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ARTICLE TYPE

Progress of 3-aminopyridinium-based synthetic receptors in anion recognition

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This review describes an overall development on synthetic receptors built on pyridinium motif with different functionalities at the 3-position in anion recognition. The review covers only the organic systems. In the designs, the pyridinium group along with the other functional motifs plays the crucial role in the binding of various anions of different shapes and sizes. Complexation characteristics are communicated through the change in ^{1}H NMR, emission, color or gelation behaviours.

Introduction

Design and synthesis of artificial receptors for anion recognition is a fertile area of research in supramolecular chemistry.[1-8] Anion recognition chemistry is rapidly developed discipline in the field of supramolecular chemistry. It started to grow in the late 1960s when Simmon and Park reported the complexation properties of series of positively charged ammonium macrocyclic hosts with halides.[9] Following Simmons and Park's report, exploration in this area took place in the mid 1970s, when Lehn and coworkers described the anion-binding properties of a variety of macrobiocyclic and macrotricyclic ammonium-based receptors.[10,11] After that, a tremendous growth on anion recognition chemistry has taken place. Receptors for anions can be of neutral and charged in nature. In anion recognition, charge receptors are much attractive than the neutral ones due to their efficacy in complexation of anions involving charge – charge interaction along with other noncovalent forces.

In the charged receptors, the cationic parts act as hosts for binding of anions and they suffer from competition from associated counter anions. In comparison, neutral hosts for anions exhibit relatively weak binding of anions and must deal with the associated counter cations. These are sometimes called ion pair binding hosts. Survey of the literature reveals that charged receptors based on guanidinium,[12,13] imidazolium,[14-16] benzimidazolium,[17-25] polyammonium[26-27] and thiourenium[28-30] motifs are known and well explored in anion recognition. Similar to these charged systems, pyridinium motif has been noted as useful and versatile motif in devising molecular receptors for anions. The pyridinium motif provides polar C-H bond as hydrogen bond donor to anions and the complex is further stabilized by charge-charge interaction. The easy incorporation of 3-aminopyridine in the desired structures with moderate to good yields, flexibility in tuning the designs are the possible factors that provide opportunity to consider pyridinium receptors for neutral as well as charged guest molecules. Thus this review aims to focus the pyridinium-based receptors (especially 3-aminopyridinium-based) related to the sensing of different anions.

Simple pyridine amine or amide is not a good motif for anion binding. But judicious placement of this motif with the quaternization of the ring nitrogen can lead to a number of structures that are capable of binding anions with considerable efficiency. Binding of anions takes place through hydrogen bonding involving polar C-H bond and the other appended functionalities of pyridinium motif. The hydrogen bonded complex is stabilized by charge-charge interactions. Figure 1 highlights the different approaches to use 3-aminopyridine as the

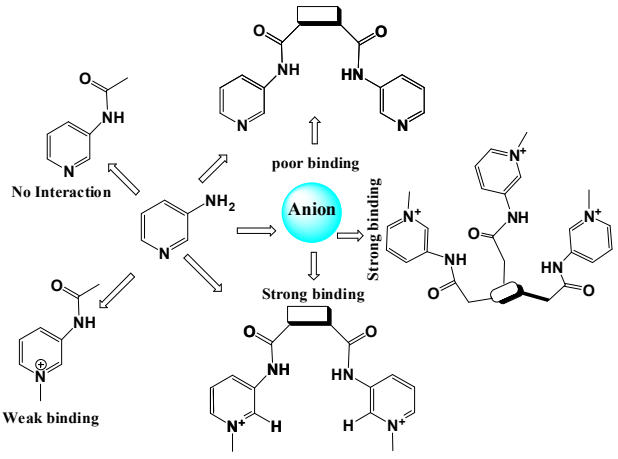

Fig 1. Strategies to use 3-aminopyridine in building up receptor structures.

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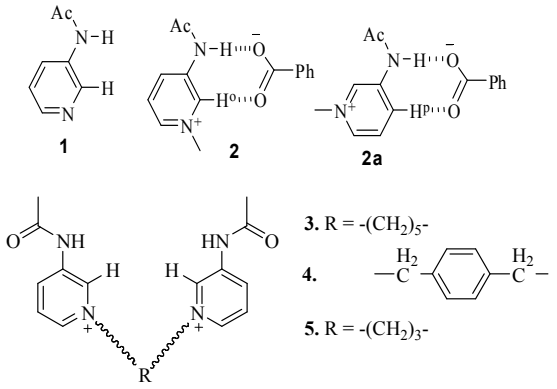
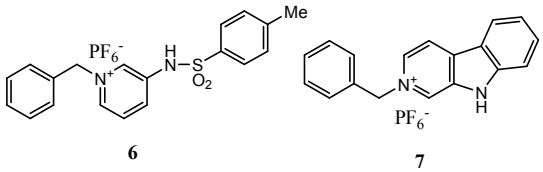
building block for various receptor structures.

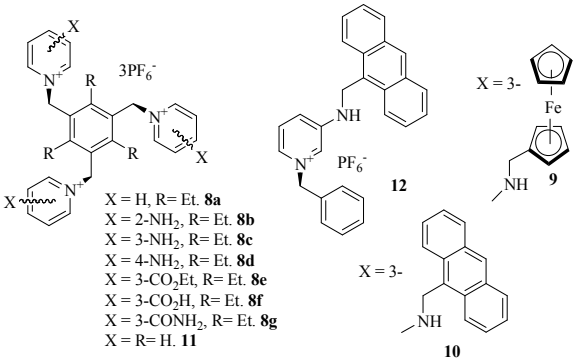
It is established that the C-H group adjacent to neutral or protonated/ alkylated nitrogen atom is often involved in hydrogen bonding in the crystal structure.[31-33] Due to weakness, C-H…X (X = O, N, Cl^-, Br^-, I^- etc.) hydrogen bonds are quite rarely incorporated into synthetic receptors as a determining force to stabilize the complexes in solution.[34] In this regard, receptors combining *N*-alkylpyridinium and amide groups were first prepared and employed for binding of carboxylate by Jeong *et al.*[35] They reported that while pyridine amide **1** binds benzoate in d_6-DMSO with a K_a of 16 M^{-1}, the alkylated pyridinium motif **2** shows an increase in K_a value (300 M^{-1}) involving different binding modes (**2** and **2a**) (Table 1).[35] Considering this feature Jeong *et al.* prepared different bispyridinium salts **3**, **4** and **5** for binding of dicarboxylates. Adipate was selectively complexed with a high association constant ($K_a > 5 \times 10^5$ M^{-1}). The alkylated pyridinium groups attached to amide nitrogen exhibited increased affinities to anions and neutral gusts as compared to their neutral counterparts. This is attributed to the increase in acidities of both NH (amide) and CH (aromatic ring) proton donors induced by quarternization of pyridine moiety. These interesting features of pyridinium moiety inspired several groups to develop pyridinium amide or urea-based receptors for anions. Of the different architectures, 3-amino or other substituted pyridines with different templates which provide different binding properties towards anions due to various binding pockets generated, have been undertaken in the discussion. Introduction of fluorogenic and chromogenic moieties to the receptors enabled easy detection of anionic species compared to the conventional ^{1}H NMR titration methods. The recognition affinities of these receptors towards the different anions are briefly summarized in Table 1.



Fabbrizzi *et al.* reported pyridinium-based structure **6** which bound anions such as AcO^-, $H_2PO_4^-$, F^- (taken as tetrabutylammonium salt) in DMSO involving both electrostatic and hydrogen bonding interactions.[36] In comparison, indole fused pyridinium compound **7** being less acidic showed only deprotonation with F^- and AcO^-. $H_2PO_4^-$ was complexed in 1:1 stoichiometric fashion with a log K_a of 3.11.[36]



Steed and co-workers described the synthesis and anion binding properties of a series of 3-aminopyridinium-based tripodal, tricationic hosts **8** - **11** for anions.[37a-b] The podand hosts were explored in the binding of halides and oxoanions. The alternating substitution around the central benzene ring preorganizes the hosts in cone conformation. While the unsubstituted tris(pyridinium) species **8a** gives K_{11} 850 M^{-1} for Br^-, structure **11** with no ethyl functionality at the core benzene ring shows the binding constant of 17 M^{-1} with Br^- ion in CD_3CN. This implied the effect of preorganization in the tripods for which the significant degree of cooperativity between the three arms in binding takes place. Among the hosts, ferrocene appended host **9** exhibited strong binding for Cl^- (K_{11} = 17,380 M^{-1}) as determined by ^{1}H NMR titration in CD_3CN. AcO^- was complexed with moderate binding constant value (K_{11} = 3680 M^{-1}). In contrast,



the anthracene appended tripodal host **10** bound AcO^- with high binding constant value (K_{11} = 49,000 M^{-1}), determined in CD_3CN by ^{1}H NMR titration. Binding was established through the involvement of N-H and C-H hydrogen bond donation from the arms around the central benzene ring. This was also realised in the solid state. For example, the X-ray crystal structure of the bromide complex of **8c** shows the chelation of Br^- ion by six fold array of two NH...Br^- and four CH...Br^- interactions (Fig. 2a). In absence of Br^-, the PF_6^- salt of **8c** assumes non-convergent partial cone conformation and also shows the engagement of N-H and C-H bonds to fluorine of PF_6^- ion (Fig. 2b).

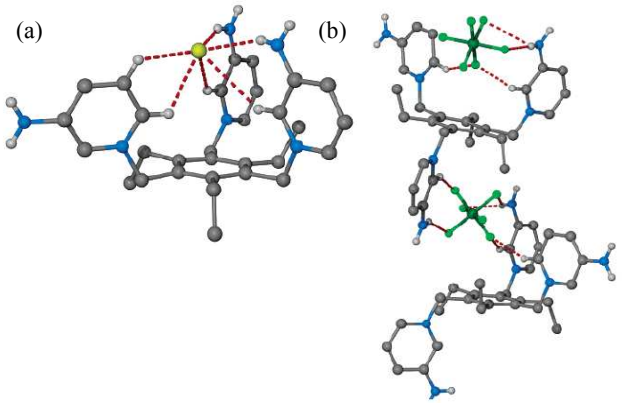
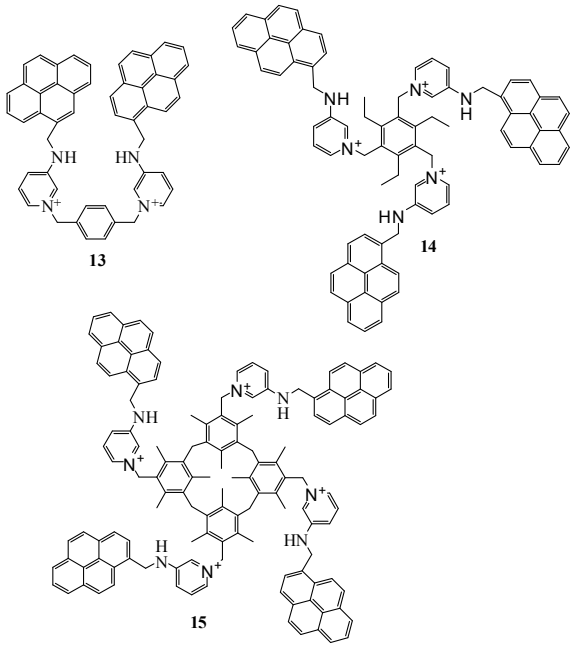


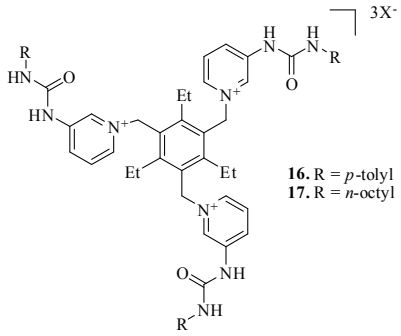
Fig 2. X-ray crystal structures of the (a) bromide salt of **8c** (three up conformation) and (b) PF_6^- salt of **8c** (partial cone conformation). Reprinted with permission from Ref. 37b. Copyright 2006 American Chemical Society.

