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Dipicolinamide and isophthalamide based fluorescent chemosensors: recognition and detection of assorted analytes

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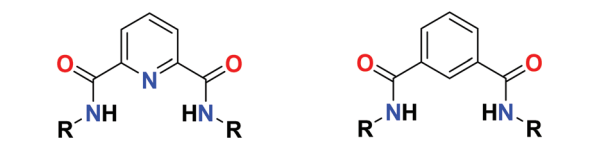
This perspective focuses on a variety of fluorescent receptors based on dipicolinamide and isophthalamide groups and their significant roles in the molecular recognition, sensing and detection of assorted analytes ranging from metal ions, anions, neutral molecules, drugs and explosives. Both the "turn-on" and "turn-off" nature of sensing highlights noteworthy applications in many fields encompassing biological, medicinal, environmental and analytical disciplines.

1. Introduction

The interdisciplinary nature of sensor research has grown enormously, connecting a number of fields of coordination, supramolecular and analytical chemistry; photo-chemistry and photo-physics; and materials science at the interface of chemistry and biology.[1] The broad applications cover health, biology and the environment.[2–11] The field of chemosensors and their usefulness in the disciplines of molecular recognition, sensing and detection is extensive and a number of reviews have appeared in the literature.[1,2,10,11] However, most of the available literature covers diverse fluorophores or assorted analytes leaving scope for a specialized review on a type of functional group. The aim of this perspective is to showcase recent yet significant progress of dipicolinamide (*i.e.*, pyridine-2,6-dicarboxamide) and isophthalamide (*i.e.*, benzene-1,3-dicarboxamide) group based chemical scaffolds in the field of chemosensing. Both dipicolinamide and isophthalamide fragment based chemical scaffolds have been extensively used as chelating pincer systems in coordination, bioinorganic and organometallic chemistry.[12–15] However, such chemical scaffolds have also emerged as effective and selective chemosensors for the detection of assorted analytes ranging from metal ions, anions and other anionic species, drugs and biomolecules to explosives (Scheme 1). The major focus of the present perspective is to illustrate the synthetic versatility of such chemical scaffolds in the detection of different analytes either *via* an emission enhancement (turn-on) or emission quenching (turn-off) mechanism. We focus on the recognition and detection of biologically relevant and/or toxic transition metal ions; assorted anions; neutral species such as drugs, biomolecules and other organic molecules; and explosives.



Dipicolinamide (pyridine-2,6-dicarboxamide) **Isophthalamide** (benzene-1,3-dicarboxamide)

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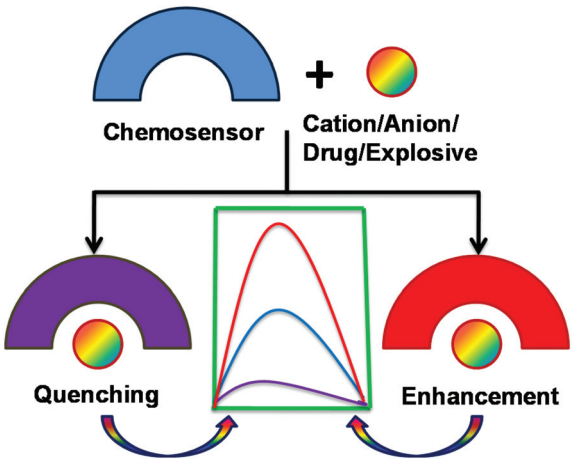

Scheme 1 Cartoon representation of a chemosensor and its interaction with an analyte (*e.g.*, cation, anion, drug or explosive) leading to either emission enhancement (turn-on) or emission quenching (turn-off).

The next few sections present selected examples of an appropriate category of chemosensors (or receptors) based on the dipicolinamide and isophthalamide fragments for showcasing a particular theme of sensing or detection application. For a better understanding, sections are classified based on either the type of chemosensors (or receptors) or the applications being offered by such chemosensors (or receptors).

2. Detection of cations

Recognition and detection of metal ions has great importance due to their relevance to many biological processes and for the purpose of environmental remediation of toxic ones.[12] A large number of dipicolinamide and isophthalamide fragment based chemical scaffolds have been developed for coordinating assorted metal ions within their chelating pincer cavity.[12–15] These examples suggest their potential role in the recognition and sensing applications of assorted metal ions if a suitable fluorophore is integrated with such scaffolds.[12] In this section, a few selected dipicolinamide and isophthalamide fragment based fluorescent chemosensors or receptors have been discussed and they have shown significant recognition and sensing abilities towards various metal ions, particularly transition metals.

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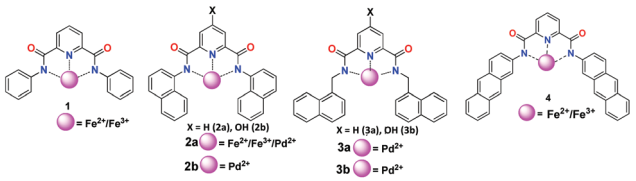

Fig. 1 Chemical structures of receptors **1–4** and their interaction with assorted cations. Adapted from ref. 16 and 17.

Gupta and co-workers[16,17] have shown the application of dipicolinamide based chemosensors, **1–4**, containing different appended arene rings as fluorophores, for the selective detection of iron and palladium ions (Fig. 1). Chemosensors **1**, **2a** and **4** exhibited significant emission quenching both for Fe^{2+} and for Fe^{3+} ions; however, **4** showed maximum selectivity for the Fe^{3+} ion with a binding constant of 3.3×10^3 M^{-1}.[16] Interestingly, while **4** was found to bind the Fe^{3+} ion in a 1 : 1 stoichiometry in THF, the isolated compound displayed a bis-chelated structure that was crystallographically substantiated.[16]

In contrast, naphthyl-based chemosensors **2** and **3** were found to be highly selective for the Pd^{2+} ion in aqueous HEPES buffer.[17] A combination of Stern–Volmer ($K_{SV} \approx 10^4$ M^{-1}) and Benesi–Hildebrand ($K_b \approx 10^3$ M^{-1}) plots and detection limits substantiated significant emission quenching-based sensing of the Pd^{2+} ion by **3a** and **3b**. Notably, both **3a** and **3b** were found to bind the Pd^{2+} ion in a 1 : 1 stoichiometry, a fact that was proved by the crystal structure of the Pd^{2+} complex of **3a**.[17] Importantly, the detection abilities of chemosensors **3a**/**3b** and **4** toward Pd^{2+} and Fe^{3+} ions, respectively, were utilized for cell imaging applications.

