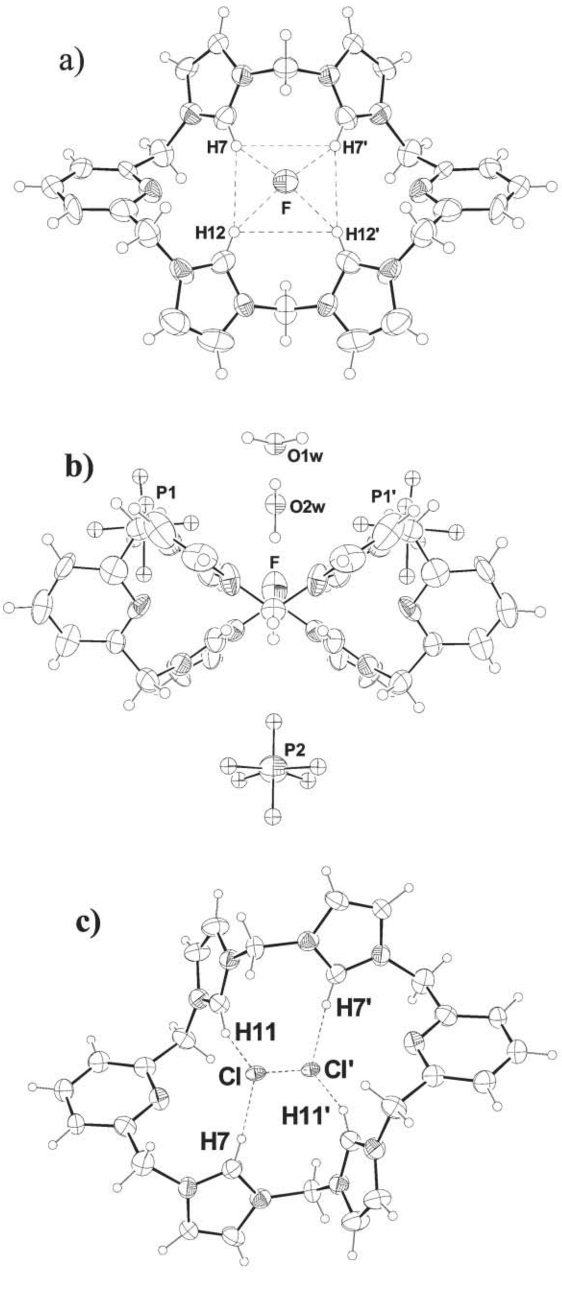
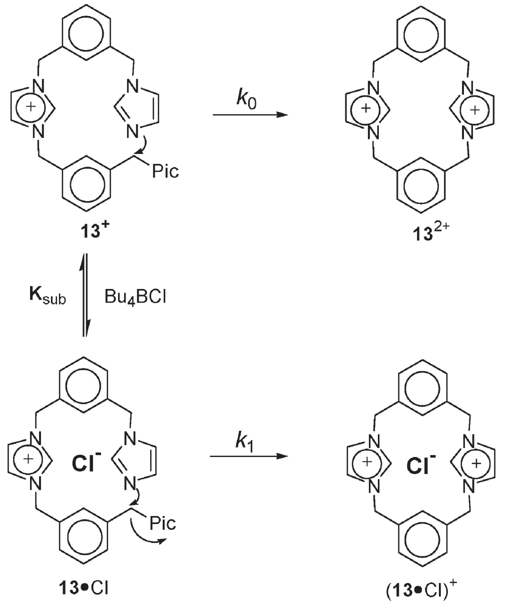


Fig. 5 Crystal structure of calix[4]imidazolium[2]pyridine **12** complexed with anions (PF_6^-, F^-, Cl^-). a) Top view of **12**·[F^-] and b) side view with 2(H_2O) for **12**·(F^-)·3[PF_6]$^-$·2(H_2O), and c) top view of **12**·2(Cl^-) for **12**·2(Cl^-)·2[PF_6]·2(CH_3CN). [Reproduced with the permission from WILEY-VCH Verlag GmbH & Co. (Ref. 11)]

Cavitand derivative

Recently, Yoon and coworkers reported a new cavitand derivative bearing four imidazolium groups (**16**) as a receptor for anions (Fig. 7).[18] The binding properties towards various anions including dicarboxylates were investigated based on the



Scheme 1 The chloride template effect in the formation of dicationic imidazoliophanes (Pic = 2,4,6-trinitrophenolate).