Steed *et al*. also synthesized a series of di-, tri-, and tetrapodal anion-binding hosts **13**, **14** and **15**, respectively based on 3-aminopyridinium units with pyrenyl reporter groups.[37c] The conformational and sensing properties of the hosts were dependent on the spacing and disposition of the binding components. The host **15** bound strongly to dicarboxylates, particularly malonate (log $\beta_1 = 5.2 \pm 0.1$, log $\beta_2 = 11.2 \pm 0.2$), in a 2:1 anion:host ratio in CH_3CN and exhibited fluorescence quenching as a result of pyrene-pyridinium charge-transfer interaction in the excited state. The higher value of second equilibrium constant than the first one indicates that complexation of the first anion favours complexation of the second anion on the opposite side of the calixarene ring through allosteric conformational changes. The host also preferred Cl^- ion



over the other monovalent anions, but the association constant for dicarboxylate was at least an order of magnitude higher than halides despite the fact that a fluorescent response was only observed upon Cl^- ion binding. In contrast, host **14** showed the highest association constants (for 1:1 and 2:1 adducts) for Cl^-, while **13** bound strongly to AcO^- ion.

However, urea-containing tripodal receptors **16** and **17** of Steed and coworkers[38] proved to be effective anion-binding hosts and represented an improvement over the amine-based systems. The



urea motifs were observed to complex anions along with some crystallizing solvents as supported by X-ray crystal structures. The X-ray crystal structures of **16** containing different counteranions represent the different geometries of host (Fig 3). To understand the binding efficacy in solution, binding constant values were determined from ^1H NMR in d_6-DMSO. Selectivity for $H_2PO_4^-$ was observed over a series of anions such as Cl^-, Br^-, I^-, NO_3^-, AcO^-, HSO_4^-, $CF_3SO_3^-$ and ReO_4^-. Log binding constants for the 1: 1 and 1:2 host/guest complexes with $H_2PO_4^-$ were found to be 3.70 and 3.68, respectively. The values of binding constants obtained with **16** in d_6-DMSO were modest due to highly polar nature of the solvent. However, titrations of more soluble octyl-substituted host **17** in CD_3CN exhibited larger binding constants (for details see Table 1). Based on experimental observations, Steed *et al*., further mentioned that there were at least two binding processes occurring during the halide titration. The first equivalent of guest gave rise to 1:1 complex, in which the value of K_{11} was, in all cases, higher than K_{12} and K_{13}. This indicated that the initial binding event may be due to a chelation of the guest by the three arms, followed by situations in which each anion binds to separate arms.

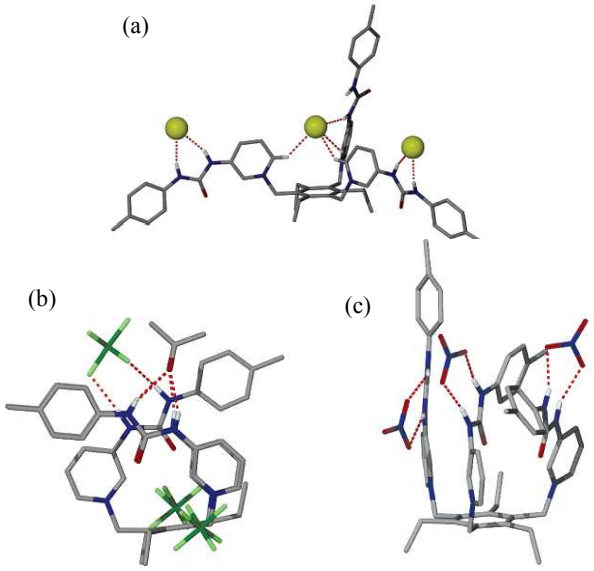
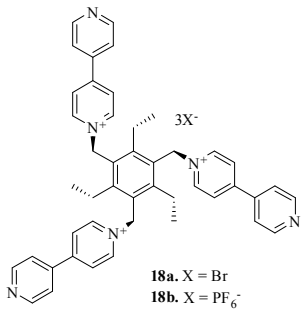


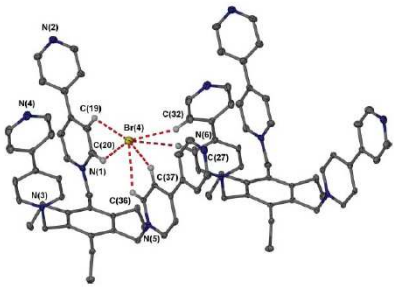
Fig 3. X-ray crystal structures of (a) bromide salt of **16** (three up conformation), (b) acetone solvate of PF_6^- salt of **16** (complexed acetone) and (c) NO_3^- complex of **16**. Reprinted with permission from Ref. 38. Copyright 2006 American Chemical Society.

In continuation, two new tripodal "pinwheel" type anion binding hosts based on a triethylbenzene core and bipyridinium unit **18a-b** were also reported by Steed *et al.*[39] These hosts complexed anions only *via* CH...anion interaction which was established by crystal structures (Fig 4a). Packing of the molecules revealed the inter host stacking (Fig 4b). ^1H NMR titration of tripod **18a** with disodium salt of ATP in D_2O/CD_3CN (1:1, v/v) resulted in significant changes to the pyridyl proton resonances. A good fit to a 1:1 binding model gave the binding constant value of 70 M^{-1}. The influence of charge-charge and π-stacking interactions played the crucial role in this recognition process.



18a. X = Br
18b. X = PF_6^-

(a)



(b)

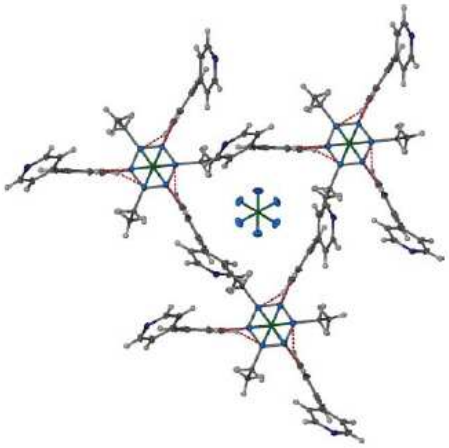
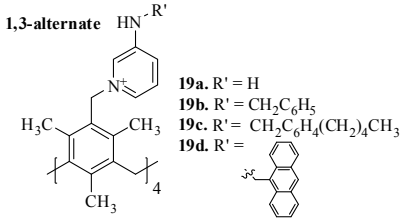
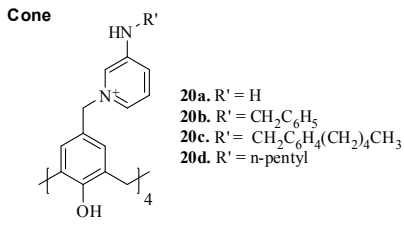


Fig 4. Crystal structures of (a) **18a** and **18b** (Reproduced from Ref. 39).

Whenever the triethylbenzene core is replaced by calixarene unit, the pyridinium-based hosts are found to be versatile in anion binding. Two types of calix[4]arene derived pyridinium-based hosts **19a-d** and **20a-d** were reported by Steed *et al.*[40]



19a. R' = H
19b. R' = $CH_2C_6H_5$
19c. R' = $CH_2C_6H_4(CH_2)_4CH_3$
19d. R' =



20a. R' = H
20b. R' = $CH_2C_6H_5$
20c. R' = $CH_2C_6H_4(CH_2)_4CH_3$
20d. R' = n-pentyl

Interestingly, while the 1,3-alternate system **19** bound dicarboxylate anions in a ditopic manner following 2:1 guest: host ratio, the cone compound **20** was deprotonated by carboxylates. The ditopic 1,3-alternate host **19c** binds malonate with K_a = 58,800 M^{-1} in CH_3CN/DMSO (60:40, v/v) with 1:2 (host:guest) ratio. The malonate anions were chelated by a pairs of pyridinium arms *via* NH...O and CH...O interactions as shown in Fig. 5. In contrast, the cone compounds due to lack of cooperativity between the arms bound small spherical anions. They were observed to bind Br^-, NO_3^- ions strongly.

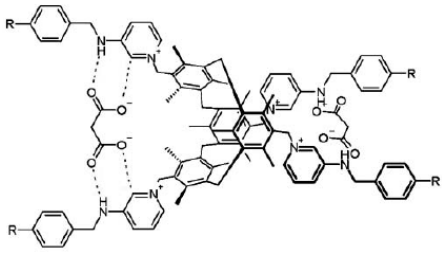
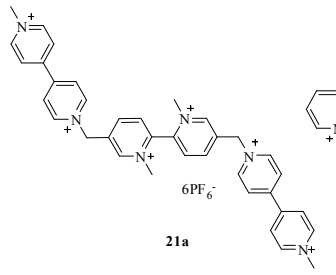
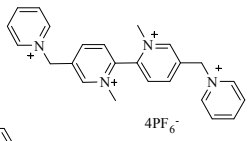


Fig 5. Binding structure of **19c** with malonate.

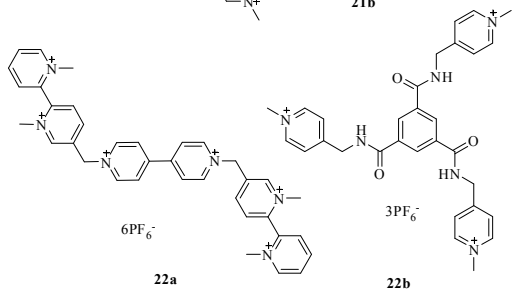
In lieu of 3-aminopyridine, quaternary bispyridinium and polypyridinium compounds **21** – **22** were also employed in anion binding.[41] ^{1}H NMR studies in d_6-DMSO revealed that the compounds have the affinity for Cl^- ion. Of the different structures, tripodal structure **22b** showed the strongest affinity for Cl^- ions (K_a = 110 M^{-1}). Due to the presence of redox active 4,4'-bipyridinium moiety, in electrochemical study the structure **22a** exhibited significant cathodic shift upon addition of Cl^- ions (ΔE = 130 mV).