These authors have further developed a dipicolinamide based receptor **5** additionally containing appended benzothiazole rings (Fig. 2).[18] This chemosensor was found to be a selective turn-off sensor for the Cu^{2+} ion both in solution and in the solid state (using single crystals). The crystallographic studies illustrated the formation of a square-planar complex between the Cu(II) ion and receptor **5** (see **A** in Fig. 2). Chemosensor **5** was further developed into low-cost peelable polystyrene films and filter paper test strips for onsite sensing applications.

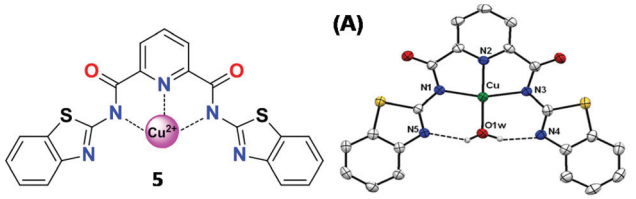

Fig. 2 Chemical structure of receptor **5** and its interaction with the Cu^{2+} ion and (A) crystal structure of **5**–Cu^{2+}. Adapted from ref. 18. Crystal structure in (A) is reproduced from ref. 18 with permission from the Royal Society of Chemistry, copyright 2016.

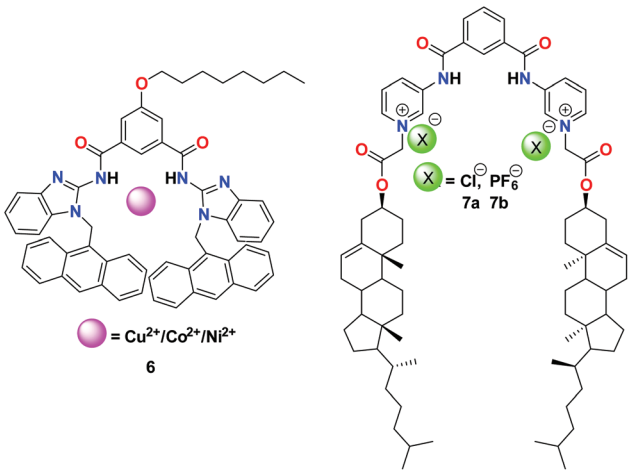

Fig. 3 Chemical structures of receptors **6** (with a suggestive site of cation interaction) and **7**. Adapted from ref. 19 and 20.

Similar to dipicolinamide based receptors, isophthalamide based receptors have also been developed for the selective sensing of transition metal ions. Ghosh and co-workers[19] have presented an anthracene-functionalized benzimidazole based chemosensor **6** for the selective detection of Cu^{2+}, Co^{2+} and Ni^{2+} ions (Fig. 3). Interestingly, detection occurred as a result of the destruction of an inherently present excimer between two closely spaced anthracene rings.[19] This chemosensor showed the highest affinity for the Cu^{2+} ion in CH_3CN among other metal ions, whereas the binding stoichiometry was found to be 1 : 1. EDTA was used to introduce reversibility that removed chelated Cu^{2+} ions from the [chemosensor-M] complex of **6**.

Ghosh and co-workers[20] have reported an interesting isophthalamide based receptor, **7a**, containing appended cholesterol units from the pyridinium groups which instantly formed a gel in $CHCl_3$ (Fig. 3). Such a gel was stable at room temperature and exhibited ionic conductivity due to the unrestricted movement of the chloride ions within the gel-network. Furthermore, gel **7a** was pH responsive and showed thermally activated ionic conductivity. Also, **7a** acted as a medium for the recognition of Ag^+ ions from a series of other cations by exhibiting a gel-to-sol transformation. Notably, PF_6^- analogue **7b**, obtained *via* anion exchange, exhibited selective recognition of the chloride ions by forming a yellow colored gel in $CHCl_3$.

3. Detection of anions

Amide-based receptors have been particularly very successful for the recognition of assorted anions and anionic species.[1c,2b,2c,21] Such a feature is related to the presence of hydrogen bonding (H-bonding) groups that amide-based receptors offer.[1c,2b,2c,22] Out of various amide-based receptors, the ones based on dipicolinamide and isophthalamide fragments are particularly successful. This is due to the fact that such receptors offer desirable orientation of the hydrogen bonds (H-bonds) while also offering a pincer cavity.[23] In this section, we present a few selected fluorescent receptors based on dipicolinamide and isophthalamide fragments for their anion recognition properties. However, such receptors have been further divided into the following two sub-categories depending on their nature: (i) neutral and (ii) charged receptors.

3.1. Neutral receptors

This section will discuss dipicolinamide and isophthalamide fragment based neutral receptors for the detection of assorted anions. In 1997, Crabtree and co-workers[24,25] have reported acyclic phenyl-appended isophthalamide and dipicolinamide as anion receptors. They noted selectivity of the phenyl-appended dipicolinamide receptors toward smaller halides (such as F^- and Cl^- ions). On the other hand, phenyl-appended isophthalamide receptors were able to coordinate much bigger bromide ion within their pincer cavity *via* H-bonds involving phenyl–CH groups and the amidic N–H groups (N···Br = 3.634 and 3.437 Å). These earlier examples led to the development of assorted amide-based receptors for the recognition and detection of various anions.

Gupta and co-workers[26] have synthesized several dipicolinamide based receptors (**2a**, **3a**, **4**, **5**, **8** and **9**) containing assorted aryl and/or heterocyclic rings as the appended groups. Such receptors were utilized for the detection of the S^{2-} ion and gaseous H_2S in aqueous media (Fig. 4). The benzothiazole ring appended receptor **5** illustrated the best sensing of the sulphide ion and gaseous H_2S when compared to the remaining receptors. The sensing of the sulphide ion was substantiated by binding studies (K_{SV} = 5.13 × 10^3 M^{-1}; K_b = 1.61 × 10^4 M^{-1}) while the detection limit was found to be 1.17 μM. It was found that the S^{2-} ion abstracted amidic N–H group(s), thus *in situ* generating the HS^- ion that remained bound within the pincer cavity. Such a fact was further confirmed by DFT studies (see **A** in Fig. 4). Importantly, a suitable proton source was found to make the sensing process reversible by protonating the cavity-bound HS^- ion. The authors illustrated the detection of the S^{2-} ion and gaseous H_2S in live

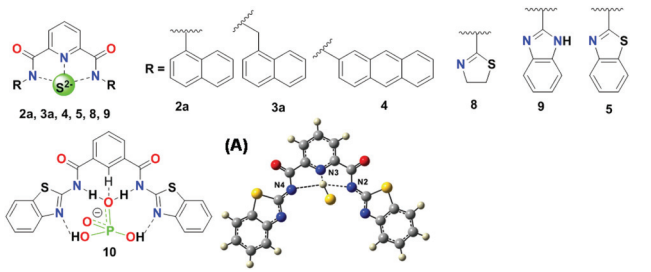

Fig. 4 Chemical structures of receptors **2a**, **3a**, **4**, **5** and **8–10** and their interaction with the selected analytes; and (A) DFT optimized structure for the **5**-HS^- species. Adapted from ref. 26 and 27. Structure in (A) is reproduced from ref. 26 with permission from the Royal Society of Chemistry, copyright 2018.

cells and further developed paper-strips for their practical applications.