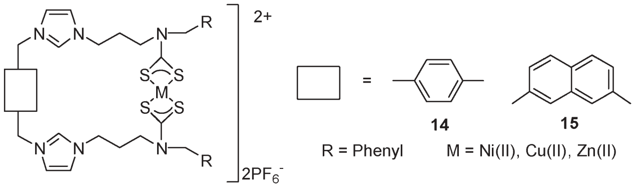
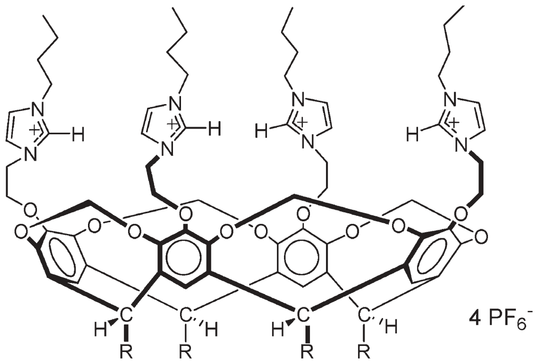


Fig. 6 Macrocyclic transition metal dithiocarbamate imidazolium receptors (**14** and **15**).



16, R = CH_2CH_2Ph

Fig. 7 Imidazolium receptors based on cavitand (**16**).

^1H NMR spectroscopic experiments in acetonitrile-d_3. The tetrabutylammonium salts of various anions, such as 1,3-adamantanedicarboxylate, adipate, terephthalate, 1,4-phenylenediacetate, succinate, acetate, Cl^-, Br^- and I^- were used for the binding study. As expected, cavitand **16** displayed 1:1 binding with dicarboxylates, while 1:2 complex formation was confirmed with acetate, Cl^-, and Br^-. In particular, among the anions examined, cavitand **16** displayed a selective binding with bis(tetrabutylammonium) 1,4-phenylenediacetate.

Fluorescent imidazolium systems

A few anthracene derivatives bearing imidazolium groups as binding sites have been recently studied by Yoon's group and by Kim's group.[19] Two imidazolium moieties were first immobilized on the 1,8-positions of the chemosensor (**17**) (Fig. 8), and a unique feature of the binding mode was predicted based on *ab initio* calculations.[19a] 1,8-Bis-imidazolium anthracene **17** effectively and selectively recognizes the biologically important $H_2PO_4^-$ ion over other anions such as I^-, Br^- and Cl^- in acetonitrile. Other than previous results of imidazolium receptors, these binding phenomena can be easily monitored *via* fluorescence quenching effects. The *ab initio* calculations also predicted high binding affinity of host **17** with $H_2PO_4^-$ and F^- ions.

We have further demonstrated that the selectivity of these imidazolium receptors against anions can be controlled by the topology of the binding site (*e.g.* enhancement of rigidity). Compared to host **17**, the greater rigidity in host **18** enhances the binding selectivity for $H_2PO_4^-$ over F^-.[19b] In both cases, anthracenes being fluorophores have the advantage of rigid templates which sense anions by the change in the fluorophore intensity due to photo-induced electron transfer (PET) mechanism. Competitive binding studies of $H_2PO_4^-$ and F^- for **18** using the fluorescent change demonstrated that there was no interference to the binding of $H_2PO_4^-$ in the presence of up to 1.5 equimolar concentrations of F^- anions, in contrast to extremely strong interference in the case of host **17**.

Recently, we reported a novel water-soluble imidazolium anthracene derivative (**19**), which not only differentiates the structurally similar compounds GTP and ATP but also acts as a potential fluorescent chemosensor for GTP in 100% aqueous solution (pH = 7.4, 10 mM HEPES).[19c] This new fluorescent chemosensor senses GTP by chelation-enhanced fluorescence quenching (CHEQ) effect, whereas it displayed a chelation-enhanced fluorescence (CHEF) effect for ATP, ADP and AMP.

A fluorescent tripodal receptor (**20**) bearing three benzoimidazolium and napthyl groups has been recently reported by Duan *et al.*[20] This host acts as an "off–on" signaling chemical sensor with high selectivity for Cl^- over Br^- and I^- through a guest-induced conformational switching process (Scheme 2). In the presence of Cl^-, the tripodal system adopts a cone conformation, which leads to the excimer fluorescence by bringing the naphthalene groups into close proximity.

