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PERSPECTIVE

# Imidazole derivatives: A comprehensive survey of their recognition properties

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Due to its amphoteric nature the imidazole ring can function as selective and effective anion and/or cation and even neutral organic molecules receptor system. As a result, the design of new multichannel imidazole-based receptors capable of recognizing different types of analytes is strongly demanded. This review summarizes the most recent and relevant advances in this area.

## Introduction

The imidazole ring is ubiquitous in nature and imidazole functionality plays a critical role in many structures within the human body, notably as histamine and hystidine. In addition, marine sponges produce a plethora of fascinating, structurally diverse secondary metabolites usually containing the imidazole moiety. Since the discovery, in 1971, of the first alkaloid of this family, oroidin, many hundreds of such compounds have been isolated.[1] On the other hand, many uses of the imidazole ring as a bioagent revolve around its ability to bond to metals as a ligand and its ability to hydrogen bond with drugs and proteins. In this context, it should be mentioned that imidazole ring of hystidine residues is one of the most common ligands at the active sites of metalloproteins.[2] The ubiquitous presence of histidine coordination has stimulated the syntheses of imidazole-containing ligand donors to perform the coordination chemistry of the biomimetic chemistry.[3]

The realisation that very simple organic compounds containing functional groups or heterocyclic rings capable of providing binding sites which can function as selective and effective ion receptor systems has led to work towards designing such kind of synthetic receptors that can selectively recognize ions and act as sensors. Among such heterocyclic units, the imidazole ring behaves as an excellent hydrogen bond donor moiety in synthetic anion receptor systems, and the acidity of the NH proton of the imidazole can be tuned by changing the electronic properties of the imidazole substituents. On the other hand, the presence of a donor pyridine-like nitrogen atom within the ring, capable of selectively binding cationic species also converts the imidazole derivatives into excellent metal ion sensors. In this sense, the binding properties of the imidazole core may be modulated by linear or angular annulation to aza-heterocycles leading to expanded imidazole derivatives bearing several binding sites.

While the positively charged imidazolium derivatives have recently been widely used and comprehensively reviewed[4] as selective anion receptors through the $C_2$–H···anion typical ionic hydrogen bond, the dual capability of the imidazole ring to act as a selective molecular sensor of anions and/or cations even as ion-pair receptors has not been reviewed.

This review covers recent important development of imidazole derivative receptors for the recognition of various anions, cations and neutral molecules. We have grouped the receptors to their structural classification which include imidazoles, benzimidazoles and imidazoles fused to additional aza-heterocycles. This review particularly focuses on the fresh reports between 2000–2011.

## Imidazole based receptors

Species containing the 2-(imidazol-2-yl)phenol ligand framework have attracted increasing attention because they are considered a model for the study of the $Tyr_z$-$His_{190}$ cofactor in photosystem II, and its luminescent properties are widely utilized in research studies of biological interest.[5] Within this framework Sun and co-workers have described the synthesis and fluorescent properties of some 2-(1*H*-imidazol-2-yl)phenols **1** and their corresponding Zn(II) complexes **2** (Fig. 1).[6] It is worth noting that due to the different substituents placed in these imidazolyl–phenol derivatives such ligands exhibited various reactivities toward the zinc salt used. Thus, the ligands with an unsubstituted phenol ring are capable of forming the respective complexes. The ligands bearing an electron-donating methoxy substituent exhibited faster precipitation of the complexes while the presence of a bulky substituent makes most reluctant the chelation process, requiring the addition of a base to aid the reaction. On the other hand, the coordination of Zn(II) with these ligands also caused enhancement or quenching effects of intensities of fluorescence relative to free ligands, depending on the substituents in

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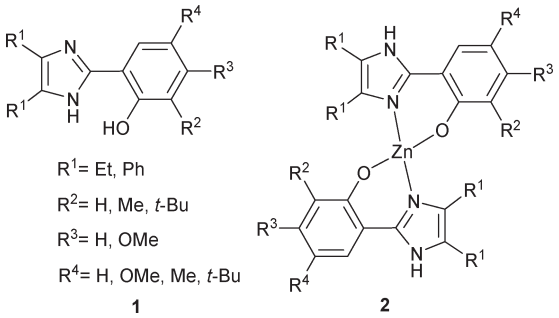



**Fig. 1** 2-(Imidazol-2-yl) phenol ligands.

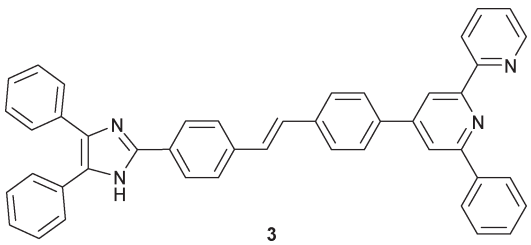



**Fig. 2** Bipyridil-imidazole fluoroionophore.

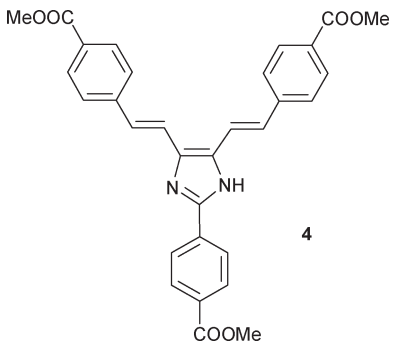



**Fig. 3** Y-shaped fluorophore bearing an imidazole ring core.

those ligands. This study shows that electron-rich substituents were suitable for ensuring better emission intensity in the zinc complexes and, as a consequence, such ligand systems are described as useful tools for the quantitative analytical estimation of free Zn(II) samples in water miscible solvents.