Jhang and co-workers[27] have noted that benzothiazole-based fluorescent receptor **10** was capable of detecting the dihydrogenphosphate anion ($H_2PO_4^-$) in a mixture of CH_3CN/DMSO/H_2O (98 : 1 : 1, v/v/v) (Fig. 4). The presence of the $H_2PO_4^-$ ion quenched the emission of chemosensor **10**, whereas the binding constant was found to be 7.9×10^3 M^{-1} by the Benesi–Hildebrand method. The authors concluded that receptor **10** offered a coordination sphere suitable for encapsulating the $H_2PO_4^-$ ion that resulted in optimum binding through N–H···O═P and PO–H···N H-bonds.

Saha and co-workers[28,29] have found that naphthalene-diimide (NDI) units bind with the F^- ion and generate an optical signal due to the anion–NDI charge transfer (CT) (Fig. 5A). The [host–guest] complex of the F^- ion with an π-electron deficient colourless NDI receptor shows CT that facilitated electron transfer (ET) from F^- to NDI and generated an orange coloured $NDI^{\bullet-}$ radical anion.[30–32] However, an excess amount of F^- ions was found to further reduce $NDI^{\bullet-}$ to a pink coloured NDI^{2-} dianion. ET events in the NDI–F^- system thus resulted in a two-step optical response, presenting a novel strategy for F^- ion sensing. To investigate the detection of assorted anions, these authors synthesized two receptors based on an isophthalamide fragment connecting two NDI units **11a** and **11b** and a control receptor **11c** without an NDI unit (Fig. 5). The selective detection of the F^- ion by NDI, **11a** and **11b**, was investigated by UV-visible, fluorescence and NMR spectral studies.

Interestingly, high concentrations (30 equiv.) of other anions did not change the emission intensity of the colorless solution of the NDI-based receptors. In contrast, the introduction of the F^- ion in different solvent systems (THF, DMSO, Me_2CO, DMF, MeCN and DMA containing 15% H_2O) immediately resulted in the color changing from colorless to orange at low F^- (5 equiv.) and to pink at high F^- ion concentrations (>5 equiv.). However, receptor **11c**, lacking in NDI units, did not detect the F^- ion. ESI-MS spectra confirmed the formation of [**11a**·F^-] and [**11b**·F^-] with the concentrations up to 1 equiv. of F, whereas species [**11a**·$2F^-$] and [**11b**·$2F^-$] were noted with 2 equiv. of F^- ions.

Fang and co-workers[33] have developed dipicolinamide based pseudo-tetrahedral cavity receptors **12** and **13** respectively containing appended cyclohexyl and (1-pyrenyl)methyl groups (Fig. 6). Both receptors showed unique recognition and sensing of phosphates such as $H_2PO_4^-$ and PO_4^{3-} over other anions such as halides, nitrate, acetate, sulfate, perchlorate and thiocyanate. Fluorescence spectra, NMR spectral titrations and X-ray diffraction analysis supported the formation of the **13**-PO_4^{3-} complex involving H-bonding interactions between the PO_4^{3-} anion and receptor **13** (Fig. 6). The authors proposed that receptor **13** can potentially work as a diagnostic tool for the detection of various phosphates, such as $H_2PO_4^-$ and PO_4^{3-}.

These authors have further reported[34] an unsymmetrically substituted receptor **14** to target the selective recognition of geranyl pyrophosphate (GPP) which is a phosphate-containing molecule having an extended "tail". The hexa-amide receptor **14** offered a large cavity with multiple H-bonds to hold the pyrophosphate end of GPP, whereas two hydrocarbon chains further enhanced the interaction with the aliphatic fragment of GPP (Fig. 6). The coumarin phosphate (CP), chosen as a fluorescence resonance energy transfer (FRET) acceptor, formed a **14**-CP complex to render FRET from the pyrene rings. The FRET in the **14**-CP complex was reduced when CP was replaced by GPP to form a **14**-GPP complex which is a stronger complex as confirmed by the binding constants (K_b *ca.* 3300 M^{-1} for GPP; 1100 M^{-1} for CP in DMSO-d_6). Notably, receptor **14** was found to selectively bind GPP in 1 : 1 stoichiometry when compared to the other anions.

Feng and co-workers[35] have reported a chemosensor **15** for the selective recognition of an iodide ion in THF/H_2O solution by various spectroscopic methods (Fig. 7A). The presence of the iodide ion was found to change colorless **15** into a yellow

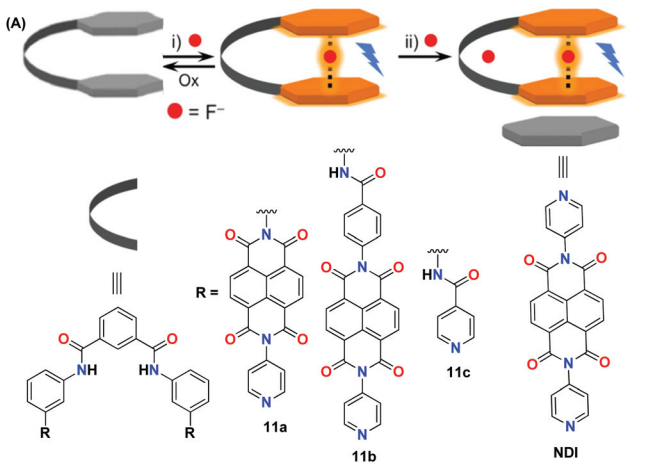

Fig. 5 Chemical structures of receptors **11a**–**11c** and **NDI** and (A) stepwise recognition of the F^- ion by receptors **11a** and **11b** through (i) anion-π; (ii) H-bonding interaction. Adapted from ref. 28 and 29. Structures in (A) are reproduced from ref. 28 with permission from the American Chemical Society, copyright 2010.