Beer and coworkers reported a new imidazolium functionalised acyclic ruthenium(II) bipyridyl receptor (**21,22**) (Fig. 9).[21]

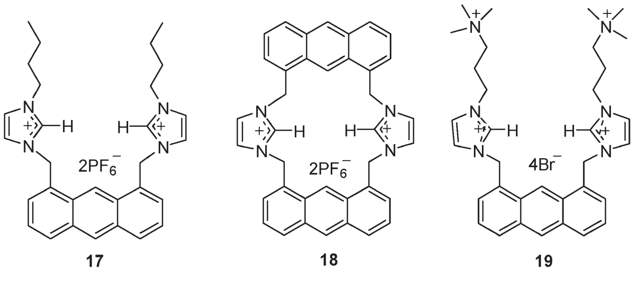
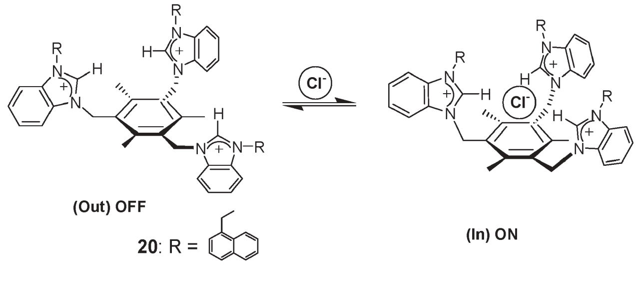


Fig. 8 Anthracene derivatives bearing imidazolium groups.



Scheme 2 Conformational switching process of **20** upon the addition of Cl^-.

Both receptors displayed a selectivity for Cl^- over the other anions in acetonitrile–water (9 : 1, v/v) and **22** sensed ATP in 50 : 50 acetonitrile–water solvent media.

Kang and coworkers reported a naphthalene derivative (**23**) which contains two methylene bridged bis-imidazolium rings (Fig. 10).[22a] The host **23** displayed a selective affinity for I^-, which was confirmed using fluorescence spectroscopy and ^1H NMR. They also reported the role of aromatic (C–H)···anion interaction on **24** in addition to the imidazolium $(C–H)^+$···anion ionic hydrogen bonding, whose strength was found to be increased with the nitro substitution on the *para* position.[22b]

Yoon and coworkers reported a fluorescent cavitand derivative bearing four imidazolium groups as well as four pyrene groups as a fluorescent receptor for GTP (Fig. 11).[23] Since host **25** contains pyrene groups, the binding properties towards various anions were investigated based on the fluorescence experiments. From the fluorescent titrations in DMSO/20 mM aqueous HEPES buffer at pH 7.4 (6:4, v/v), the association constants for GTP, ATP and CTP are reported as 73800, 14040 and 7700 M^{-1}, respectively.

Ferrocenyl imidazolium receptor

Howarth *et al.* reported an imidazolium receptor which contains two ferrocene groups (**26**) (Fig. 12).[24] Cyclic voltammetry revealed that this ferrocenylimidazolium salts selectively make complexes with guest anions and electrochemically recognize them. ^1H NMR spectroscopy indicated the formation of 1 : 2 stoichiometric complexes with Cl^-, Br^- and I^- and 1 : 1 stoichiometric complexes with NO_3^- and HSO_4^-.

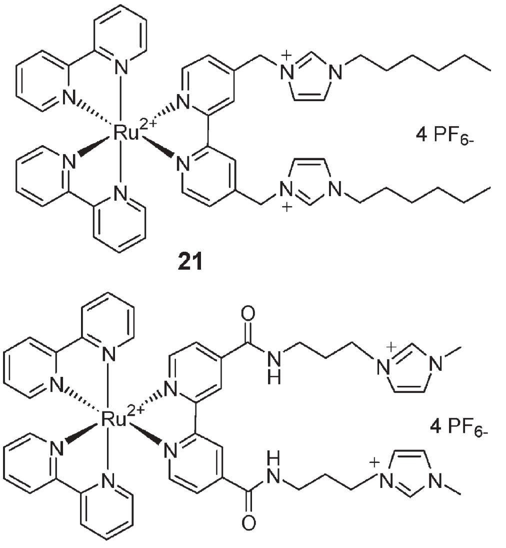


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Fig. 9 Structures of fluorescent hosts **21** and **22**.