The asymmetric substituted imidazole derivative **3** (Fig. 2), based on 2,4,5-triphenylimidazole and 6-phenyl-2,2′-bipyridine has been used as a fluorophore in the cation sensing field. Thus, it can be applied to recognize Fe(III) with high selectivity in aqueous solution (THF/$H_2O$, 1 : 1, v/v), by the appearance of emission bands attributed to the emission of the newly formed **3**·Fe(III) complex.[7]

Structurally related is the ligand **4** (Fig. 3). This novel Y-shaped fluorophore with an imidazole ring core, bearing two stilbene-type conjugated substituents at the 2 and 3 position of the aromatic ring, has been described as a ratiometric fluorescent sensor for $F^-$ anions with high selectivity. Upon addition of $F^-$anions this receptor shows an obvious change in emission colour from green to brown, which is due to the deprotonation of the imidazole core of the ligand. Importantly, during the process,

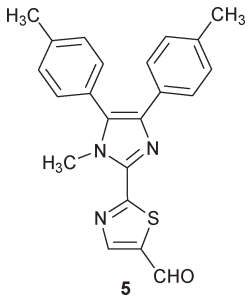



**Fig. 4** Chemosensor based on imidazole-thiazole units.

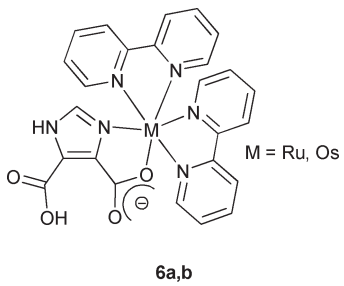



**Fig. 5** Mononuclear Ru(II) and Os(II) complexes derived from bipyridine and imidazole.

an obvious variation in the maximum wavelength of the two-photon excited fluorescence (TPEF) peak was observed from 490 to 565 nm, indicating that this receptor is an excellent ratiometric TPEF-sensor for $F^-$ anions.[8]

A similar structure is found in a new class of Y-shaped ligand **5** (Fig. 4) possessing an imidazole–thiazole core which has proven to be an excellent fluorescent chemosensor for Hg(II) ions in water–acetonitrile (7 : 3). The addition of Hg(II) led to a fluorescence reduction, and this quenching is accompanied by a shift of the emission band. Both quenching and shift are concentration-dependent: as Hg(II) concentration increases, so do the quenching and shift.[9]

On the other hand, by using metals as directing elements or templates it has proven possible to arrange simple organic components into arrays of hydrogen bond donors producing receptors with high selectivity for particular anions.[10] Within this research field, Baitalik and co-workers have recently studied in detail the structural, spectroscopic and physico-chemical properties of mixed-ligand mononuclear ruthenium(II) **6a** and osmium (II) **6b** complexes (Fig. 5), derived from 2,2′-bipyridine (bipy) and imidazole-4,5-dicarboxylic acid ($H_3$Imdc), that act as triple channel sensors for $F^-$, $AcO^-$ and $H_2PO_4^-$.[11] In fact, their binding properties have been confirmed by absorption, emission and $^1$H NMR spectroscopic techniques and also by electrochemical studies. Binding studies show that although at relatively lower concentrations of anions, a 1 : 1 H-bonded adduct is formed, in the presence of excess anions deprotonation of the imidazole N–H fragment occurs, which is accompanied by a distinct change of colour.

More recently, the Baitalik group have also exploited the $F^-$ ion signalling potential of the imidazole NH group and transition metal ion binding ability of the terpyridine moiety, by using the

terpyridil-imidazole base bifunctional receptor **7** (Fig. 6).[12] In fact, this tridentate ligand has been capable of acting as a triple channel (colorimetric, fluorescent and electrochemical) sensor for both Fe(II) and $F^-$ ions in solution. The binding site for the Fe(II) cation in the system has been unambiguously established by single-crystal X-ray diffraction study of the Fe(II) complex of the receptor.

Imidazole-based systems capable of recognizing neutral molecules have also been developed. In this context, Xie and co-workers have reported the synthesis of chiral imidazole cyclophane receptors **8** from L-histidine (Fig. 7) and their enantioselective recognition for amino acid methyl esters.[13] The binding constants of the inclusion complexes formed were determined on the basis of UV studies showing a 1 : 1 complex formation. It is worth noting that receptor **8** exhibits stronger binding and better enantioselectivity for amino acid esters containing an aromatic group than for those possessing an aliphatic side chain, inferring that the π–π stacking interaction between the receptor and the aromatic side chain of the amino acid is the principal attractive interaction involved. This receptor also exhibits better enantioselectivities for amino acid esters hydrochlorides than their corresponding amino acid esters, suggesting that this enhanced chiral recognition ability should arise from the cation-π interaction and hydrogen bonding between $NH_3^+$ of the amino acid ester hydrochloride and the receptor **8**.

Neutral imidazole–aminopyridine-based receptors **9**,[14] **10** and **11**[15] have been established as highly effective and selective carbohydrate receptors (Fig. 8). The recognition process, studied by $^1$H NMR and fluorescence spectroscopy, involves multiple interactions, including neutral hydrogen bonds and CH···π interactions between the carbohydrate CH groups and the aromatic rings of the receptors.

Studies in the field of synthetic chemosensors have paid special attention to the preparation of flexible molecules, among which bis(imidazole)-type ligands are of particular interest. They

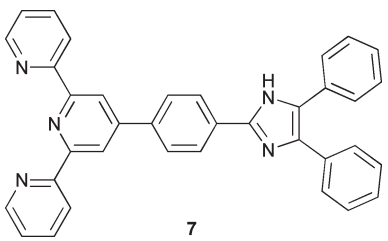



**Fig. 6** Chemosensor based on imidazole–terpyridine units.

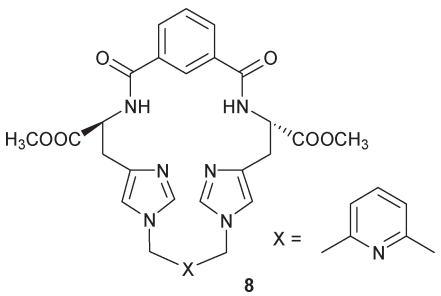



**Fig. 7** Chiral imidazole cyclophane receptor.

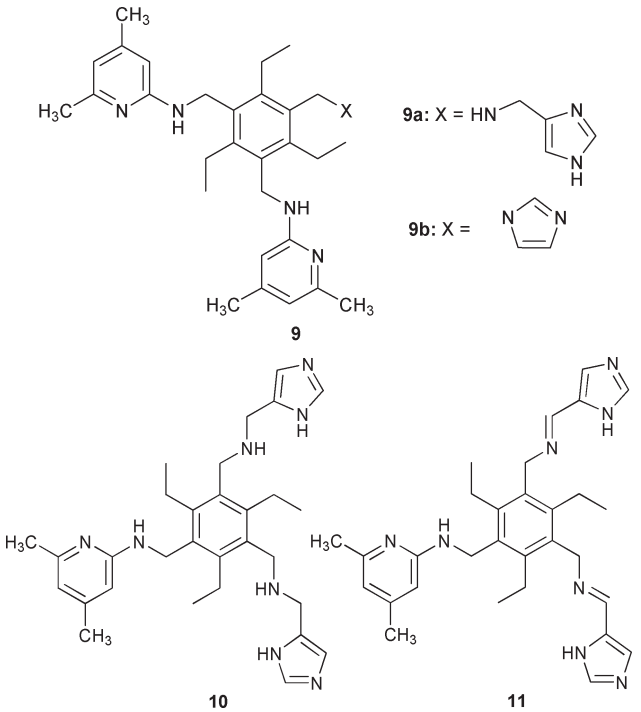



**Fig. 8** Imidazole–aminopyridine receptors.

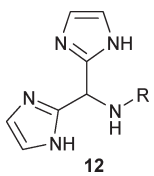



**Fig. 9** BINAM receptors.

not only play key roles as supporting ligands in a diverse array of metalloprotein active sites, but also they are important and useful building blocks for the design and construction of polydentate ligands.