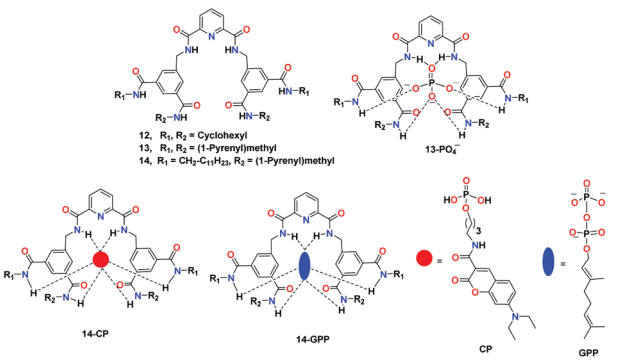

Fig. 6 Chemical structures of receptors **12**–**14** and their interaction with assorted phosphates. Adapted from ref. 33 and 34.

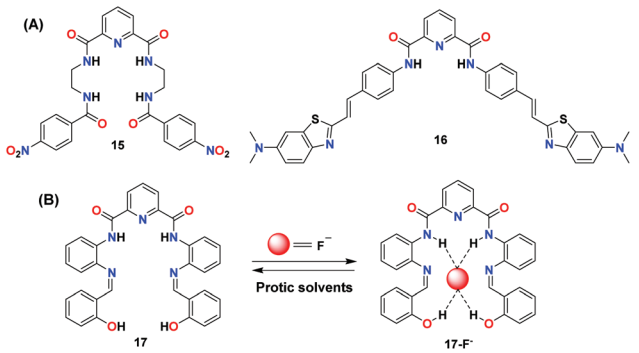

Fig. 7 (A) Chemical structures of receptors **15** and **16**. (B) Chemical structure of receptor **17** and its H-bonding based interaction with the fluoride anion. Adapted from ref. 35–37.

solution accompanied by a bathochromic shift in both the absorption and emission spectra. The emission spectral quenching of receptor **15** by the iodide ion was due to the complexation *via* intermolecular change transfer.

Rurack and co-workers[36] have reported a dipicolinamide based fluorescent receptor **16** consisting of two styryl based chromophores that showed an intramolecular charge transfer (ICT) (Fig. 7A). Receptor **16** showed a change in fluorescence spectra in the presence of $H_2PO_4^-$ and CH_3COO^- anions. An X-ray diffraction analysis of **16** helped in better understanding the charge-transfer mechanisms of anion sensing. The crystal structures of **16**-DMF and **16**-DMSO showed that solvent molecule stays in the pincer cavity *via* H-bonding. The key step for the detection of $H_2PO_4^-$ and CH_3COO^- anions was the replacement of such a cavity-bound solvent molecule by an anion, supported by H-bonds and responsible for the signal output.

Bao and co-workers[37] have reported a dipicolinamide based receptor **17** for the recognition of a fluoride ion (Fig. 7B). The detection of an F^- ion was investigated by the UV-Vis, colorimetric, fluorescence and proton NMR spectral studies in DMSO. Emission spectral enhancement was seen after the addition of F^- ion to a solution of receptor **17**. In the UV-Vis spectra, the presence of an F^- ion gradually reduces the original peak at 326 nm accompanied by the generation of a new peak at 425 nm with a binding constant of 2.31×10^4 M^{-1}. Receptor **17** acted as a selective colorimetric probe, producing a yellow-green solution after interaction with the F^- ion. Interestingly, the addition of protic solvents (H_2O or CH_3OH) in a DMSO solution of **17**-F^- reversed the color change, indicating that the detection of the F^- ion was purely based on H-bonding (Fig. 7B).

Gunnlaugsson and co-workers[38] have reported a series of hybrid dipicolinamide-thiourea based receptors **18–20** (Fig. 8). Receptors **19a** and **19b** possessed a glycol chain at the *para* position of the pyridyl ring to promote water solubility. Receptors **20a** and **20b** containing two pincer cavities were connected by a *para*-substituted poly(ethyleneglycol) chain. Receptors **19a**, **19b**, **20a** and **20b**, containing glycol chains, showed anion recognition in alcohol or aqueous/alcohol

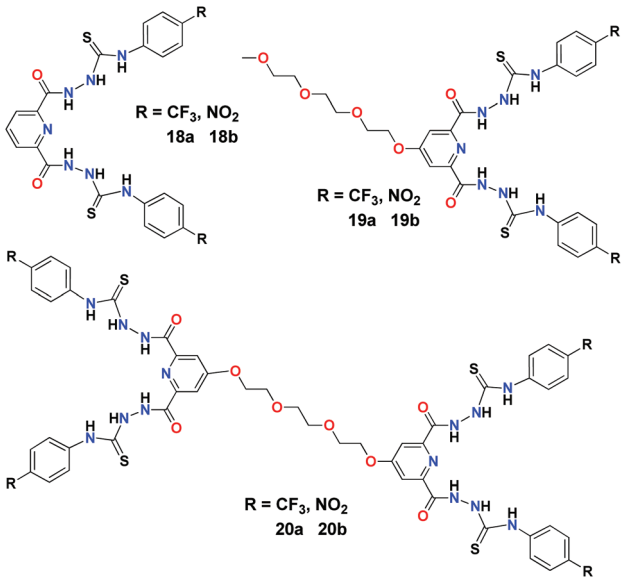

Fig. 8 Chemical structures of receptors **18–20**. Adapted from ref. 38.

media. In contrast, precursors, **18a** and **18b**, which lacked these glycol chains, only detected anions in DMSO. Absorption and emission spectral titrations of receptors **18–20** showed changes with different anions, such as halides, CH_3COO^-, oxo-anions, $H_2PO_4^-$, $HP_2O_7^{3-}$ and adenosine phosphates. Mechanistic investigations confirmed that H-bonding and deprotonation of the receptors played an important role in the sensing.