21a



21b



22a **22b**

Tuning of the structural features of polypyridinium compounds introduced some new viologen – based receptors **23**-**24**.[42] NMR titration results in CD_3CN intimated that the hosts bind to two Cl^- ions with log K_{11} = 3.95 and log K_{12} = 3.21 for **23**, and log K_{11} = 3.55 and log K_{12} = 3.39 for **24**. Interestingly, binding of carboxylate anions, particularly acetate, malonate and succinate by pyridinium derivative **23** in CH_3CN resulted in an intense purple colouration (Fig 6a). Theoretical calculation on

representative system **23**.malonate revealed that the origin of color was due to charge-transfer from the anion to the bipyridinium unit. In contrast, anion binding by **24** did not initially result in colour change because anions were complexed at the periphery of the receptor. But addition of more than two equivalents of acetate or more than one equivalent of dicarboxylates gave intense pink color (Fig 6b).

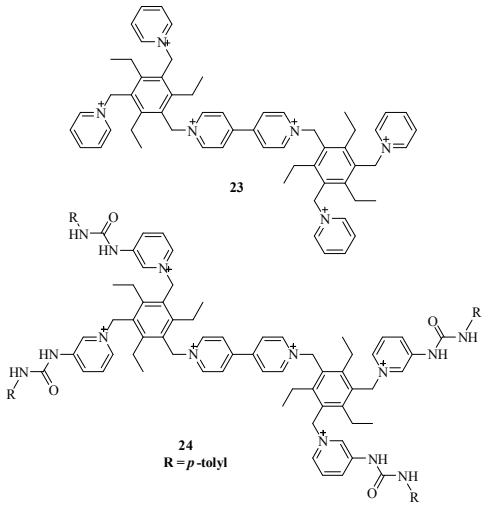
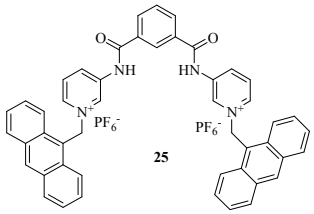


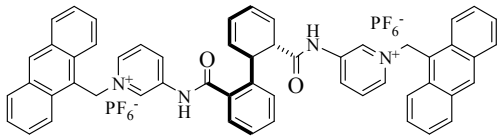
Fig 6. Change in color of the host solutions (c = 1 x 10^{-4} M): (a) host **23** in presence of 1 equiv. of tetrabutylammonium succinate, malonate, acetate, chloride, bromide, nitrate and perrhenate (from left to right); (b) host **24** with 4 equiv. of same anions (from left to right). Reproduced from Ref. 42 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Our group exhaustively used the pyridinium motif in building up a series of synthetic receptors which showed potentiality in anion binding. Simple design **25** from our group strongly bound basic anions such as AcO^-, $H_2PO_4^-$ and F^- with affinity constant on the order of 10^4 M^{-1} in CH_3CN.[43] Analysis of the fluorescence behaviour of **25** towards a series of anions interpreted that the

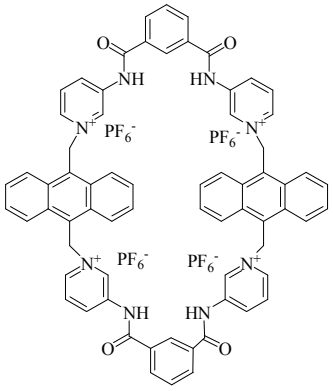


cleft of **25** can distinguish aliphatic carboxylates form aromatic carboxylates and is also able to report the selective binding of tetrahedral shaped $H_2PO_4^-$ ions through strong excimer formation between the pendant anthracenes.

Change of isophthaloyl spacer in **25** by biphenyl unit led to a new structure **26** that showed selective complexation of isophthalate and $H_2PO_4^-$.[44] Addition of $H_2PO_4^-$, HSO_4^- and isophthalate to the solution of **26** in $CHCl_3$ containing 2% CH_3CN caused change in monomer emission of anthracene followed by appearance of excimer. The greater intensity of the excimer emission in the presence of $H_2PO_4^-$ distinguished it from the other anions. Analysis of the fluorescence titration results revealed the K_a value of 1.22 x 10^4 M^{-1} for $H_2PO_4^-$. It is mentionable that such anthracene labelled bispyridinium diamide not only shows propensity for dihydrogenphosphate sensing but also exhibits good interaction with DNA. The compounds of this class are cell permeable and useful for cell staining.[45]

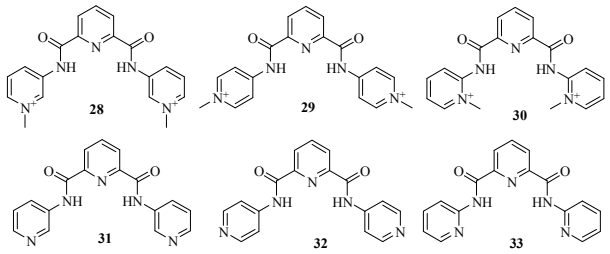


The tuning of the structure **25** was further done in our laboratory by macrocyclisation. The synergistic effect of hydrogen bonding, weak π-stacking and charge-charge interactions enabled the macrocycle **27** to complex 1,4-phenylenediacetate (K_a = 3.34 x 10^5 M^{-1}) selectively. During complexation a considerable increase in emission of anthracene was observed.[46]

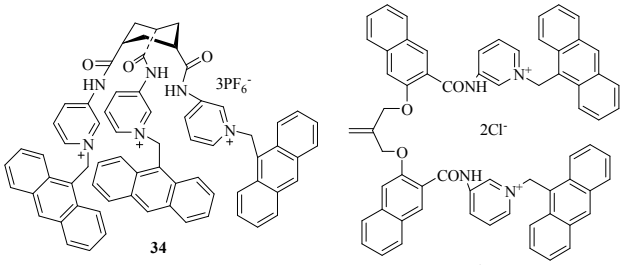


Referring our work on **25**, Yatsimirsky and co-workers reported a series of known isomeric dicationic *N*-methylated pyridyl derivatives[47] (**28** - **30**) of three isomers of *N,N'*-bis(pyridyl)-2,6-pyridine dicarboxamide **31** – **33**.[47] The binding of the cationic compounds were studied and compared with the neutral analogues. Cationic receptors offered higher affinity and selectivity for anions in CH_3CN (log K in the range 3.5-6.5) than their corresponding neutral versions. Indeed, the dicationic compounds showed pronounced selectivity for Cl^- ions and in some cases for AcO^-.[47] The stoichiometry of the complexes was established as 1:1 and also 1:2 (host:guest) which varied with the isomer. The solid state binding of the three isomers was also

highlighted by Yatsimirsky and co-workers. Analysis of four crystal structures of chloride and triflate complexes of the three isomers revealed the binding of anion in the cleft involving amide NH and CH – interactions.



On the other hand, based on the observation on receptor **25**, Gong *et al*. reported a tripodal fluorescent chemosensor **34** with 3-aminopyridinium as binding motif for $H_2PO_4^-$.[48] Upon complexation of $H_2PO_4^-$ the tripodal receptor **34** in CH_3CN/EtOH (9:1, v/v) gave a strong excimer which was diagnostic to distinguish $H_2PO_4^-$ from the other anions. In continuation the same group reported another chemosensor **35** by changing the spacer. The dipodal sensor **35** exhibited solvent polarity dependant conformational behaviour. They focused that intramolecular hydrogen bonding of the pyridinium *ortho* proton with the amide carbonyl oxygen regulated the cleft dimension and in both $CHCl_3$ and CH_3CN the sensor **35** selectively sensed $H_2PO_4^-$.[49a]



Gong *et al* also synthesized dipodal[49b] and tripodal[49c] receptors for colorimetric sensing of AcO^- over a series of other anions based on the utilization of amide-pyridinium as recognition site and nitro-benzene as signalling unit. Addition of AcO^- induced clear color change of the receptor solutions from colorless to yellow.

The rational design of unsymmetrical bispyridinium amide is another strategy to make anion binding host. In this regard, in 2011, we reported the hetero bisamide **36** which selectively recognised tetrabutylammonium benzoate over a range of aliphatic monocarboxylates in $CHCl_3$ containing 2% CH_3CN by showing concomitant increase in emission of pyrene. The

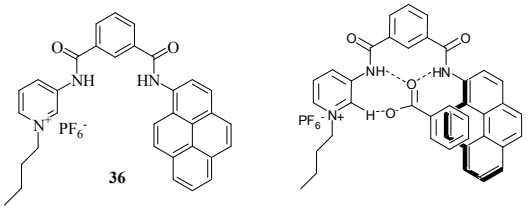
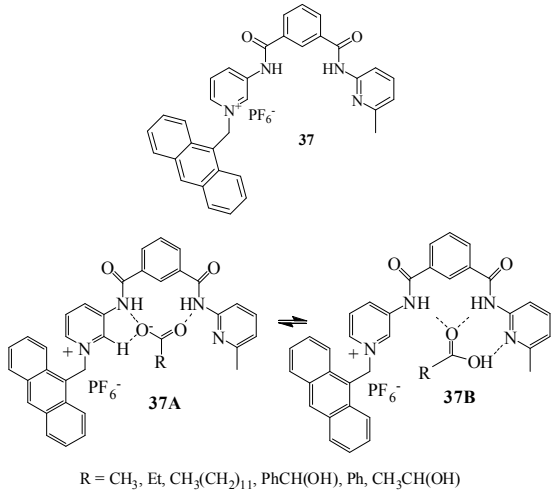


Fig 7. Suggested benzoate complex of **36**.

hydrogen bonding, charge-charge interaction and the π-stacking effect as displayed in Fig. 7 corroborated the selective sensing of benzoate (K_a = 3.46 x 10^3 M^{-1}). Moreover, the cleft of **36** showed selective sensing of HSO_4^- (K_a = 1.87 x 10^3 M^{-1}) over $H_2PO_4^-$ ion by exhibiting much change in emission of **36**.[50]

In continuation, we addressed another hetero bisamide **37** that contains anthracene in a selective position to create a PET (photoinduced electron transfer) sensor.[51] The fluorescent hetero bisamide **37** exhibited selective binding of monocarboxylates over their conjugate acids in spite of the presence of binding complementarity to both carboxylate and carboxylic acid (Fig 8).