In this context, Soto and co-workers have reported 3,3-bis(2-imidazolyl)propionic acid (HBIP),[16] bis(imidazol-2-yl)bis (methoxycarbonyl)-methylmethane (BIBM)[17] 2-di(1*H*-imidazol-2-yl)methylmalonate (DIMMAL)[18] and bis(imidazol-2-yl) methylaminomethane (BINAM).[19] BINAM derivatives **12**, with two imidazole groups and –NH amine functionalities in the side chain (Fig. 9), are flexible ligands that use two N-donor atoms to form interesting complexes with copper ions. In addition to metal binding sites, these ligands also contain hydrogen-bonding functionalities that are retained upon complexation leading to a broad variety of metal–organic coordination networks. The same research group has also recently reported the binding properties of a new tripodal bis(imidazole)-containing ligand toward Cu(II) metal cations with structural X-ray crystallographic elucidation of the dinuclear copper(II) compound formed.[20]

Based on the optical properties of the Ru(II)-bipyridine (Ru-bipy) moiety and the biimidazole ($H_2$biim) unit as an anion receptor *via* the formation of hydrogen bonding, Ye and co-workers have described the metalloreceptor **13** (Fig. 10), in which the *syn* conformation of the $H_2$biim is fixed and therefore

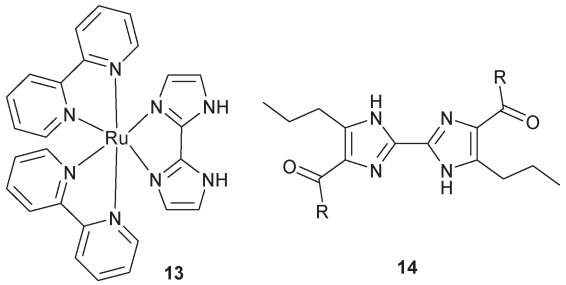
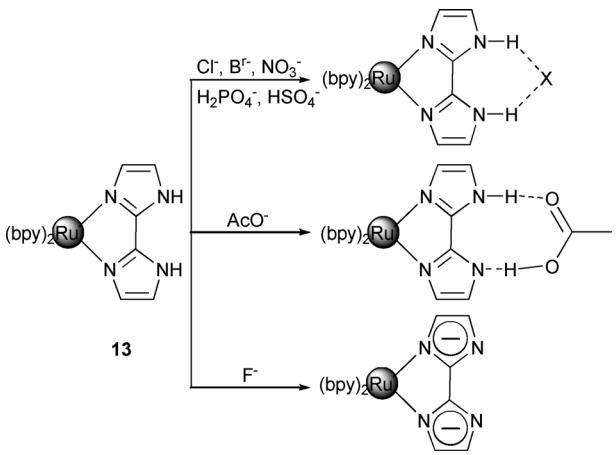



**Fig. 10** Receptors bearing a biimidazole core.




**Scheme 1** Schematic representation of the interaction between **13** and anions.

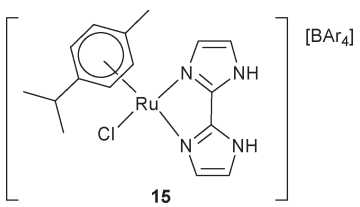



**Fig. 11** Ru(II)-biimidazole receptor.

optimally preorganized for anion binding,[21] features which do not occur in the biimidazole diamides **14** used by Causey and Allen in the coordination of $H_2PO_4^-$ and $Cl^-$.[22]

Ye's study reports that **13** is an appropriate receptor for anions *via* formation of N–H···X hydrogen bonding, mono-proton-transfer system, or deprotonation depending on the interaction anions (Scheme 1). These processes are signalled by the change of vivid colors, resulting from the second sphere donor–acceptor interactions between Ru(II)-$H_2$diim and the anions, and can be distinguished visually. These interactions are not only determined by the basicity of the anion but also by the strength of hydrogen bonding. Fluoride is a particular case because it has a high affinity toward the N–H group, rather than forming hydrogen bonding with the receptor.

A structurally related metal biimidazole complex is **15** which stabilises strong non-selective interactions with several simple inorganic anions such as bromide, nitrate, hydrogensulfate, iodide or perrhenate (Fig. 11).[23]

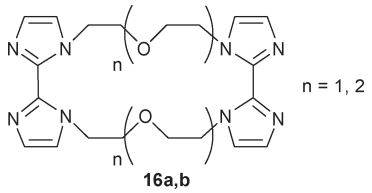



**Fig. 12** Macrocyclic receptors based on biimidazoles.

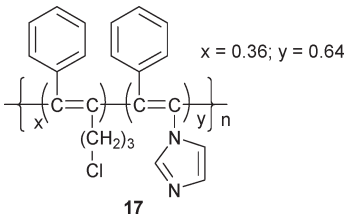



**Fig. 13** Imidazole-functionalized disubstituted polyacetylene.

More recently, a cyclophane containing four imidazole rings linked by ether chains, **16**, has also been used for the recognition of amino acid esters (Fig. 12).[24]

Fluorescent conjugated polymers (CPs) have emerged as improved selective recognition and transduction materials for chemical sensing purposes.[25] CPs are polyunsaturated compounds with alternating single and double bonds along the polymer chain. This conjugation between each repeated unit creates a semiconductive "molecular wire", providing the polymers with very useful optical and optoelectronic properties. CPs which can exhibit a strong luminescence, are extremely sensitive to minor external structural perturbations or to electron density changes within the polymer. CPs have the ability to self-amplify their fluorescence quenching response[26] due to perturbation of the electronic network upon binding of analytes.