Kondo and co-workers[39,40] have developed three related isophthalamide based receptors, **21–23**, bearing appended pyrene rings while also containing a hexyl chain at the *para* position (Fig. 9). Receptor **21** showed ratiometric fluorescence spectral responses after the addition of the following anions: CH_3COO^-, $H_2PO_4^-$, $(EtO)_2PO_2^-$ and Cl^- with binding constants varying between 10^3 and 10^4 M^{-1}.[39] In spectral titrations, monomer emission was found to enhance with a concomitant decrease in the excimer emission, allowing the sensing

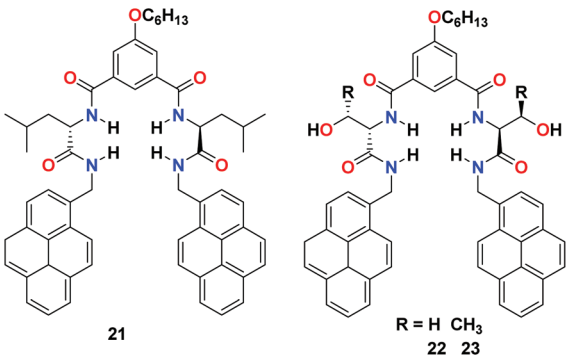

Fig. 9 Chemical structures of receptors **21–23**. Adapted from ref. 39 and 40.

of anions with the following trend: $(EtO)_2PO_2^-$ > CH_3COO^- > $H_2PO_4^-$ > Cl^-.

These authors[40] subsequently presented related receptors **22** and **23** offering hydroxyl groups from serine and threonine side chains to enhance the H-bonding propensity to a guest (Fig. 9). As expected, the binding affinities for the identical anions were found to be two orders of magnitude larger than those of receptor **21**. Such a remarkable enhancement in the binding was due to the involvement of six H-bonds: four from amidic N–H groups and two from the serine/threonine O–H side chains. Interestingly, both receptors **22** and **23** were also found to bind the F^- ion quite strongly.

3.2. Charged receptors

The dipicolinamide and isophthalamide group based chemical systems have also been functionalized to introduce positive charge(s). The introduction of positive charge(s) was considered to enhance their anion recognition abilities as a result of electrostatic attraction. Typically, positive charge(s) have been introduced either by the protonation or by the alkylation of nitrogen containing heterocyclic rings (*e.g.*, pyridine). This section discusses the anion recognition and sensing abilities of a few positively charged dipicolinamide and isophthalamide fragment based receptors.

Yatsimirsky and co-workers[41,42] have developed a series of dicationic dipicolinamide based fluorescent receptors for the detection of various anions in aqueous medium. Such receptors offered either *N*-methylated pyridinium groups (**24a–24c**) or *N*-methylated quinolinium groups (**25a–25c**) and exhibited significant affinity towards anionic analytes such as halides and acetate as well as neutral guests such as amides and ureas (Fig. 10).

Such positional isomeric receptors containing different N–Me^+ centers with respect to the –CO–NH– groups nicely tuned the electronic and optical properties of the receptors. Notably, receptors **25a–25c** exhibited affinity to detect pyrophosphate (PPi) and nucleotides. Highly fluorescent *N*-methylquinolinium based receptors **25a** and **25b** showed emission quenching in the presence of acetate, halides and PPi anions in a buffer solution of pH 6.5. Receptor **25a** differed from **25b** due to the presence of a large and open cavity with more acidic *N*-methylquinolinium groups, and formed comparatively more stable complexes with PPi and acetate anions while preferring larger Br^- ions over other smaller halides. In contrast, **25c** showed unexpected behavior, exhibiting negligible emission quenching in the presence of Cl^- and PPi anions and very weak emission change with Br^- ions. The authors noted that the interaction of an anion to a receptor was governed by the receptor cleft rather than by the electrostatic forces. However, the significant detection abilities of receptors **25a** and **25c** towards ATP were mainly due to the π···π interaction of the adenine ring to that of quinolinium rings of the receptor (Fig. 10B).

Yatsimirsky and co-workers[43] have also developed a dicationic dipicolinamide based fluorescent receptor **26** for the detection of a Cl^- ion in an aqueous buffer of pH 5.0 (Fig. 11). The

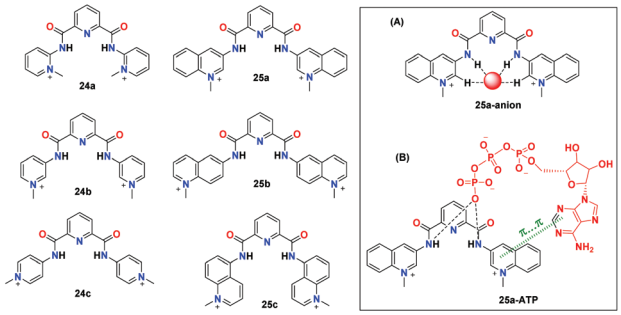

Fig. 10 Chemical structures of receptors **24a–24c** and **25a–25c** and their roles in (A) anion and (B) ATP binding. Adapted from ref. 41 and 42.

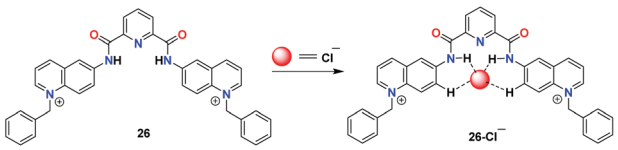

Fig. 11 Chemical structure of receptor **26** and its H-bonding based interaction with the chloride ion. Adapted from ref. 43.

significant change in the absorption spectrum and emission spectral quenching of **26** with increasing chloride ion concentration illustrated its strong affinity for the Cl^- ion with binding constants of 126 M^{-1} and 20 M^{-1} (at pH 5.0), respectively. NMR spectral titrations, crystal structure and theoretical calculations confirmed that the Cl^- ion was bound in the pincer cavity of the receptor by two short CH···Cl bonds and two N–H···Cl H-bonding interactions. The authors proposed a photo-induced electron transfer quenching mechanism and the formation of a **26**-Cl^- complex based on spectroscopic and theoretical studies.

Ghosh and co-workers[44,45] have reported isophthalamide and dipicolinamide based fluorescent receptors **27a** and **27b** containing pyridinium-appended groups for the detection of various anions (Fig. 12). Both receptors **27a** and **27b** strongly bound basic anions such as CH_3COO^-, $H_2PO_4^-$ and F^- ions in CH_3CN. Interestingly, the presence of the $H_2PO_4^-$ ion greatly increased the emission of **27a** and **27b** due to the formation of an excimer between anthracene rings. However, the presence of the F^- and CH_3COO^- ions only slightly changed the emission of receptors **27a** and **27b** without any excimer formation. Furthermore, UV-Vis spectral titration of **27a** in the presence of the $H_2PO_4^-$ ion showed a red shift in the absorption peaks of anthracene, indicating strong H-bonding within the pincer cavity of **27a**. However, receptor **27b** in the presence of $H_2PO_4^-$ showed gradual decreases in the absorbance of anthracene with a 5 nm red shift. The binding constants for the detection of these anions were found to be in the order of 10^3–10^4 M^{-1} in CH_3CN from the UV-Vis and emission spectral titrations. Similar to **27a** (Fig. 12), Ghosh and co-workers[46,47] have reported two unsymmetrical pyridinium-based receptors, containing singly appended pyrene and anthracene rings as the