R = CH_3, Et, $CH_3(CH_2)_{11}$, PhCH(OH), Ph, $CH_3CH(OH)$

Fig 8. Possible modes of complexation of **37** with carboxylates and carboxylic acids.

Binding analysis indicated that AcO^- (K_a = 1.16 x 10^4 M^{-1}) and $CH_3CH_2COO^-$ (K_a = 1.04 x 10^4 M^{-1}) anions were preferred in the cleft over their conjugate acids by giving significant change in emission (Fig 9).

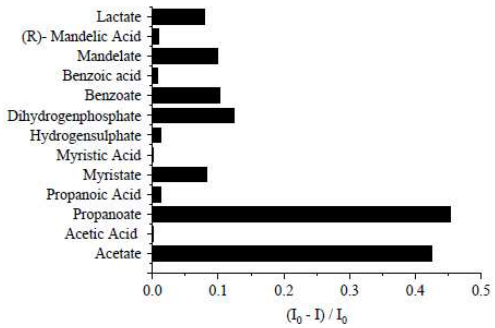


Fig 9. Change in fluorescence ratio of **37** (c = 6.27 x 10^{-5} M) at 412 nm upon addition of 2 equiv. of guests in CH_3CN. Reproduced from Ref. 51, permission is not yet received.

Of the different solvent combinations, 2% CH_3CN in $CHCl_3$ was a better choice for better selectivity in the recognition process. While the emission of **37** upon addition of aliphatic carboxylate guest in CH_3CN was perturbed to the lesser extent, it was found to be significant with a new emission at ~512 nm in less polar solvent $CHCl_3$ containing 2% CH_3CN. Figure 10 illustrates this

aspect. The binding affinity of the cleft of **37** for anion was further realized from the analysis of global electrophilic character by DFT calculation.[51]

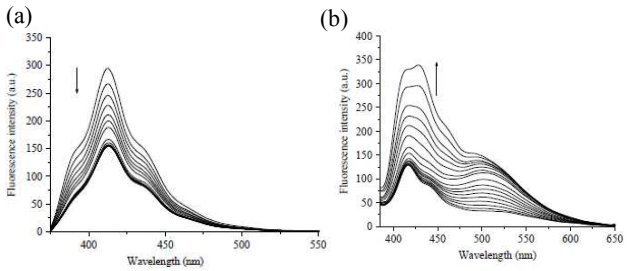
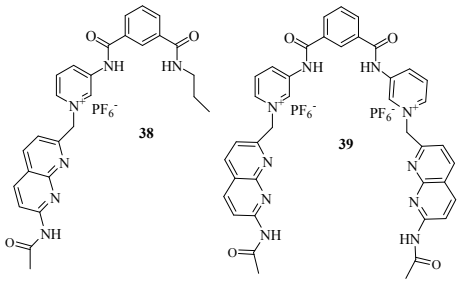
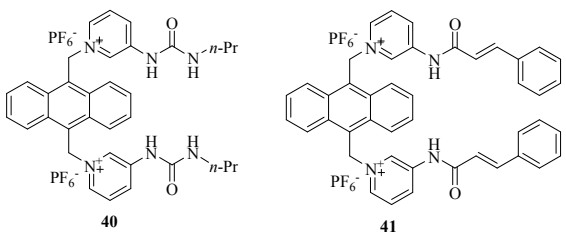


Fig 10. Change in emission of **37** (c = ~ 10^{-5} M) upon addition of (a) propanoate in CH_3CN and (b) acetate in $CHCl_3$ containing 2% CH_3CN. . Reproduced from Ref. 51, permission is not yet received.

The carboxylate binding affinity of the cleft of hetero bis amides as discussed above was further utilized in our laboratory in the selective sensing of tetrabutylammonium salt of biotin (K_a varies in between 10^2 M^{-1} and 10^4 M^{-1}) over biotin ester by naphthyridine appended pyridinium salts **38** and **39**.[52] Biotin is an essential cofactor for a number of enzymes that have diverse metabolic functions.[53] In spite of not using fluorophore, the emission feature of naphthyridine was used to assess the binding characteristics. The diamide clefts of the receptors bound carboxylate functionality involving NH...O, CH...O hydrogen bonds and charge-charge interactions. The bicyclic urea part of biotin was complexed by the pendant naphthyridine motifs due to which the emission of naphthyridine was enhanced considerably. The fluorometric titration was carried out in CH_3CN containing 1.2% DMSO. Binding was also understood by ^1H NMR titration. The unsymmetrical receptor **38** gave improved binding over the symmetrical diamide **39**. The less steric feature at the naphthyridine site in **38** allowed comfortable binding of the bicyclic urea part of biotin.



In an effort to recognise dicarboxylates (larger anions), the ureidopyridyl groups were coupled with anthracene unit to make chemosensor **40**. ^1H NMR, fluorescence and UV-vis studies



established the compound **40** as a selective sensor for 1,4-phenylenediacetate (log K = 8.93) over a series of other aliphatic dicarboxylates in DMSO.[54]

Based on this observation, we further moved to another new system **41** where the ureidopyridyl unit is replaced by *trans*-pyridylcinnamide. *Trans*-pyridylcinnamide motif was used as an alternative of urea to make hydrogen bonded complex with the carboxylate in the mode shown in Fig. 11. However, the sensor **41** showed moderate selectivity for long chain pimelate over a wide range of dicarboxylates by exhibiting good fluorescence 'On-Off' switchability. The switching mode was noted to be reverse to that of urea analogue **40**. The interplay of N-H...O, C-H...O hydrogen bonds and charge-charge interactions contribute to the selectivity in the recognition process.[55]

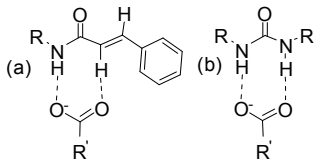
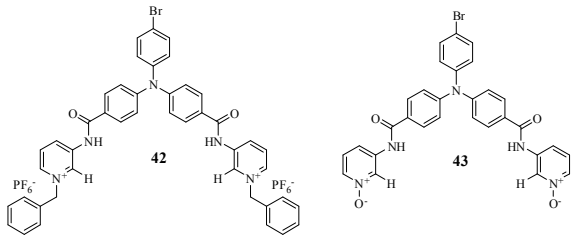


Fig 11. Hydrogen bonded complexes of carboxylate with (a) cinnamide and (b) urea derivatives.

Instead of anthracene, triphenylamine was used in building up pyridinium-based ditopic receptor **42** for dicarboxylates.[56] In the design, the triphenylamine acts as spacer as well as fluorescent probe to illustrate the recognition process. From fluorescence titration the open cleft of receptor **42** was selective for pimelate (log K = 5.00 ± 0.01). Upon complexation (suggested mode in shown Fig.12) the emission intensity gradually decreased to the significant extent. In comparison, under similar condition the pyridine-N-oxide analogue **43** was less efficient in the recognition process. This experimental fact indicated the greater electrophilic character of the pyridinium amide for complexation of anion. This was further explained by calculating the global electropilicity using DFT calculation.



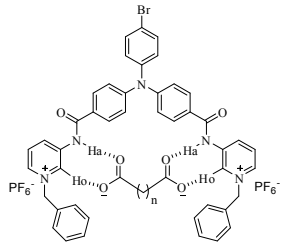


Fig 12. Suggested binding mode of dicarboxylate in the cavity of **42**.

Variation of the synthetic spacer in the designed-molecule draws attention. The placement of pyridinium motifs on *ortho*-phenylenediamide core resulted in compound **44**[57] which bound selectively $H_2PO_4^-$ in CH_3CN giving excimer emission at 456 nm due to π-π stacking between the pendant naphthalene units. The sensor **44** also fluorometrically distinguished ATP from ADP and AMP in $CH_3CN–H_2O$ (1: 1, v/v) at pH 6.5 by exhibiting a more intense band of exciplex formed due to favorable stacking of the adenine ring in between the pendant naphthalenes (Fig. 13).

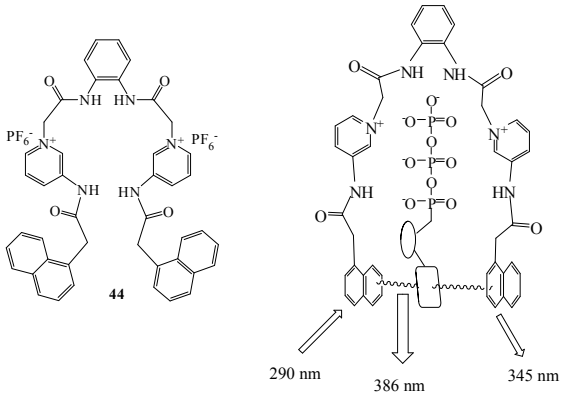
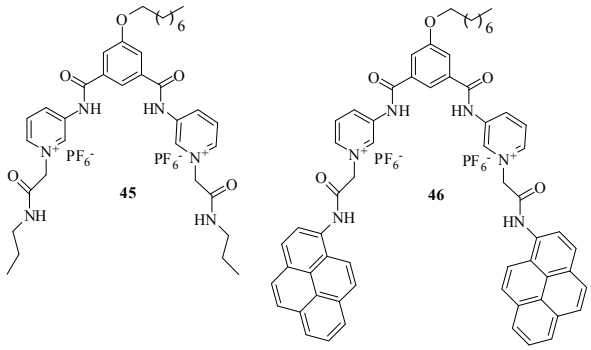


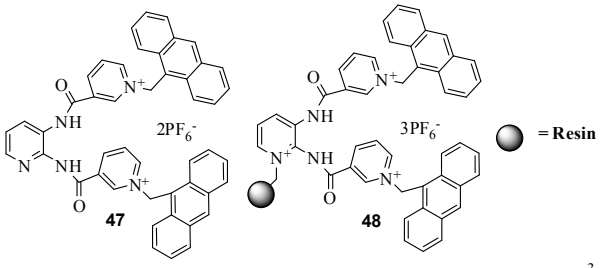
Fig 13. Possible binding structure of **44** with ATP.

The pyridinium-based architectures were also used in Indicator displacement assay (IDA) technique for sensing of anions. In this technique, an indicator is first allowed to bind reversibly to a receptor and then a competitive analyte is introduced into the system causing the displacement of the indicator from the host which in turn modulates the optical signal.[58] Pyridinium-based symmetrical receptors **45** and **46** for the first time were applied in IDA technique for the selective sensing of carboxylate guests.[59]



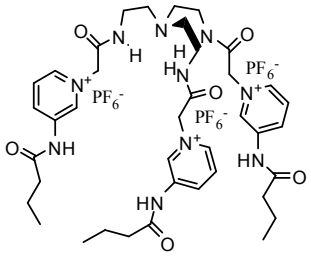
Both the receptors responded in CH_3CN/H_2O (4:1, v/v) at pH 6.3 for the selective naked-eye detection of citrate over a series of guests. Additionally, receptor **46** (c = 6.29 x 10^{-3} M) formed stable gel selectively with citrate in CH_3CN. It was focused that conventional N-H...O and unconventional C-H...O hydrogen bonds, charge-charge interactions and pyrene with large π-surface interplayed altogether to set up a network in solution in the presence of citrate for which gelation took place. The non responsive behaviour of **45** in formation of gel indicated the role of pyrene in **46**. However, both the receptors gave binding constant values of the order of 10^4 M^{-1} with 1:1 stoichiometry.