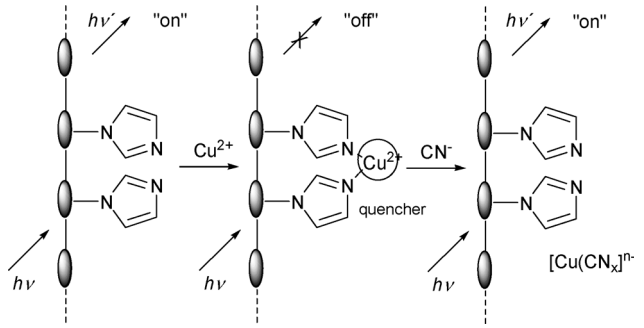
Fluorescent CPs have been employed in different sensing applications, and particularly as sensitive probes for the detection of metal ions.[27] Importantly, CP chemosensors should then contain in their structure some acceptor units to trap the metal ions, such as bipyridyl, terpyridyne, quinoline or imidazole units.

Thus, combining the advantages of the strong luminescence of disubstituted polyacetylenes and the metal ion-coordinating ability of imidazoles Li and co-workers have described a novel kind of highly effective chemosensor **17** (Fig. 13). This receptor can report the presence of Cu(II) selectively, based on the fluorescence "turn-off". Moreover, it can also indirectly probe the presence of trace $CN^-$ both selectively and sensitively (Scheme 2).

Alternating polyfluorene copolymers with imidazole rings as receptor units in the pendent side chains have also been used in the chemosensors field. These systems take advantage of the effective π-conjugation and strong luminescence properties of the polyfluorene and metal ion-coordinating ability of imidazoles to develop novel classes of highly effective transitional metal-sensitive chemosensors. As a consequence of the interest of these type of systems several sensitive probes for Cu(II) metal ions and cyanide (*i.e.* **18** and **19** (Fig. 14)), by using a fluorescence turn off–turn on strategy, have been published following






**Scheme 2** Schematic representation of Cu(II) and $CN^-$ sensors based on the fluorescence "turn-off" and "turn-on" of the polyacetylene.

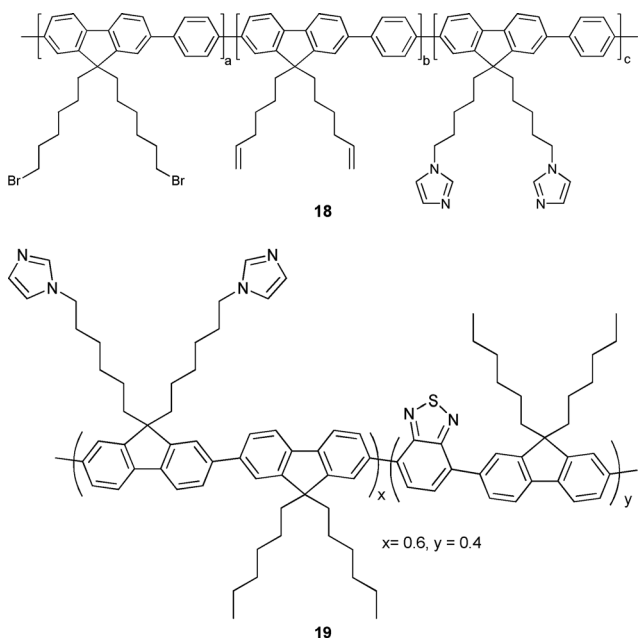



**Fig. 14** Polyfluorene copolymers functionalized with imidazole rings.

this approach.[28] Typically, the imidazole unit appended to the conjugated polymer selectively recognizes Cu(II) promoting the turn off of the fluorescence which is recovered on addition of cyanide ions.

## Benzimidazole receptors

Benzimidazole has also been commonly used in molecular recognition of all cations, anions and neutral molecules due to the emissive properties of this aromatic ring. As a result, this moiety has been used not only as a binding unit for cations and anions, as the imidazole derivatives do, but also as a fluorogenic antenna. Apart from its photochemical properties it is also worth noting another difference with the imidazole ring which involves the different acidity of the NH proton caused by the electronic effect of the benzene ring.

In the field of molecular recognition of cations the macrocyclic ligand **20** reported by García and co-workers should be mentioned (Fig. 15). In this system the N and S atoms act as recognition sites while the two benzimidazole units act as

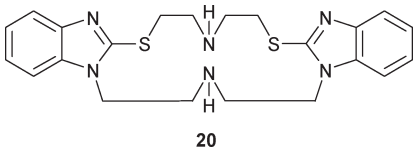



**Fig. 15** Macrocyclic receptor based on benzimidazole.

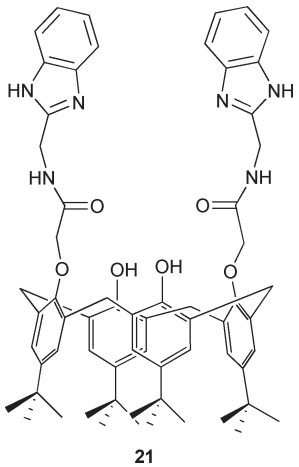



**Fig. 16** Benzimidazole-substituted calixarene receptor.

fluorescent antenna for the detection of transition metal cations in water.[29] Upon addition of the corresponding cations, the receptor's UV-Vis bands experience a bathochromic shift due to the metal coordination. Titration experiments carried out by using this technique were used to calculate the association constant of the different complexes, showing a higher affinity towards Cr(III), followed by the Fe(II) cation, while other metal cations as Hg(II) or Cd(II) have much smaller association constants. The selectivity found in this receptor has been attributed to the relative Lewis acidity of the cations that dominates the coordination capabilities of the receptor. Fluorescence of **20**, that is partially quenched by the donor groups in the macrocycle and other structural issues, is gradually vanished when a large excess of metal guests are added. The small selectivity in the process indicates that fluorescence quenching has a diffusive behaviour.

The benzimidazole-substituted calix[4]arene **21** has been reported by Rao and co-workers for the selective recognition of Hg(II) *versus* a large number of divalent cations (Fig. 16).[30] Solvents used were not only MeOH and anhydrous $CH_3CN$ but also different aqueous mixtures of this organic solvent. In 50% aqueous solution, a 10-fold quenching in the fluorescence was observed only in the case of Hg(II), whereas all other divalent metal cations tested exhibited almost no quenching in fluorescent intensity. However, when the amount of water decreases, the selectivity for this cation also decreases, due to the effect of a less competitive media. Binding of Hg(II) has been attributed, by $^1$H-NMR experiments, to the nitrogen atoms in the benzimidazole ring and the oxygen atoms of the amide bridge, as the theoretical calculations also predicted. The **21**·Hg(II) complex formed has been isolated, characterized and studied on surface by TEM, SEM and AFM microscopies.