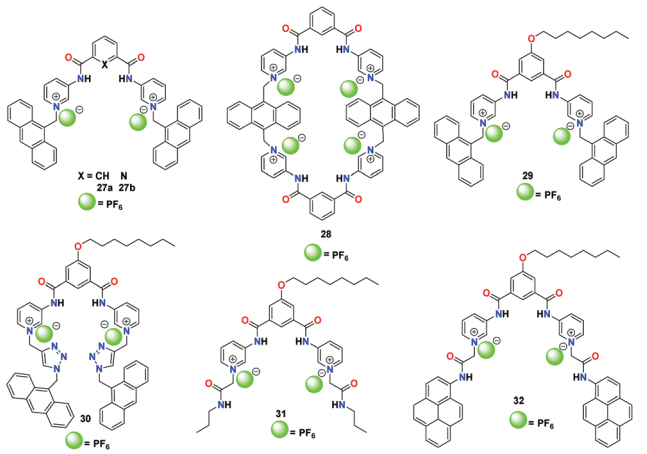

Fig. 12 Chemical structures of charged receptors **27–32**. Adapted from ref. 44, 45 and 48–50.

fluorophores, for the selective recognition of benzoate over a range of aliphatic mono-carboxylates in $CHCl_3$ (2% CH_3CN).

Ghosh and co-workers[48] have synthesized an anthracene-functionalized pyridinium-based macrocyclic receptor **28** (Fig. 12). Receptor **28** exhibited selective binding of 1,4-phenylenediacetate with large enhancement in its emission intensity when compared to other dianions. The authors observed a red-shift in the anthracene based absorption in the presence of the guest. The complexation of 1,4-phenylenediacetate was suggested at the positively charged sites of **28**, whereas binding constants were found to be 3.35×10^5 M^{-1} and 3.63×10^4 M^{-1} from emission and absorption spectral titrations, respectively. The reasonably high binding was attributed to the synergistic effect of H-bonding, π···π stacking and charge–charge interaction between the macrocycle **28** and the guest.

These authors[49] have further developed receptors **29** and **30** by the insertion of a long alkyl chain at the *para* position of the benzene ring, although **30** also contained a 1,2,3-triazole ring (Fig. 12). Receptor **30** selectively recognized the $H_2PO_4^-$ ion in the form of emission spectral quenching and the formation of a stable gel in $CHCl_3$ (10% CH_3CN), although receptor **29** did not produce a gel with $H_2PO_4^-$ under identical conditions but exhibited emission enhancement due to the excimer formation. These contrasting results supported the role of the triazole ring in the gel formation.

Ghosh and co-workers[50] have used the indicator displacement assay (IDA) technique[51] for the detection of an anion by using isophthalamide based receptors **31** and **32** (Fig. 12). In the IDA technique, an indicator first binds reversibly to a host and then an analyte (*e.g.*, anion) displaces the indicator from the host, resulting in an optical response.[51] Receptors **31** and **32** were found to be effective for the recognition of the citrate ion over other anions *via* the IDA technique in the CH_3CN/H_2O mixture (4 : 1, v/v, pH 6.3). The binding constants for both receptors **31** and **32** were computed to be in the order of 10^4 M^{-1} with a 1 : 1 stoichiometry. In addition, receptor **31** selectively formed a stable gel with the citrate ion in CH_3CN. The authors proposed that the charge–charge interaction, H-bonding and large π-surface of the pyrene ring in **31** created a network in solution in the presence of the citrate ion, which is necessary for gelation.

4. Detection of neutral molecules

Detection and sensing of a neutral guest is comparatively more challenging in the absence of any electrostatic interaction.[1,2] As a result, very few examples are available under this category, particularly, those based on fluorescent receptors. However, the majority of the biologically significant molecules are neutral and therefore their recognition and detection is very critical.[1,2] This section discusses the detection of a few neutral molecules by using dipicolinamide and isophthalamide group based fluorescent receptors. The neutral molecules include assorted organic molecules, drugs and explosives.

4.1. Detection of organic and drug molecules

Ghosh and co-workers[52] have developed an isophthalamide based receptor **33** and its pseudo-macrocyclic analogue **34** containing appended anthracene groups for the recognition of urea and thiourea (Fig. 13). Both receptors **33** and **34** were found to bind urea and thiourea effectively in $CHCl_3$ and exhibited a significant change in the intrinsic fluorescence of the anthracene groups. In non-polar solvent $CHCl_3$, macrocyclic receptor **34** showed a much higher selectivity towards urea (1.97×10^6 M^{-1}) and thiourea (1.35×10^6 M^{-1}) than non-macrocyclic analogue **33** (urea: 1.14×10^5 M^{-1}; thiourea: 2.71×10^4 M^{-1}). Interestingly, in polar solvent CH_3CN, the binding constants for urea were much lower in magnitude ($\approx 10^3$ M^{-1}) for both the receptors, whereas negligible binding was noted for thiourea. The authors concluded that a polar solvent, CH_3CN, potentially reduced the H-bonding interactions

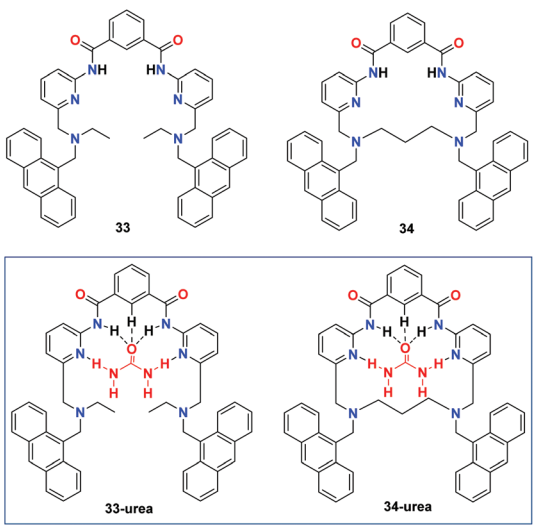

Fig. 13 Chemical structures of receptors **33** and **34** and their interaction with urea. Adapted from ref. 52.