Using the IDA technique, tetrabutyammonium hydrogenphosphate was recognized over a series of other anions in both CH_3CN and aq. CH_3CN (CH_3CN: H_2O = 4:1, v/v, pH = 6.5) by receptor structures **47** and **48**.[60] In the unsymmetrical receptors, pyridinum motifs were manipulated using 3-picolinic acid. Compound **47** showed binding constant value of (9.59 ± 1) x 10^4 M^{-1} for $HP_2O_7^{3-}$. However, the Merrifield resin supported bead **48** was of practical use to detect $HP_2O_7^{3-}$ by naked eye in CH_3CN:H_2O (4:1 v/v) as well as in pure water at pH 6.5 *via* IDA technique. Moreover, the experiments with blood serum



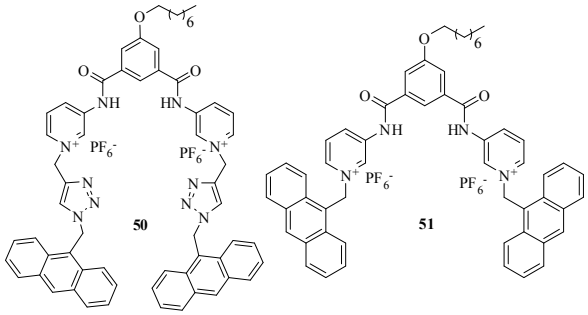
suggested that the sensor bead **48** is capable of sensing $HP_2O_7^{3-}$ selectively in complex biological system. It is to be pointed out that the selective detection of hydrogen pyrophosphate or pyrophosphate (PPi) is an important aspect in supramolecular chemistry research. PPi is a biologically important target which arises from ATP hydrolysis under cellular conditions.[61] It is involved in DNA sequencing/replication etc.[62] It has physiological relevance in energy storage and signal transduction. Therefore, the detection of PPi has become important in cancer research.[62,63] Patients with calcium pyrophosphate dehydrate (CPPD) crystals and chondrocalcinosis are usually found to have a high synovial fluid PPi level.[64]

Following IDA technique using uranine dye, water soluble tripodal receptor **49** was established from our laboratory as chemosensor for the naked eye recognition of AMP (**K_a** = 5.96 x 10^3 M^{-1}) over ADP and ATP in aqueous environment.[65] Complexation of AMP was supported by both experimental and theoretical investigations. Furthermore, the tripod was used to recognise the intercellular AMP as well as ALP mediated conversion of ATP/ADP *via* IDA technique.

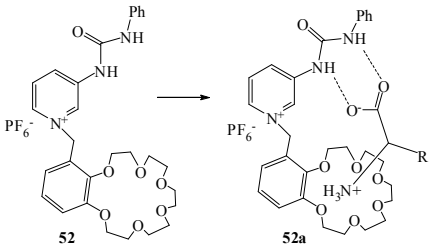


Modification of the substituent of pyridine ring nitrogen by using 1,2,3-triazole ring which is surrogate of amide was also performed and structure **50** was synthesized in our laboratory. The receptor structure **50** selectively recognized $H_2PO_4^-$ by exhibiting ratiometric change in emission and formed stable gel in $CHCl_3$ containing 10% CH_3CN. This was useful in visual sensing of $H_2PO_4^-$.[66a] In comparison, receptor **51** which is devoid of triazole motif did not form gel with $H_2PO_4^-$ under similar condition. Upon interaction with $H_2PO_4^-$, the intensity of

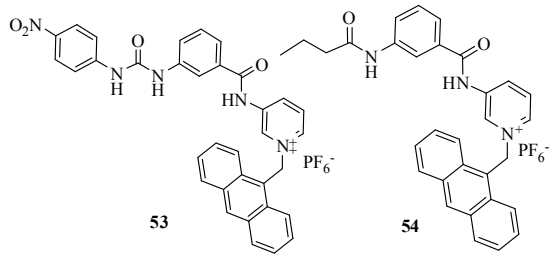
monomer and excimer emission peaks of **51** increased markedly without giving any ratiometric nature in the spectra. Moreover, F^- ion induced greater quenching of monomer emission in both **50** and **51** in non ratiometric manner distinguished it from other anions examined. These observations underlined the key role of the triazole ring in **50** in the recognition of anion. Indeed, triazole is a well established motif in anion binding.[66b] Job's plot analysis of the flurescence titration spectra gave 2:1 (Guest: Host) complex between $H_2PO_4^-$ and **50**. This was also true for F^-. On the basis of 2:1 stoichiometry in the excited state, the association constants of **50** for $H_2PO_4^-$ and F^- were established to be (K_{11} = 2.45 ± 0.1 x 10^4 M^{-1}, K_{12} = 2.21 ± 0.1 x 10^4 M^{-1}) and (K_{11} = 1.06 ± 0.08 x 10^4 M^{-1}, K_{12} = 8.21 ± 0.8 x 10^3 M^{-1}), respectively. The receptor **51** followed 2:1 (Guest: Host) binding stoichiometries with both $H_2PO_4^-$ and F^- in the excited state like that of **50** and gave relatively lower binding constant values [(K_{11} = 2.09 ± 0.16 x 10^4 M^{-1}, K_{12} = 1.40 ± 0.12 x 10^4 M^{-1} for $H_2PO_4^-$) and (K_{11} = 1.84 ± 0.40 x 10^4 M^{-1}, K_{12} = 5.19 ± 0.16 x 10^3 M^{-1} for F^-)].



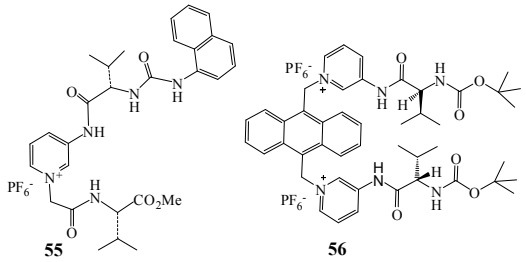
Pyrdinium-based receptor module has also been used to bind zwitterionic α-amino acids. In this context, Jeong *et al*. made a new simple compound **52** which is composed of two components namely, benzo-18-crown-6 and urea functionality for binding the ammonium and carboxylate groups of zwitterionic α-amino acids (**52a**), respectively.[67] They examined the amino acid binding property by solid-liquid and liquid-liquid extractions at 24±1 °C and also applied it in the transportation of amino acids across a $CHCl_3$ liquid membrane. The transport efficiency was established as Phe > Trp > Ile > Leu > Val >> Ala > Ser >> Asp, His.



For fluorometric sensing of a particular α-amino acid derivative, pyridinium amide was used in conjunction with urea motif by our group using the PET sensor **53**.[68] Fluorescence studies of **53** in CH_3CN (λ_{ex} = 370 nm) revealed a moderate quenching of the emission at 415 nm upon addition of L-*N*-acetylproline, (S)-mandelate, pyruvate, and L-*N*-acetylglycine, whereas L-*N*-acetylalanine and L-*N*-acetylvaline resulted in increase of emission along with the appearance of a broad emission at 492 nm of moderate intensity. The peak at 492 nm which was more significant in presence of L-*N*-acetylvaline than L-*N*-acetylalanine, was attributed to the formation of a charge transfer complex between the excited state of anthracene and the electron deficient nitrophenyl urea. This was confirmed by considering amide-amide analogue **54**. Fluorometric titrations revealed 1:1 binding of L-*N*-acetylvaline (K_a = 2.60 x 10^3 M^{-1}) with receptor **53** in CH_3CN.



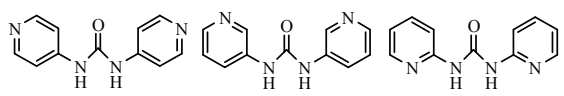
Attachment of chiral amide or urea segment to the side chain of the 3-aminopyridinium unit resulted in chiral sensors such as **55** and **56**. The chiral receptors were found to be useful in chiral recognition of hydroxyl carboxylates such as lactate and tartrate.



Synthetic fluorescent chemosensor that discriminates the enantiomers of a particular chiral guest by exhibiting different fluorescence behaviors draws attention in the area of molecular recognition. The simple pyridinium-based chiral receptor **55** containing L-valine as the chiral source fluorometrically recognizes D-lactate [(K_a = 4.17 ± 0.7) x 10^3 M^{-1}] over L-lactate in CH_3CN with enantiomeric fluorescence ratio (*ef*) of 5.32.[69] While upon gradual addition of D-lactate to the solution of **55** the monomer emission at ~400 nm increases significantly, a small increase in emission with the addition of L-lactate was observed. Similarly, using L-valine as chiral source anthracene-based chiral chemosensor **56** was established as efficient enantioselective sensor for L-tartrate (ef = 29.38) over D-tartrate in DMSO.[70] In the presence of tetrabutylammonium salt of L-tartaric acid the monomer emission of **56** at 432 nm was considerably enhanced giving a binding constant value of (6.31 ± 0.05) x 10^3 M^{-1}.

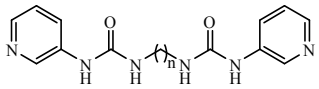
The versatility of pyridinium motif in molecular recognition is commendable. It cannot be completed if its use in gel chemistry is not discussed. Gels are considered as viscoelastic solid or liquid like materials (called gelators), comprised of cross-linked networks and a solvent, the major component. Multiple non-covalent interactions among the gelators are the key to establish the network in solution. For this, several functional groups are found in gelator molecules. Usually amide, hydroxyl and urea groups are incorporated into the structures of gelators for the

formation of self-associated chains that contribute to the gelation of solvent molecules.[71] In 2003, Kato *et al.,* reported some pyridyl ureas that acted as gelators and produced fibrous self-assembly.[72] Dostidar and co-workers investigated the gelation properties of the pyridyl ureas such as **57**, **58** and **59**.[73] Among the three, only compound **57** exhibited gelation ability in pure water. The isomeric compounds **58** and **59** are non gelators. A theoretical calculation on this aspect was recently done by Xie *et al.*[74] They have studied the conformational and hydrogen bonding behaviours of the three isomers (**57**, **58** and **59**) in details.