The anthracene-linked bis(benzimidazole) diamide **22** (Fig. 17) has also been described as a simple receptor for the

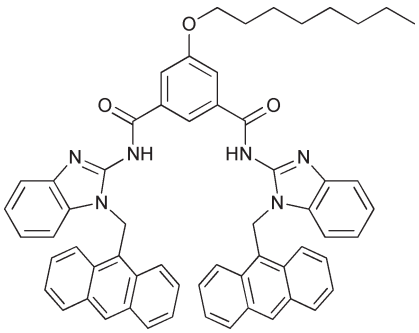



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**Fig. 17** Anthracene-linked bis(benzimidazole) diamide receptor.

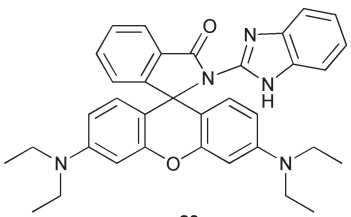


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**Fig. 18** Benzimidazole containing rhodamine B receptor.

selective detection of metal ions and organic sulfonic acids.[31] Differences in the monomer/excimer ratio of fluorescent emission of the anthracene moieties were used to detect the presence of diverse organic acids in $CHCl_3$ and $CH_3CN$/water (4 : 1) solutions. Therefore, the change in emission was considerable in the presence of methanesulfonic acid and *p*-toluenesulfonic acid while the addition of acetic, mandelic or trifluoacetic acids perturbed less the emission of receptor **22**. This difference in the fluorescence emission can be attributed to the protonation of host by the most acidic sulfonic acids and the formation of different ion pairs. Changes in the absorption spectrum correlate well with the fluorescence results. Moreover, metal complexation was studied in $CH_3CN$ and addition of increasing amounts of transition metal cations decreases both the monomer and the excimer emission, although the effect on the excimer band is more pronounced. Cu(II), Co(II) and Ni(II) cause the most marked changes in comparison to the other transition metals.

A different approach has been followed by Tang and Nandhakumar who designed a Rhodamine B colorimetric chemosensor based on the chemical changes induced by Cu(II) anion (Fig. 18).[32] UV-Vis experiments demonstrated that upon addition of Cu(II) a new low energy band appears in the complex formed which is responsible for the change of colour in the solution from colourless to pink. This colour change has been attributed to a ring-opening process of the spirolactam form of **23**. Addition of other metal cations does not produce such changes in the absorption spectrum and does not disturb the effect of Cu(II) in competitivity experiments. The reversibility of the process has confirmed by the addition of EDTA to the medium that cause the disappearance of colour, returning the solution to the initial colourless appearance.

Wang and co-workers synthesized a dehydroabietyl molecule **24** with a benzimidazole unit for the molecular recognition of metal cations (Fig. 19).[33] Receptor **24** decreases its fluorescent emission at $\lambda_{em}$ = 540 nm upon addition of Cu(II) whilst the rest of the cations do not modify or increase the fluorescent emission. Moreover, addition of up to 2 equiv. of Cu(II) also modifies the absorption spectrum of **24**. A Job's plot of the UV-Vis data yielded a 1 : 1 stoichiometry for the Cu(II) complex.

Interestingly, imidazo–benzocrown ether-based ionophores **25–27** bearing arylthienyl and bithienyl π-conjugated bridges have also been evaluated as fluorimetric sensors for metal cations (Fig. 20). In fact, selectivity and sensitivity for Cu(II) and Pd(II) was observed for all systems. More over, systems **26** and **27** have also proved to be efficient sensors for basic anions such as $F^-$, due to changes in emission after deprotonation of the imidazole NH by the $F^-$ ion.[34]

In the field of molecular recognition of anions, the receptors **28** and **29** (Fig. 21), reported by Jang and co-workers, in which

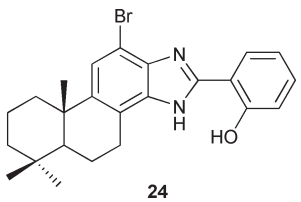


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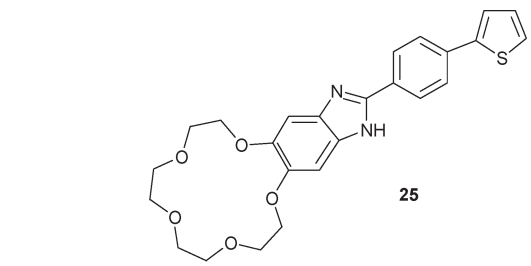
**Fig. 19** Receptor based on the 2-(2′-hydroxyphenyl)benzimidazole core.

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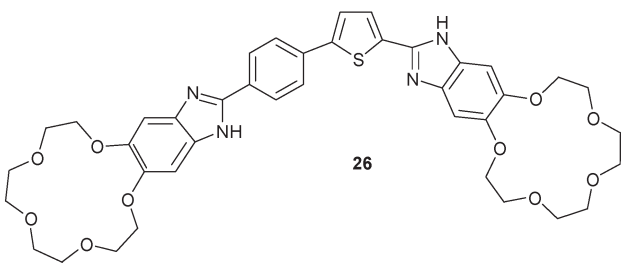


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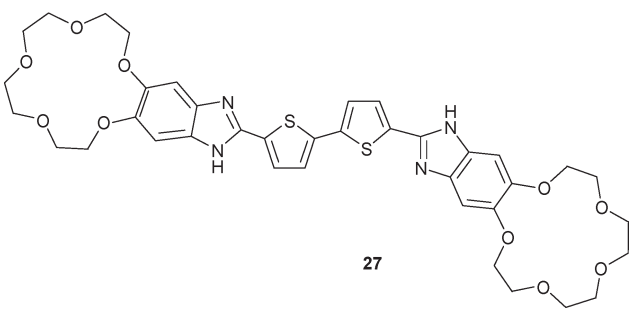
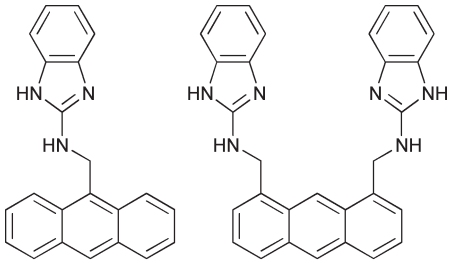