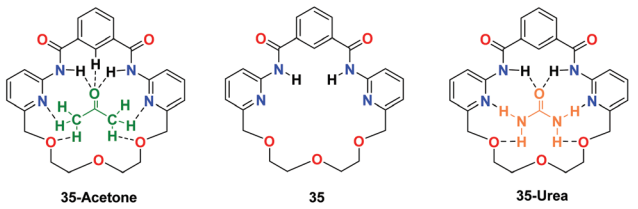

Fig. 14 Chemical structure of receptor **35** and its binding with acetone and urea based on crystal structures. In the crystal structure of the **35**–urea complex, the stoichiometry between **35** and urea is 2 : 1; however, only one molecule of **35** is shown for clarity. Adapted from ref. 53.

between a receptor and a guest. The detection mechanism involved anthracene-based PET for the sensing of the guest.

Ghosh and co-workers[53] have reported an isophthalamide based polyether-chain containing non-fluorescent macrocyclic receptor **35** for the detection of neutral molecules, acetone and urea (Fig. 14). The replacement of the originally bound acetone within the macrocyclic cavity by urea was investigated by the absorption and NMR spectral studies in $CHCl_3$. Crystallographic analyses illustrated that while both conventional (N–H···O) and unconventional (C–H···O and C–H···N) H-bonds were found to effectively bind acetone within the macrocyclic cavity of **35**, the moderate inclusion of the biologically relevant metabolite urea was due to only the conventional (N–H···O and N–H···N) H-bonds.

These authors[54] have further reported an isophthalamide based receptor **36** for the recognition of biologically relevant guests, biotin methyl ester and urea in $CHCl_3$ (containing 1% CH_3CN) (Fig. 15). Such a detection was evaluated by measuring enhancement in the emission intensity of **36** and the binding constant was found to be 9.8×10^3 M^{-1} for biotin methyl ester and 6.2×10^3 M^{-1} for urea. In the host–guest complex, one phenyl C–H, two amidic N–H and two benzothiazole-N atoms were involved in H-bonding interactions with the guests, biotin methyl ester and urea. The authors found that a less polar solvent was better suited for monitoring the effective interaction of a guest with receptor **36**. Such a fact was related to less interference from a less polar solvent that potentially enhanced the binding.

Hamilton and co-workers[55] have reported a series of isophthalamide and dipicolinamide group based macrocyclic receptors, **37–39**, capable of binding a family of barbiturates, a class of sedative and sleep-inducing drugs (Fig. 16). Binding

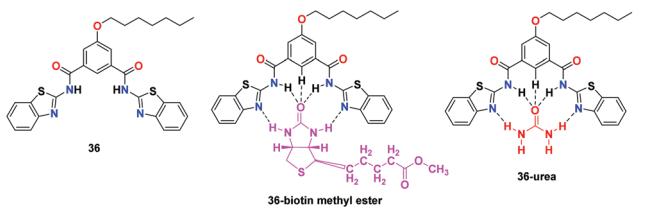

Fig. 15 Chemical structure of receptor **36** and its interaction with biotin-methyl-ester and urea. Adapted from ref. 54.

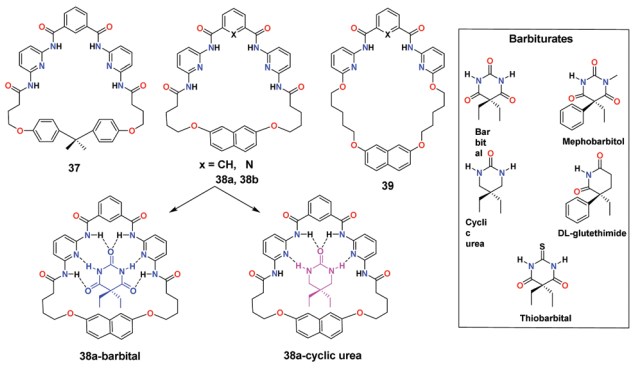

Fig. 16 Chemical structures of receptors **37–39** and different barbiturates, and the interaction of barbital and cyclic urea with receptor **38a**. Adapted from ref. 55.

constants (M^{-1}) by the fluorescence spectral titrations for receptors **37**, **38a** and **38b** toward barbital were found to be 6.0×10^5, 2.5×10^5 and 4.1×10^4, respectively. Substrate binding studies, NMR spectra and X-ray crystallography substantiated that six H-bonds were formed between receptor **38a** and barbital. However, receptor **39**, in which H-bond donating amide groups were replaced by the H-bond accepting ether groups, formed a weaker complex with barbital with only four H-bonds. Receptors **37** and **38a** showed very weak interactions with cyclic urea, mephobarbitol, DL-glutethimide and thiobarbital ($K_b \approx 10^2$ M^{-1}). Notably, cyclic urea, mephobarbital and DL-glutethimide offered fewer H-binding sites as compared to barbital, and hence showed weaker binding potentials than barbital.

Goswami and co-workers[56] have developed isophthalamide based fluorescent receptors **40** and **41** for the recognition and solubilization of tartaric acid in $CHCl_3$ (Fig. 17). The addition of solid L-(+)-tartaric acid to a $CDCl_3$ solution of **40** and **41** led to its facile dissolution, confirmed by the appearance of methyne protons of tartaric acid at δ 5.00 ppm and a downfield shift of the amidic protons of receptors **40** and **41**. The binding of tartaric acid in $CHCl_3$ was also established by the emission spectral enhancement on complexation. The pres-

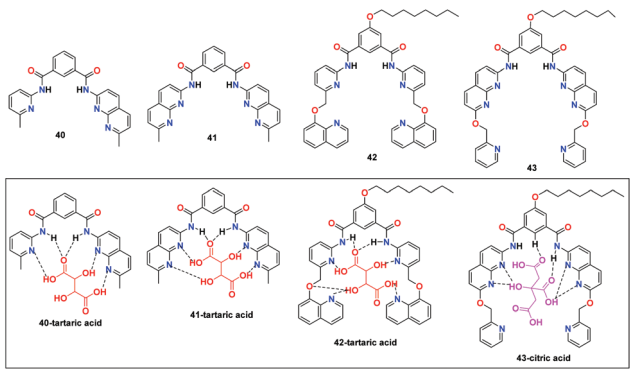

Fig. 17 Chemical structures of receptors **40–43** and their interactions with tartaric acid and citric acid. Adapted from ref. 56–58.

ence of tartaric acid also shifted the absorption spectral profile of receptors and the binding constants were found to be 1.6 × 10^4 M^{-1} and 1.7 × 10^4 M^{-1} for **40** and **41**, respectively. The 1 : 1 binding stoichiometry for tartaric acid was established by NMR, emission and absorption spectral titrations.