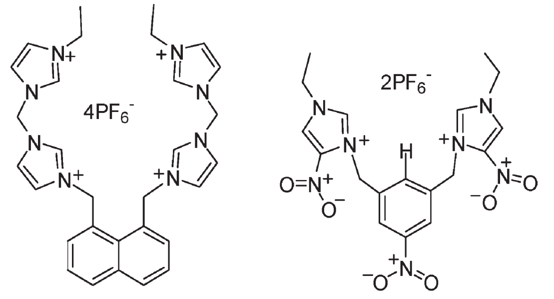

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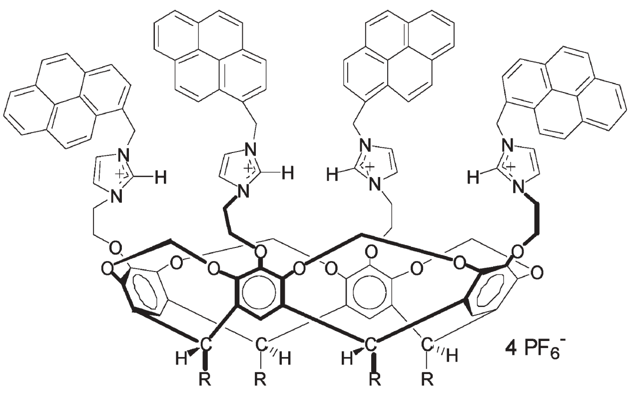
Fig. 10 Structures of hosts **23** and **24**.



25, R = CH_2CH_2Ph

Fig. 11 Imidazolium receptors based on cavitands (**25**).

Polymeric imidazolium receptor

Leclerc *et al.* reported a new colorimetric and fluorometric chemosensor based on a cationic polythiophene derivative for iodide-specific detection.[25] The aqueous solution of the cationic polymer **27** was yellow with a maximum absorption wavelength at 406 nm (Fig. 13). When NaI was added to the solution, the color of the solution instantly changed from yellow to red-violet (λ_{max} = 543 nm). Furthermore, a selective fluorescence emission quenching effect was observed when NaI was added to the solution of polymer **27**.

Miscellaneous imidazlium receptors

A series of organoboron molten salts (**28**, **29**) were prepared by hydroboration of allyl imidazolium type salts with various

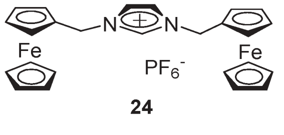


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Fig. 12 Structures of ferrocenyl imidazolium receptors **26**.

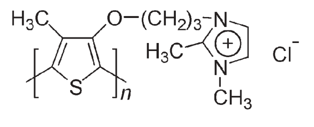

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Fig. 13 Polythiophene imidazolium derivative.

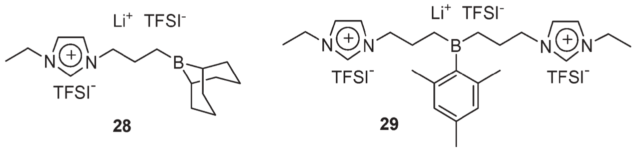

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Fig. 14 Imidazolium receptors containing organoboron groups (**28** and **29**).

hydroborating reagents and anion exchange (Fig. 14).[26] These molten salts bearing anion receptors exhibited selective lithium transporting properties with ionic conductivity of 7.79×10^{-5}–6.25×10^{-6} S cm^{-1} at 323 K.

Imidazolium based ionic liquids $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$ could also be used as alternative solvents for the recovery of some amino acids (L-tryptophan, L-phenylalanine, L-tyrosine, L-leucine and D-valine) from aqueous media.[1c] Therefore, an understanding of the nature and magnitude of the ionic hydrogen bonding or the ion-pair electrostatic interaction force between imidazolium moiety and various anions would provide a knowledge for the better design of improved molten salts/imidazolium based anion receptors.

Concluding remarks

Imidazolium derivatives have recently been utilized as anion receptors by virtue of forming strong $[C–H]^+\cdots$anion ionic hydrogen bonds. With fine tuning and carefully designed topological features of the organic systems, imidazolium receptors could be widely used for sensing various anions. In this regard, we have reviewed various type of receptors containing imidazolium moieties as the binding sites in benzene tripodal, cyclophane and calix-[n]-imidazolium, fluorescent imidazolium, ferrocenyl imidazolium, cavitand, and polymeric imidazolium systems.

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