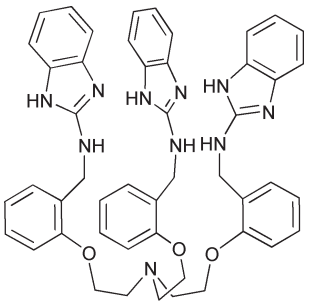

27

**Fig. 20** Imidazo-benzocrown ether receptors.



28 29

**Fig. 21** Fluorescent receptors based on 2-aminobenzimidazole.



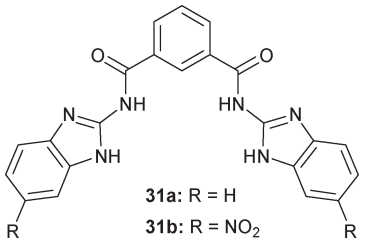
30

**Fig. 22** Benzimidazole-based tripodal receptor.

one or two 2-aminobenzimidazole groups are connected to an anthracene ring should be mentioned.[35] Receptor **28** displayed strong fluorescence emission in $CH_3CN$, which is quenched with the addition of halide, $AcO^-$ and $H_2PO_4^-$ anions. The quenching mechanism has been attributed to a photoinduced electron transfer (PET) process. Compound **29**, bearing two benzimidazole units, presents similar results and selectivities, though higher association constants were found and a preference for $AcO^-$ over $F^-$ was also observed.

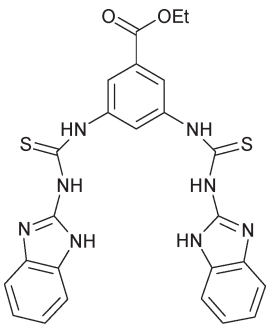
A similar receptor **30** was also prepared by Jang and coworkers, though with a tripodal 2,2′,2″-trioxiethylamine linker (Fig. 22).[36] The recognition behaviour of the receptor toward various anions was evaluated in $CH_3CN$/water (9 : 1) buffered with HEPES to neutral pH and a good selectivity for $I^-$ was found. Thus, fluorescence of the receptor **30** is selectively and strongly quenched with the addition of $I^-$ while the other anions tested do not modify significantly its emission spectrum. In this example, complementarity between the host and iodide predominates over basicity of the anions. The $^1$H-NMR titration with iodide showed that this anion is fundamentally bound by the NH protons of the benzimidazole moiety.

Within the concept of two-arms receptors, these authors synthesized two isophthalamide receptors containing benzimidazole **31a** and nitrobenzimidazole **31b** units[37] (Fig. 23) and a 1,3-bisurea bearing two benzimidazole moieties **32** (Fig. 24).[38] Compound **31b** experiences a bathocromic shift of the UV-Vis bands with the addition of $F^-$ and $AcO^-$ anions in $CH_3CN$/DMSO (99 : 1) that is observable at "naked-eye", while the rest of the anions tested do not cause important variations. When the same titrations are carried out on the related receptor **31a**, it exhibited no change in the absorption spectrum upon addition of any of the anions assayed.



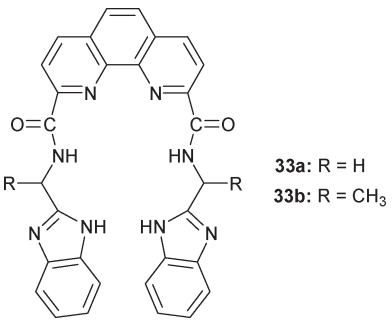
**31a:** R = H
**31b:** R = $NO_2$

**Fig. 23** Two arm isophthalamide–benzimidazole based receptors.



32

**Fig. 24** Benzimidazole and thiourea conjugated receptor.

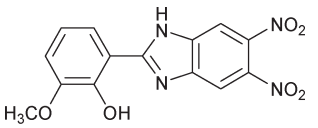


**33a:** R = H
**33b:** R = $CH_3$

**Fig. 25** Two-arm phenanthroline-benzimidazole based recptors.

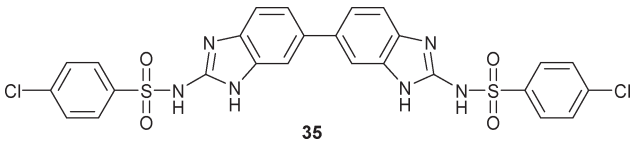
In the case of **32**, after addition of 5 equiv of the sodium salt of a large variety of anions, only the phosphate anion quenches the fluorescence of the receptor in a DMSO/water mixture while the other anions do not modify importantly the fluorescence emission. A PET quenching process has been addressed to explain the fluorescence changes. The $^1$H-NMR titration of the receptor with phosphate exhibits an upfield shifting of the thiourea and benzimidazole NH protons involved in the recognition process that points to the presence of hydrogen bonds in the neat receptor that are stronger than in the complex.

The popularity of the tweezer-like structures for anion recognition is again demonstrated with the preparation of two molecules bearing a phenanthroline, two imide and two benzimidazole moieties as receptor units.[39] In **33a** (R = H) and **33b** (R = $CH_3$) receptors (Fig 25), two different fluorescent responses were found: a quenching of the fluorescence emission for $F^-$ and $AcO^-$ and an enhancement of the fluorescence for $Cl^-$, $Br^-$ and $I^-$ anions. These opposite behaviours were rationalized by a photo-induced electron mechanism (PET) and the increase of the rigidity of the host molecules. In particular, $Cl^-$



34

**Fig. 26** Chromogenic functionalized benzimidazole receptor.



35

**Fig. 27** Bis-benzimidazole-based conformationally restricted receptor.

anion could be recognized selectively according the changes in the fluorescence spectrum.

H. Lin and co-workers published a chromogenic "naked-eye" anion receptor **34** (Fig 26) in an aqueous media, with a dinitrobenzimidazole unit connected to a phenol donating group.[40] The presence of the nitro groups increases the polarity of the molecule, making it more suitable for chromogenic detection and increases the acidity of the NH group of benzimidazole. Addition of $F^-$ to a solution of compound **34** induces a clear colour change that is not observable with other halide anions. In the UV-vis spectrum of the complex formed, a new charge-transfer band appears which is responsible for this colour change. The $^1$H-NMR study carried out to investigate the coordination modes illustrates that the NH group of the benzimidazole and the phenolic OH are responsible for the $F^-$ coordination.

Structurally related is the receptor **35** reported by Jang and co-workers to distinguish adipate over other dicarboxylates (Fig. 27).[41] Receptor **35**, that coordinates adipate in a 1 : 1 fashion, presents a ratiometric response of fluorescence emission in $CH_3CN$/DMSO (99 : 1) that is not found with the addition of other dicarboxylates. This response consists in a blue shifting of the fluorescence emission that has been attributed to a restriction of the molecular free rotation. In this compound, the important factor in the discrimination of the different dicarboxylates is the distance between the two recognition units that makes the receptor more suitable for adipate than for the other dicarboxylates.