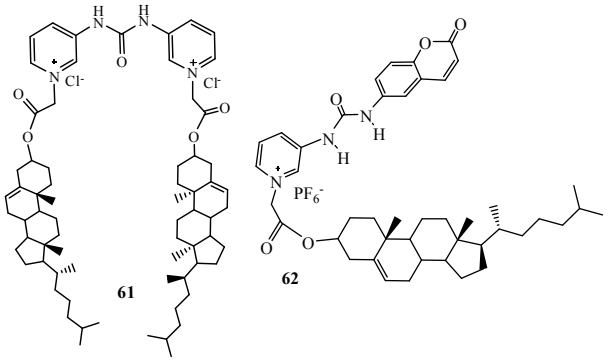
57 **58** **59**

Bispyridyl ureas **60** with flexible linkers also ordinarily did not show any gelation property. But on interaction with both Ag^+ and Cu^{2+} salts they exhibited gelation tendency. Cross linking role of the metals introduced gelation of the systems.[75]



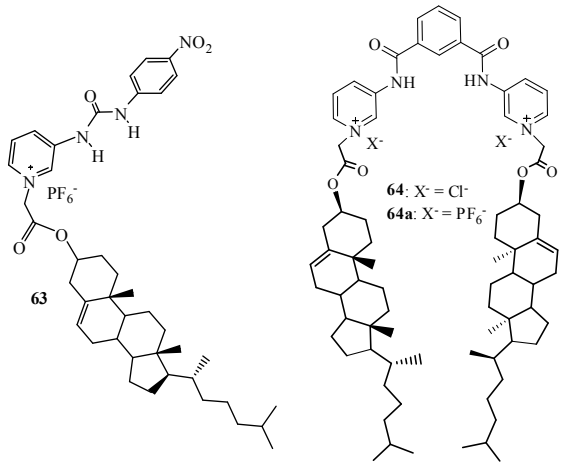
60 n = 2-8

Besides the metal ions, the introduction of the cholesteryl unit onto the pyridine ring nitrogen in dipyridyl urea **58** modified its gelation property. In relation to this, compound **61** was observed to exhibit gelation in $CHCl_3$.[76] The gel was anion responsive. In the presence of F^- the gel state was transformed into the sol and validated the visual sensing of F^-. On the other hand, unsymmetrical pyridyl urea salt **62** fluorimetrically distinguished F^- from the other anions in both CH_3CN and DMSO with appreciable binding constant values.[76] Interestingly, while the compound **62** formed gel in DMSO in the presence of F^-, compound **61** underwent transition from gel to sol state in $CHCl_3$ in the presence of same anion. Usually anions are gel breaker. But the appearance of gel in the presence of F^- in case of **62** is



61 **62**

noteworthy. We explained this due to effective aggregation of gelators. The dianionic species obtained from fluoride induced deprotonation of urea motif in **62** and the resulting HF_2^- are involved in intermolecular contacts to set up a network in solution. The stabilization of network is influenced by large hydrophobic surface of the cholesterol part. Replacement of the coumarin substituent in **62** by nitrophenyl motif resulted in a similar type of compound **63** which acted as low molecular weight gelator in DMSO:H_2O (1:1, v/v) in the presence of F^- (Fluoride source: KF, NaF, CsF and tetrabutylammonium fluoride).[77] During gelation the color change was useful in naked eye detection of F^-. The deprotonation of urea proton and subsequent delocalization of the charge to the nitrophenyl motif introduced the color change. Furthermore, the gel state was reported to be good semiconductor and also a medium to detect Cu^{2+} and Pb^{2+} ions by showing a transition from gel to sol.



63 **64**: $X^- = Cl^-$ **64a**: $X^- = PF_6^-$

Not only the pyridinium ureas but also cholesterol appended bis pyridinium amides were found to be interesting as low molecular weight gelator. Recently, we have demonstrated that cholesterol appended pyridinium diamide **64** gives instant gel from chloroform.[78] The gel is pH responsive and exhibits ionic conductivity due to movement of unrestricted Cl^- ions within the network. The gel acted as a media to recognize Ag^+ ion over a series of other cations by exhibiting gel to sol transformation. The gel state reappeared in the presence of chloride salt and indicated the reversibility in the process. It was further observed that hexafluorophosphate analogue **64a** which was obtained from **64** on anion exchange allowed the selective recognition of Cl^- over other halides by forming transparent yellow colored gel in $CHCl_3$.

Conclusion

Significant progress in the design and synthesis of receptors (both non fluorescent and fluorescent) of various architectures based on pyridinium motif has been made over the past several years. The approach of using 3-aminopyridine and related derivatives has provided different strategies for the design of chemosensors for the recognition of anions such as halides, phosphate derivatives, phosphate-based nucleotides, DNA, dicarboxylates etc. The enantioselective sensing of hydroxyl carboxylates by pyridinium –based chiral fluororeceptors has also been explored. It has also been observed that incorporation of hydrophobic surfaces into pyridinium-based urea or amide receptors draws much attention as the compounds of this class are useful in gel chemistry. Gels are stimuli responsive and much appealing in anion recognition. Though an increasing number of receptors/probes have been developed based on 3-aminopyridine unit, further developments in the fabrication of new sensing systems (e.g., chiral receptors, stimuli responsive gelators, nano particle- hooked sensors etc.)

with high sensitivity and selectivity are still desired. Moreover, in continuation of our work on the systems **47** and **48**, there is enough scope to use 3-aminopyridine to develop solid supported receptor beads that are to be useful to detect anions in aqueous environment.

Acknowledgements

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Table 1. Binding characteristics of different pyridinium –based hosts.

Receptors	Binding constant (K_a) values with some selected anions (host:guest stoichiometry, solvent and methods used)
1, **2**, **3**, **4**, **5**(Jeong*et al* ; Ref. 35)	**1** with $PhCOO^-$: K_a = 16 M^{-1} (1:1, d_6-DMSO, ^{1}HNMR) **2** with $PhCOO^-$: K_a = 300 M^{-1} (1:1, d_6-DMSO, ^{1}HNMR) **3**, **4** and **5** individually withadipate: K_a> 5 x 10^5 M^{-1} (1:1, d_6-DMSO, ^{1}HNMR) **3**, **4** and **5** individually withadipate: K_a> 10^3 M^{-1} (1:1, 10% D_2O/DMSO, ^{1}HNMR). (Anions were used as $N^nBu_4^+$ salts.)
6 and **7** (Fabbrizzi*et al;* Ref. 36)	**6** with CH_3COO^-, F^- and $H_2PO_4^-$: log K_a >6 (1:1, DMSO, UV-vis) **7** with CH_3COO^-: logK_a = 5.10 ± 0.05 (1:1, DMSO, UV-vis) **7** with F^-: log K_a = 4.77 ± 0.02 (DMSO; UV-vis) **7** with $H_2PO_4^-$: log K_a = 3.11 ± 0.01 (DMSO; UV-vis) (Anions were used as $N^nBu_4^+$ salts.)
8a-g, **9**, **10**, **11** and **12** (Steed *et al*; Ref. 37a)	**8a** with Br^-: K_{11} = 850 M^{-1} (1:3; CD_3CN, ^{1}HNMR) **8c** with Cl^-: K_{11}> 100 000 M^{-1} (1:3; CD_3CN, ^{1}HNMR) **8c** with Br^-: K_{11} = 13800 M^{-1} (1:3; CD_3CN, ^{1}HNMR) **8c** with AcO^-: K_{11} = 10 500 M^{-1} (1:3; CD_3CN, ^{1}HNMR) **8c** with Cl^-: K_{11} = 15 M^{-1} (1:3; d_6-DMSO, ^{1}HNMR) **8d** with Cl^-: K_{11} = 8 M^{-1} (1:3; d_6-DMSO, ^{1}HNMR) **8c** with Cl^-: K_{11} = ca. 82 000 M^{-1} (1:3; d_6-DMSO/CD_3CN 50% v/v, ^{1}HNMR) **8d** with Cl^-: K_{11} = ca. 3000 M^{-1} (1:3; d_6-DMSO/CD_3CN 50% v/v, ^{1}HNMR) **9** with Cl^-: K_{11} = 17,380 M^{-1}(1:3; CD_3CN, ^{1}HNMR) **9** with AcO^-: K_{11} = 3680 M^{-1}(1:3; CD_3CN, ^{1}HNMR) **10** with CH_3COO^-: K_{11} = 49,000 M^{-1}(1:3; CD_3CN, ^{1}HNMR) **11** with Br^-: K_{11} = 17 M^{-1}(1:3; CD_3CN, ^{1}HNMR) **12** with CH_3COO^-: K_{11} = 7 M^{-1} (1:3; CD_3CN, ^{1}HNMR) (Anions were used as $N^nBu_4^+$ salts.)
13, **14** and **15** (Steed *et al*; Ref. 37b)	**13** with Cl^-: log K_a = 9.2 ± 0.3 (2:1; CH_3CN, UV-vis); log K_a = 4.2 ± 0.1 (1:1; CH_3CN, UV-vis) **13** with AcO^-: log K_a = 12.7 ± 0.2 (2:1; CH_3CN, UV-vis); log K_a = 6.0 ± 0.3 (1:1; CH_3CN, UV-vis); log K_a = 10.5 ± 0.3 (1:2; CH_3CN, UV-vis) **13** with succinate: log K_a = 5.0 ± 0.2 (1:1; CH_3CN, UV-vis) **13** with malonate: log K_a = 5.4 ± 0.2 (1:1; CH_3CN, UV-vis) **14** with Cl^-: log K_a = 12.1 ± 0.4 (2:1; CH_3CN, UV-vis); log K_a = 5.7 ± 0.3 (1:1; CH_3CN, UV-vis) **14** with AcO^-: log K_a = 11.6 ± 0.3 (2:1; CH_3CN, UV-vis); log K_a = 5.5 ± 0.2 (1:1; CH_3CN, UV-vis); log K_a = < 4(1:2; CH_3CN, UV-vis) **14** with succinate: log K_a = 10.5± 0.6(1:1; CH_3CN, UV-vis);); log K_a = 5.3 ± 0.3 (1:1; CH_3CN, UV-vis); log K_a = < 4(1:2; CH_3CN, UV-vis) **14** with malonate: log K_a = 10.0 ± 0.3(2:1; CH_3CN, UV-vis); log K_a = 4.7± 0.3 (2:1; CH_3CN, UV-vis) **15** with Cl^-: log K_a = 4.2 ± 0.2 (1:1; CH_3CN, UV-vis); log K_a = 7.7 ± 0.4 (1:2; CH_3CN, UV-vis) **15** with AcO^-: log K_a = 3.8 ± 0.2 (2:1; CH_3CN, UV-vis); log K_a = 5.6 ± 0.2 (1:1; CH_3CN, UV-vis); log K_a = < 4(1:2; CH_3CN, UV-vis) **15** with succinate: log K_a = 5.5 ± 0.1 (1:1; CH_3CN, UV-vis);); log K_a = 11.2 ± 0.2(1:2; CH_3CN, UV-vis) **15** with malonate: log K_a = 5.2 ± 0.1 (1:1; CH_3CN, UV-vis); log K_a = 11.2± 0.2(2:1; CH_3CN, UV-vis) (Anions were used as $N^nBu_4^+$ salts.)
	16 with Cl^-: log K_{11} = 2.64, log K_{12} = 2.18, log K_{13} = 1.40 (1:3; d_6-DMSO, ^{1}H NMR) **16** with Br^-: log K_{11} = 3.46, log K_{12} = 2.99, log K_{13} = 1.21 (1:3; d_6-DMSO, ^{1}H NMR) **16** with I^-: log K_{11} = 1.61, log K_{12} = 0.60, log K_{13} = 1.05 (1:3; d_6-DMSO, ^{1}H NMR) **16** with NO_3^-: log K_{11} = 2.54, log K_{12} = 2.22, log K_{13} = 0.68 (1:3; d_6-DMSO, ^{1}H NMR)