Ghosh and co-workers[57] have developed an interesting isophthalamide-quinoline based receptor **42** to detect tartaric acid through H-bonding mediated complexation (Fig. 17). The complexation of tartaric acid with **42** was investigated by proton NMR, absorption, and emission spectral studies while the binding constant was found to be 9.8 × 10^4 M^{-1} by the UV-Vis spectral titration. The emission spectral quenching of **42** by tartaric acid followed intramolecular excimer emission upon H-bond mediated complexation. These authors[58] have further reported a naphthyridine-based receptor **43** for the detection of assorted carboxylic acids (Fig. 17). Although the complexation of **43** with different carboxylic acids was studied by several spectroscopic methods, it showed strong affinity towards citric acid with binding constants of 1.6 × 10^5 M^{-1} and 9.3 × 10^4 M^{-1} by absorption and emission spectral methods, respectively. Importantly, the presence of citric acid enhanced the emission of receptor **43** in $CHCl_3$, *i.e.*, turn-on behavior.

4.2. Detection of explosives

The detection of explosive materials is very important due to security reasons.[59,60] In recent times, considerable efforts have been devoted to developing effective sensors for the detection of explosive materials.[59,60] Out of various explosive materials, nitroaromatics have been extensively used as explosives and therefore their detection has been considerably targeted.[61] In this section, a few selected chemosensors that successfully detected nitroaromatics have been discussed.

Sessler and co-workers[62] have designed dipicolinamide (**44**) and isophthalamide (**45**) group based receptors containing appended pyrene groups (Fig. 18). Receptor **44** adopted a supramolecular oligomeric structure, both in $CHCl_3$ solution and in the solid state, due to the presence of intramolecular H-bonding interactions between pyridine-N and amide-NH groups. In contrast, receptor **45** did not show such NH···N H-bonding interactions and thus a supramolecular structure. Interestingly, linear supramolecular array of **44** was found to de-aggregate in the presence of electron-deficient substrates, such as trinitrobenzene (TNB) and trinitrotoluene (TNT). Such a host–guest complexation was confirmed spectroscopically and by X-ray crystallography (Fig. 18A). Receptor **44** showed characteristic pyrene

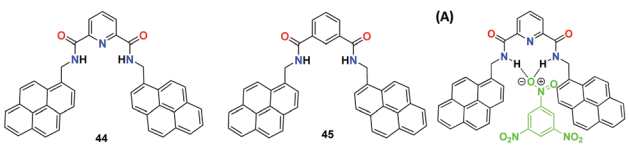

Fig. 18 Chemical structures of receptors **44** and **45**; and (A) adduct [**44**-TNB] based on the single crystal X-ray diffraction analysis. Adapted from ref. 62.

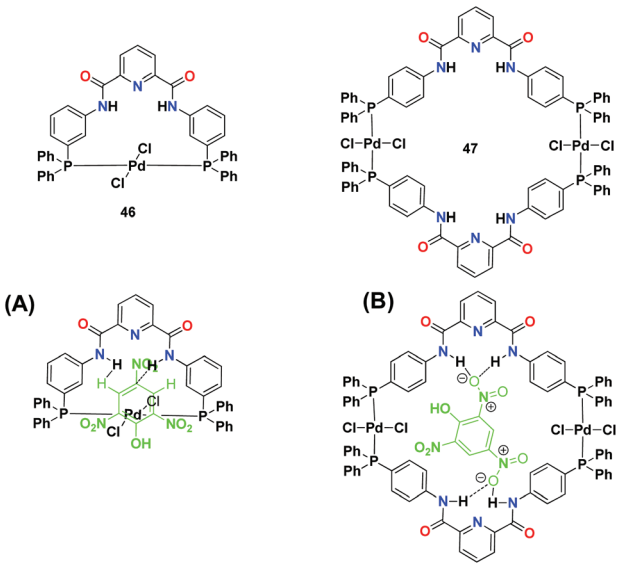

Fig. 19 Chemical structures of Pd-based receptors **46** and **47** and their interaction with picric acid (A) and (B). Adapted from ref. 63.

monomer emission along with a broad excimer emission at 470 nm in $CHCl_3$. In contrast, receptor **45** displayed only pyrene monomer emission at 375 nm and 400 nm; however, no excimer formation was observed due to the absence of intramolecular π···π interactions. The emission intensities of **44** and **45** were quenched effectively both by TNB and by TNT in $CHCl_3$ accompanied by sharp color changes from colorless to red (**44**) and orange (**45**). The binding constants (M^{-1}) for receptor **44** were found to be 7.3 × 10^4 and 7.7 × 10^2 for TNB and TNT respectively from ^{1}H NMR spectral titrations.

Gupta and co-workers[63] have reported two Pd-based fluorescent macrocycles, **46** and **47**, displaying either a 1 + 1 or 2 + 2 self-assembly of dipicolinamide based ligand(s) to Pd(II) ion (s) (Fig. 19). Receptor **46** offered a smaller macrocyclic cavity of 6.49 × 4.90 $Å^2$ dimensions while **47** exhibited a much larger cavity of 14.92 × 12.78 $Å^2$. Such dipicolinamide group based Pd-macrocycles were utilized for the efficient sensing of picric acid and other nitroaromatics in EtOH. The emission spectral titrations allowed the calculation of binding constants that were found to be 2.5 × 10^4 M^{-1} and 1.0 × 10^5 M^{-1} for **46** and **47**, respectively. Notably, while the larger receptor **47** was able to encapsulate picric acid within its macrocyclic cavity with the help of multiple H-bonds, **46** was able to only partially interact with picric acid due to its smaller macrocyclic cavity (Fig. 19A and B). As a result, the larger receptor **47** not only illustrated nano-molar detection of picric acid but also allowed its significant transport from the aqueous to the organic phase within a few minutes.

5. Conclusions and future prospects

A mosaic of examples comprising recognition, sensing and detection discussed in this perspective have adequately illus-

trated the importance of receptors based on both dipicolinamide and isophthalamide groups. Analytes vary from diverse cations to assorted anions including complex ones such as ATP, to distinct organic molecules, to drugs and even explosives. The noteworthy applications encompass many fields including biological, medicinal, environmental and analytical domains. The recognition event is primarily controlled either by the pincer cavity or by the H-bonding pocket being offered by such receptors depending upon the type of analyte. Such a fact, in a way, simplifies the design strategies and one can easily envision a variety of possible receptors emerging either from a dipicolinamide or an isophthalamide core by simply picking a suitable appended group. Such a fact together with straightforward synthesis yet diversified design approaches involving both dipicolinamide and isophthalamide groups is likely to create enormous opportunities for the development of next-generation chemosensors.

Conflicts of interest

There are no conflicts to declare.

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