Ruthenium and osmium complexes coordinated to imidazole and benzimidazole ligands have been used as anion receptors. The stability of these complexes and their redox and chromogenic properties make them good candidates for molecular sensing. Thus, coordination of the metal to the nitrogen atoms in these ligands enhances the acidity of the NH groups and makes them able to recognize the presence of basic anions by deprotonation or by coordination of the less basic ones. Moreover, the effect of the benzene in benzimidazole with respect to imidazole units makes them more acidic, favouring the anion-induced deprotonation. In this sense, ruthenium complexes **36** and **37**, osmium-ruthenium complex **38a** and osmium complex **38b** have been used as molecular receptors of basic anions (Fig. 28).[42] $^1$H-NMR titrations of **36** and **37** with anions revealed that NH groups of the benzimidazole are in charge to coordinate the anions: the downfield/disappearance of their peaks and the remarkable upfield of the neighbouring protons indicates a

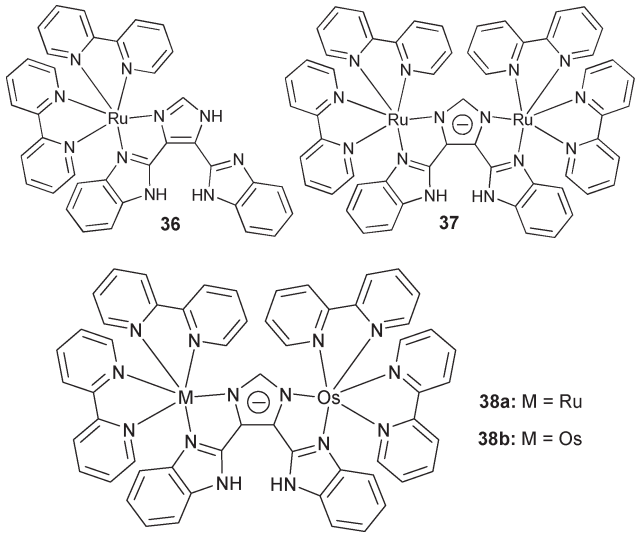
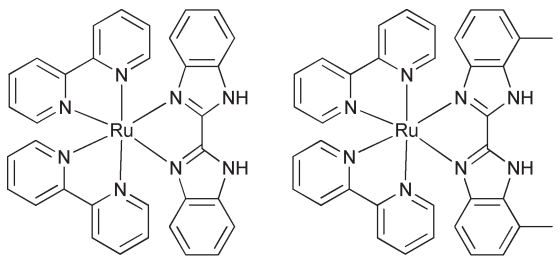



**Fig. 28** Monometallic Ru(II), homobimetallic Os(II) and heterobimetallic Ru(II)-Os(II) bipyridyl complexes containing 4,5-bis(benzimidazole-2-yl)imidazole units.



39 40

**Fig. 29** Ru(II) bipyridine complexes with 2,2′-bis(benzimidazole) receptors.

strong hydrogen bond formation or a neat deprotonation. In the UV-Vis titrations, it is observed that a 1 : 1 hydrogen-bonded adduct was formed with $F^-$, $AcO^-$ and $H_2PO_4^-$ anions. However, in the presence of an excess of $F^-$, stepwise deprotonation of the two benzimidazole NH fragments occurred. Less basic anions ($AcO^-$ and $H_2PO_4^-$) induce deprotonation of only one NH. Photoluminiscence titrations exhibit a strong quenching when $F^-$, $AcO^-$ and $H_2PO_4^-$ anions are added. The redox properties of **36** and **37** are also affected by the anion coordination and a new wave appears, cathodically shifted in relation to the initial ones. The structurally related osmium complexes **38a** and **38b** presented the same spectroscopic and electrochemical behaviour when they were titrated with $F^-$ and $AcO^-$ anions.

Following with the family of ruthenium complexes, Ye and co-workers prepared mononuclear complexes with 2,2-bisbenzimidazole and the corresponding 4,4′-bismethylated ligand (Fig. 29).[43] In a similar way as in the aforementioned complexes, compounds **39** and **40** experienced successive deprotonations in $CH_3CN$ with $F^-$ and $AcO^-$ that were followed by UV-Vis, emission spectroscopy, $^1$H-NMR and electrochemical methods. Additionally, a strong hydrogen bond coordination of the less basic anions is observed in emission spectroscopy and $^1$H-NMR experiments. A theoretical paper published by Zhang and co-

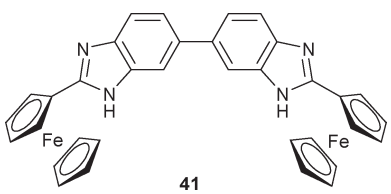
workers studies the coordination/deprotonation process in this sort of ruthenium bis(benzimidazol-2-yl)imidazole complexes.[44] Computational results, obtained with (TD)-DFT methods in the Gaussian09 program, support a proton transfer process for the spectroscopic and electrochemical changes experienced in these compounds.

It is worth mentioning that a series of ruthenium complexes containing bis-benzimidazole derivatives have been identified as able to target mitochondria and induce caspase-dependent apoptosis in cancer cells through superoxide overproduction.[45]

The novel 2,2′-diferrocenyl-5,5′-bis(benzimidazole) **41** has been synthesized and studied as a multichannel molecular sensor for anions (Fig. 30).[46] Thus, **41** behaves as a selective redox, chromogenic and fluorescent chemosensor for $H_2PO_4^-$ and $HP_2O_7^{3-}$ in DMSO/water. Upon complexation, the ferrocene redox wave displays a cathodic shift of $\Delta E = -90$ to $-80$ mV. Moreover, the absorption spectrum undergoes a perturbation characterized by a bathocromic shift of the lower energy band. Importantly, emission spectrum of the receptor is also perturbed and a 37-fold enhancement of initial fluorescence intensity is obtained.

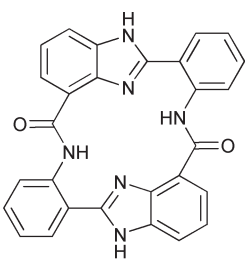
The pre-organization provided by macrocyclic structures has also been used for the design of anion receptors. A conformationally-restricted structure has less freedom to accommodate diverse guests and a higher selectivity is expected. Using this concept, Eichen and co-workers prepared a cyclo[2]benzimidazole receptor **42** for the fluorescent detection of anions (Fig. 31).[47] The binding affinity was studied in DMSO containing 0.1% of water and $F^-$, $H_2PO_4^-$, and benzoate caused a strong emission enhancement up to 150-fold in the case of $F^-$, that eventually deprotonates the receptor **42**. The observed enhancement of fluorescence has been attributed to an Excited-Estate Intramolecular Proton Transfer (ESIPT) due to the existence of different energy-accessible tautomers in the molecule.