16 and **17** (Steed *et al*; Ref. 38)	**16** with AcO^-: log K_{11} = 3.21, log K_{12} = 3.70(1:1 and 1:2; d_6-DMSO, ^1H NMR) **16** with $H_2PO_4^-$: log K_{11} = 3.70, log K_{12} = 3.68(1:1 and 1:2; d_6-DMSO, ^1H NMR) **17** with Cl^-: log K_{11} = 3.85, log K_{12} = 1.96, log K_{13} = 2.93 (1:3; CD_3CN, ^1H NMR) **17**. Br^-: log K_{11} = 3.62, log K_{12} = 2.24, log K_{13} = 1.96 (1:3; CD_3CN, ^1H NMR) **17**. NO_3^-: log K_{11} = 3.46, log K_{12} = 2.66, log K_{13} = 1.89 (1:3; CD_3CN, ^1H NMR) **17**. AcO^-: log K_{11} = 4.61, log K_{12} = 2.30, log K_{13} = 3.67(1:3; CD_3CN, ^1H NMR) (Anions were used as $N^nBu_4^+$ salts.)
18a and **18b** (Steed *et al*; Ref. 39)	**18a**. Na_2ATP: K_a = 70 M^{-1} [1:1; D_2O/CD_3CN (1:1, v/v), ^1H NMR]
19a-d and **20a-d** (Steed *et al*; Ref. 40)	**19c**. Br^-: K_{11} = 446 M^{-1}, K_{12} = 467 M^{-1} (1:2; CD_3CN, ^1H NMR) **19c**. NO_3^-: K_{11} = 3090 M^{-1}, K_{12} = 302 M^{-1} (1:2; CD_3CN, ^1H NMR) **20c**. Br^-: K_{11} = 24 550 M^{-1}, K_{12} = 1990 M^{-1} (1:2; CD_3CN, ^1H NMR) **20c**. NO_3^-: K_{11} = 51 290 M^{-1}, K_{12} = 912 M^{-1} (1:2; CD_3CN, ^1H NMR) **19c**.malonate: K_{11} = 58 800 M^{-1}, K_{12} = 83 M^{-1} [1:2; CD_3CN/d_6-DMSO (60/40, v/v), ^1H NMR] **19c**.malonate: K_{11} = 2720 M^{-1}, K_{12} = 15 M^{-1} (1:2; d_6-DMSO, ^1H NMR) **19c**. succinate: K_{11} = 2690 M^{-1}, K_{12} = 37 M^{-1} (1:2; d_6-DMSO, ^1H NMR) (Anions were used as $N^nBu_4^+$ salts.)
21a-b and **22a-b** (Beer *et al*; Ref. 41)	**21a**. Cl^-: K_a = 40 M^{-1} (1:1; d_6-DMSO, ^1H NMR) **22b**. Cl^-: K_a = 110 M^{-1} (1:1; d_6-DMSO, ^1H NMR)
23 and **24** (Steed *et al*; Ref. 42)	**23**. Cl^-: log K_{11} = 3.95, log K_{12} = 3.21 (1:2; CD_3CN, ^1H NMR) **24**. Cl^-: log K_{11} = 3.55, log K_{12} = 3.39 (1:2; CD_3CN, ^1H NMR) (Anions were used as $N^nBu_4^+$ salts.)
25 (Ghosh *et al*; Ref. 43)	**25**. F^-: K_a = 1.85 x 10^3 M^{-1} (1:1; CH_3CN, fluorescence) **25**. $H_2PO_4^-$: K_a = 1.03 x 10^4 M^{-1} (1:1; CH_3CN, fluorescence) **25**. AcO^-: K_a = 6.99 x 10^3 M^{-1} (1:1; CH_3CN, fluorescence) **25**. propanoate: K_a = 5.07 x 10^3 M^{-1} (1:1; CH_3CN, fluorescence) **25**. $C_6H_5COO^-$: K_a = 4.12 x 10^2 M^{-1} (1:1; CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts.)
26(Ghosh *et al*; Ref. 44)	**26**. $H_2PO_4^-$: K_a = 1.22 x 10^4 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**. HSO_4^-: K_a = 2.36 x 10^3 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**.isophthalate: K_a = 2.73 x 10^3 M^{-1}(1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**. phthalate: K_a = 8.37 x 10^2 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**. terephthalate: K_a = 5.03 x 10^2 M^{-1}(1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**. glutarate: K_a = 1.71 x 10^2 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**. malonate: K_a = 3.52 x 10^2 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **26**. succinate: K_a = 6.95 x 10^2 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
27 (Ghosh *et al*; Ref. 46)	**27**. oxalate: K_a = 7.94 x 10^3M^{-1} (1:1; CH_3CN, fluorescence) **27**. adipate: K_a = 5.78 x 10^3M^{-1} (1:1; CH_3CN, fluorescence) **27**. pimelate: K_a = 2.59 x 10^4M^{-1} (1:1; CH_3CN, fluorescence) **27**.1,4-phenylenediacetate: K_a = 3.34 x 10^5M^{-1} (1:1; CH_3CN, fluorescence) **27**. terephthalate: K_a = 8.16 x 10^3M^{-1} (1:1; CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
28-**33** (Yatsimirsky *et al*; Ref. 47)	**28**. F^-: log K_a = 5.28 (1:1; CH_3CN, UV-vis) **28**. Cl^-: log K_a = 5.27 (1:1; CH_3CN, UV-vis) **28**. Br^-: log K_a = 5.24 (1:1; CH_3CN, UV-vis) **28**. I^-: log K_a = 3.80 (1:1; CH_3CN, UV-vis) **28**. $H_2PO_4^-$: log K_a = 4.20 (1:1; CH_3CN, UV-vis) **28**. AcO^-: log K_a = 4.40 (1:1; CH_3CN, UV-vis) **28**. NO_3^-: log K_a = 4.11 (1:1; CH_3CN, UV-vis) **29**. F^-: log K_a = 4.36 (1:1; CH_3CN, UV-vis) **29**. Cl^-: log K_a = 5.65 (1:1; CH_3CN, UV-vis) **29**. Br^-: log K_a = 4.29 (1:1; CH_3CN, UV-vis) **29**. I^-: log K_a = 3.57 (1:1; CH_3CN, UV-vis) **29**. $H_2PO_4^-$: log K_a = 5.18 (1:1; CH_3CN, UV-vis) **29**. AcO^-: log K_a = 5.38 (1:1; CH_3CN, UV-vis)

	29. NO_3^-: log K_a = 4.34 (1:1; CH_3CN, UV-vis) **30**. Cl^-: log K_a = 5.85 (1:1; CH_3CN, UV-vis) **30**. Br^-: log K_a = 5.40 (1:1; CH_3CN, UV-vis) **30**. I^-: log K_a = 3.80 (1:1; CH_3CN, UV-vis) **30**. NO_3^-: log K_a = 4.40 (1:1; CH_3CN, UV-vis) Neutral analogues **31**, **32** and **33** exhibited weak binding. (Anions were used as $N^nBu_4^+$ salts)
34 (Gong *et al*; Ref. 48)	**34**. $H_2PO_4^-$: log K_a = 4.28 [1:1; CH_3CN/EtOH (9:1, v/v), fluorescence] (Anions were used as $N^nBu_4^+$ salts)
35 (Gong *et al*; Ref. 49)	**35**. $H_2PO_4^-$: K_a = (3.0 ± 0.3) x 10^4 M^{-1} (1:1; $CHCl_3$, fluorescence); K_a = (5.0 ± 0.2) x 10^4 M^{-1}(1:2; $CHCl_3$, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
36 (Ghosh *et al*; Ref. 50)	**36**.$C_6H_5COO^-$: K_a = 3.46 x 10^3 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **36**. 4-butoxybenzoate: K_a = 8.69 x 10^2 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **36**. pyridine-3-carboxylate: K_a = 5.48 x 10^2 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **36**. HSO_4^-: K_a = 1.87 x 10^3 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
37(Ghosh *et al*; Ref. 51)	**37**. AcO^-: K_a = 1.08 x 10^4 M^{-1} (1:1; CH_3CN, fluorescence) **37**. propanoate: K_a = 1.25 x 10^4 M^{-1} (1:1; CH_3CN, fluorescence) **37**. AcO^-: K_a = 1.16 x 10^4 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **37**. propanoate: K_a = 1.04 x 10^4 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **37**. $C_6H_5COO^-$: K_a = 3.02 x 10^3 M^{-1}(1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) **37**. $H_2PO_4^-$: K_a = 9.56 x 10^3 M^{-1} (1:1; $CHCl_3$ containing 2% CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
38 and **39**(Ghosh *et al*; Ref. 52)	**38**. biotin carboxylate: K_a = 5.12 x 10^4 M^{-1} (1:1; CH_3CN containing 1.2% DMSO, fluorescence) **38**. biotin methyl ester: K_a = 3.69 x 10^3 M^{-1} (1:1; CH_3CN containing 1.2% DMSO, fluorescence) **38**. AcO^-: K_a = 5.14 x 10^4 M^{-1} (1:1; CH_3CN containing 1.2% DMSO, fluorescence) **38**. biotin carboxylate: K_a = 1.89 x 10^4 M^{-1} (1:1; DMSO, fluorescence) **38**. biotin methyl ester: K_a = 6.33 x 10^3 M^{-1} (1:1; DMSO, fluorescence) **38**. AcO^-: K_a = 1.19 x 10^4 M^{-1} (1:1; DMSO, fluorescence) **39**. biotin carboxylate: K_a = 4.22 x 10^4 M^{-1} (1:1; CH_3CN containing 1.2% DMSO, fluorescence) **39**. biotin methyl ester: K_a = 7.05 x 10^2 M^{-1} (1:1; CH_3CN containing 1.2% DMSO, fluorescence) **39**. AcO^-: K_a = 1.91 x 10^4 M^{-1} (1:1; CH_3CN containing 1.2% DMSO, fluorescence) **39**. biotin carboxylate: K_a = 9.70 x 10^3 M^{-1} (1:1; DMSO, fluorescence) **39**. biotin methyl ester: K_a = 4.17 x 10^3 M^{-1} (1:1; DMSO, fluorescence) **39**. AcO^-: K_a = 1.95 x 10^4 M^{-1} (1:1; DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
40 (Ghosh *et al*; Ref. 54)	**40**. malonate: log K_a = 4.28 (1:1; DMSO, fluorescence) **40**. succinate: log K_a = 4.93 (1:1; DMSO, fluorescence) **40**. glutarate: log K_a = 5.73 (1:1; DMSO, fluorescence) **40**. adipate: log K_a = 6.87 (1:1; DMSO, fluorescence) **40**. pimelate: log K_a = 7.32 (1:1; DMSO, fluorescence) **40**. 1,4-phenylenediacetate: log K_a = 8.93 (1:1; DMSO, fluorescence) **40**. benzoate: log K_a = 5.19 (1:1; DMSO, fluorescence) **40**. acetate: log K_a = 5.52 (1:1; DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
41 (Ghosh *et al*; Ref. 55)	**41**. malonate: K_a = 2.09 x 10^4 M^{-1} (1:1; DMSO, fluorescence) **41**. succinate: K_a = 1.15 x 10^4 M^{-1} (1:1; DMSO, fluorescence) **41**. glutarate: K_a = 4.21 x 10^4 M^{-1} (1:1; DMSO, fluorescence) **41**. adipate: K_a = 4.68 x 10^4 M^{-1} (1:1; DMSO, fluorescence) **41**. pimelate: K_a = 8.60 x 10^3 M^{-1} (1:1; DMSO, fluorescence)

	41. suberate: $K_a = 7.29 \times 10^4\ M^{-1}$ (1:1; DMSO, fluorescence) **41**. terephthalate: $K_a = 4.75 \times 10^4$ M (1:1; DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
42 and **43** (Ghosh *et al*; Ref. 56)	**42**. malonate: log $K_1 = 4.44 \pm 0.02$, log $K_2 = 3.36 \pm 0.03$ (1:2; DMSO, fluorescence) **42**. succinate: log $K_1 = 4.36 \pm 0.03$, log $K_2 = 3.36 \pm 0.05$ (1:2; DMSO, fluorescence) **42**. glutarate: log $K_1 = 4.40 \pm 0.04$, log $K_2 = 3.63 \pm 0.05$ (1:2; DMSO, fluorescence) **42**. adipate: log $K_a = 4.21 \pm 0.02$ (1:1; DMSO, fluorescence) **42**. pimelate: log $K_a = 4.42 \pm 0.04$ (1:1; DMSO, fluorescence) **42**. suberate: log $K_a = 4.17 \pm 0.03$ (1:1; DMSO, fluorescence) **43**. malonate: log $K_1 = 3.74 \pm 0.02$, log $K_2 = 4.31 \pm 0.04$ (1:2; DMSO, fluorescence) **43**. succinate: log $K_1 = 3.69 \pm 0.03$, log $K_2 = 4.37 \pm 0.05$ (1:2; DMSO, fluorescence) **43**. glutarate: log $K_a = 4.14 \pm 0.08$ (1:1; DMSO, fluorescence) **43**. adipate: log $K_a = 4.73 \pm 0.02$ (1:1; DMSO, fluorescence) **43**. pimelate: log $K_a = 5.00 \pm 0.01$ (1:1; DMSO, fluorescence) **43**. suberate: log $K_a = 4.89 \pm 0.01$ (1:1; DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
44 (Ghosh *et al*; Ref. 57)	**44**. $N^nBu_4^+$ $H_2PO_4^-$: $K_a = 9.07 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **44**. Na_2ATP: $K_a = 3.36 \times 10^2\ M^{-1}$ [1:1; H_2O/CH_3CN (1:1, v/v), fluorescence] **44**. Na_2ADP: $K_a = 1.79 \times 10^2\ M^{-1}$ [1:1; H_2O/CH_3CN (1:1, v/v), fluorescence]
45 and **46** (Ghosh *et al*; Ref. 59)	**45**. citrate: $K_a = (2.34 \pm 0.01) \times 10^4\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. pimelate: $K_a = (4.05 \pm 0.05) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. adipate: $K_a = (1.05 \pm 0.01) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. glutarate: $K_a = (1.17 \pm 0.02) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. succinate: $K_a = (1.62 \pm 0.01) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. F^-: $K_a = (1.12 \pm 0.01) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. Cl^-: $K_a = (9.94 \pm 0.07) \times 10^2\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. Br^-: $K_a = (8.98 \pm 0.07) \times 10^2\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. I^-: $K_a = (9.96 \pm 0.07) \times 10^2\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. $H_2PO_4^-$: $K_a = (1.01 \pm 0.03) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **45**. AcO^-: $K_a = (1.61 \pm 0.02) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. citrate: $K_a = (7.02 \pm 0.7) \times 10^4\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. pimelate: $K_a = (1.62 \pm 0.04) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. adipate: $K_a = (1.50 \pm 0.02) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. glutarate: $K_a = (1.49 \pm 0.02) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. succinate: $K_a = (1.54 \pm 0.01) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. F^-: $K_a = (1.18 \pm 0.01) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. Cl^-: $K_a = (1.07 \pm 0.02) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. $H_2PO_4^-$: $K_a = (1.81 \pm 0.03) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] **46**. AcO^-: $K_a = (8.21 \pm 0.02) \times 10^3\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), UV-vis] (Anions were used as $N^nBu_4^+$ salts)
47 (Ghosh *et al*; Ref. 60)	**47**.$(N^nBu_4^+)_3HP_2O_7$: $K_a = (9.59 \pm 1) \times 10^4\ M^{-1}$ [1:1; CH_3CN/H_2O (4:1, v/v), fluorescence]
49 (Ghosh *et al*; Ref. 65)	**49**. Na-salt of ATP: $K_a = 6.80 \times 10^2\ M^{-1}$ (1:1; H_2O, UV-vis) **49**. Na-salt of ADP: $K_a = 8.85 \times 10^2\ M^{-1}$ (1:1; H_2O, UV-vis) **49**. Na-salt of AMP: $K_a = 5.96 \times 10^3\ M^{-1}$ (1:1; H_2O, UV-vis)
50 and **51** (Ghosh *et al*; Ref. 66a)	**50**. $H_2PO_4^-$: $K_{11} = (2.45 \pm 0.1) \times 10^4\ M^{-1}$, $K_{12} = (2.21 \pm 0.1) \times 10^4\ M^{-1}$ (1:2; CH_3CN, fluorescence) **50**. F^-: $K_{11} = (1.06 \pm 0.08) \times 10^4\ M^{-1}$, $K_{12} = (8.21 \pm 0.8) \times 10^3\ M^{-1}$ (1:2; CH_3CN, fluorescence) **51**. $H_2PO_4^-$: $K_{11} = (2.09 \pm 0.16) \times 10^4\ M^{-1}$, $K_{12} = (1.40 \pm 0.12 \times 10^4)\ M^{-1}$ (1:2; CH_3CN, fluorescence) **51**. F^-: $K_{11} = (1.84 \pm 0.4) \times 10^4\ M^{-1}$, $K_{12} = (5.19 \pm 0.16) \times 10^3\ M^{-1}$ (1:2; CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
53 and **54** (Ghosh *et al*; Ref. 68)	**53**. L-*N*-acetylvaline: $K_a = 1.87 \times 10^4\ M^{-1}$ (1:1; CH_3CN, fluorescence) **53**. L-*N*-acetylalanine: $K_a = 2.60 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **53**. L-*N*-acetylproline: $K_a = 1.38 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **53.** L-*N*-acetylphenylglycine: $K_a = 1.31 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **53**. AcO^-: $K_a = 2.20 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **53**. (S)-mandelate: $K_a = 1.60 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence)

	54. L-*N*-acetylvaline: $K_a = 1.30 \times 10^4\ M^{-1}$ (1:1; CH_3CN, fluorescence) **54**. L-*N*-acetylalanine: $K_a = 6.50 \times 10^2\ M^{-1}$ (1:1; CH_3CN, fluorescence) **54**. AcO^-: $K_a = 1.70 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
55 (Ghosh *et al*; Ref. 69)	**55**. D-lactate: $K_a = (4.17 \pm 0.7) \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **55**. L-lactate: $K_a = (1.92 \pm 0.33) \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
56 (Ghosh *et al*; Ref. 70)	**56**. L-tartrate: $K_a = (6.31 \pm 0.056) \times 10^3\ M^{-1}$ (1:1; DMSO, fluorescence) **56**. D-tartrate: $K_a = (8.18 \pm 0.55) \times 10^3\ M^{-1}$ (1:1; DMSO, fluorescence) **56**. *R*- mandelate: $K_a = (2.79 \pm 0.39) \times 10^3\ M^{-1}$ (1:1; DMSO, fluorescence) **56**. *S*- mandelate: $K_a = (2.07 \pm 0.22) \times 10^3\ M^{-1}$ (1:1; DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
61 and **62** (Ghosh *et al*; Ref. 76)	**61**. F^-: $K_a = 3.14 \times 10^3\ M^{-1}$ (1:1; $CHCl_3$, UV-vis) **61**. Cl^-: $K_a = 4.20 \times 10^4\ M^{-1}$ (1:1; $CHCl_3$, UV-vis) **62**. F^-: $K_a = 2.07 \times 10^3\ M^{-1}$ (1:1; CH_3CN, fluorescence) **62**. F^-: $K_a = 3.21 \times 10^3\ M^{-1}$ (1:1; DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)
63 (Ghosh *et al*; Ref. 77)	**77**. F^-: $K_a = 8.93 \times 10^3\ M^{-1}$ (1:1; DMSO, UV-vis) (Anions were used as $N^nBu_4^+$ salts)
64a (Ghosh *et al*; Ref. 78)	**64a**. Cl^-: $K_a = 1.31 \times 10^4\ M^{-1}$ (1:1; $CHCl_3$ containing 0.2% DMSO, fluorescence) **64a**. F^-: $K_a = 3.2 \times 10^4\ M^{-1}$ (1:1; $CHCl_3$ containing 0.2% DMSO, fluorescence) **64a**. Br^-: $K_a = 3.38 \times 10^3\ M^{-1}$ (1:1; $CHCl_3$ containing 0.2% DMSO, fluorescence) **64a**. I^-: $K_a = 3.30 \times 10^4\ M^{-1}$ (1:1; $CHCl_3$ containing 0.2% DMSO, fluorescence) **64a**. OH: $K_a = 2.64 \times 10^4\ M^{-1}$ (1:1; $CHCl_3$ containing 0.2% DMSO, fluorescence) (Anions were used as $N^nBu_4^+$ salts)