As already commented in the section concerning the imidazole receptors, conjugated polymers (CP) have also been used as receptors for different species. Thus, the recognition properties




41

**Fig. 30** 5,5′-Bis(benzimidazole) receptor.




42

**Fig. 31** Cyclo[2]benzimidazole receptor.

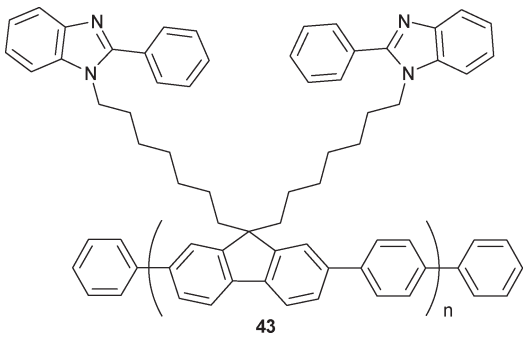



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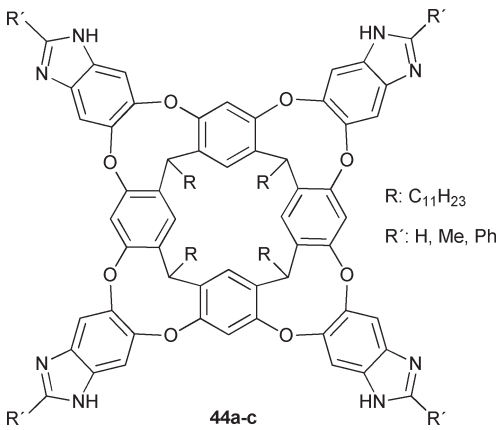
**Fig. 32** Polyfluorene derivative functionalized with benzimidazole units.




44a-c

**Fig. 33** Tetrabenzimidazole cavitands.

can add to the optoelectronic properties of these materials. One of these polymers, synthesized by Iyer and co-workers, connects benzimidazole moieties to a polyfluorene-*alt*-1,4-phenylene backbone (Fig. 32).[48] This polymer, **43**, is able to coordinate selectively Fe(III) in THF/water (4 : 1) at pH = 7.4 that originates a strong static quenching of the emission in μM concentrations. Besides, the iron complex fully recovers its original fluorescence emission when it is treated with $H_2PO_4^-/HPO_4^{2-}$ or $HP_2O_7^{3-}$ at low concentration while halogens, other oxoanions or cyanide do not affect significantly the emission spectrum. In fact, recovery of the initial fluorescence is caused by the decomplexation of Fe(III) induced by the different phosphate species in solution. The selectivity of these processes has successfully been applied to the detection of phosphate in saliva, giving satisfactory results when they were compared to commonly used analytical techniques.

In the field of molecular recognition, as well as in other fields of the supramolecular chemistry, pre-organization and conformationally-restricted equilibriums have been repeatedly used in order to control and optimize the intermolecular interactions. It is well known that a good match between the host and the guest increases the possibilities of success. One of the best established backbone structures are cavitands – hollow circular molecules that create a well defined cavity in them. Rebek and co-workers prepared a family of resorcinarene cavitands (**44a–44c**, Fig. 33) with four units of benzimidazole forming a cavity that has been used in the molecular recognition of cationic and anionic guests.[49] These compounds, differently to other cavitands, stay

as monomers in water or alcohol saturated chloroform (hydrogen bond solvents are required to maintain the supramolecular structure of the receptor) and the methyl-substituted cavitand **44b** forms a strong 1 : 1 complex with tetramethylphosphonium bromide while complexation with triethylammonium chloride presents a very small association constant and does not respond upon addition of tetraethylphosphonium and ammonium bromides. In the same conditions, adamantine and 1-hydroxyadamantane are incorporated to the cavity of the receptor.[49a] These authors, in a related article, described the influence of the counterion for the most stable tautomer in the complexation of ammonium salts using $^1$H-NMR.[49b] In this study, it is shown how chelation of anion by the NH moieties in the benzimidazole moiety modifies the structure of the complex with the organic cation.

The supramolecular properties of these versatile molecules continued with the work of Choi and co-workers, who described that receptor **44a** complexes neutral amide molecules.[50] When 4-methyl-*N*-4-tolylbenzamide was added in excess to a solution of **44a** in water-saturated chloroform, a large upfield shift of the $^1$H-NMR signal of the methyl group of the benzamide was observed as evidence of the inclusion of the molecule into the receptor cavity. However, no evidence of a similar shift in the other terminal methyl group was observed. This unexpected selectivity was confirmed with model molecules in which one of the *p*-tolyl groups was replaced by a methyl group. The reason for such selectivity was attributed to the formation of one hydrogen bond when the guest is placed one side or the other. This extra energetic contribution makes possible the existence of only one complex.

A related structure **45** of Rebek's team, functionalized with four carboxylates on the benzimidazole moieties, has demonstrated to encapsulate the alkyl chains of surfactants in water (Fig. 34).[49c] In this interesting paper it is observed by NMR how the long alkyl chains of sodium dodecylsulfate (SDS) and dodecylphosphocholine (DPC) are introduced in the apolar cavity formed by the receptor. These surfactants introduced in the cavity in a coiled form up to the sixth carbon atom, and the complex is stabilized by C–H/π interactions, solvophobic effects and a good complementarity between the inner volume of the receptor and the guest. Receptor **45** also exhibits the capability of incorporating in water important biological targets such as acetylcholine and choline preferentially to L-carnitine with kinetic and thermodynamic stability.[49d] The complexation process was followed by $^1$H-NMR and isothermal titration calorimetry (ITC) exhibiting a good selectivity of this enthalpy and entropy driven process. **45** was also able to dissolve and encapsulate solid adamantane by sonication in water. In a more recent article the affinity of this cavitand for biomolecules, as neurotransmitters or anti-influenza drugs (amino adamantanes), has been extended.[49e] The results derived from this study reveal that host discrimination between guests with similar charges and shapes is not to be derived from specific host–guest contacts but from differences in guest hydration and hydrophobicity. Therefore, factors that affect solvation (pH, the presence of buffers or salts) change decisively the complexation behaviour. In the aforementioned article and in a previous communication[49f] the presence of SDS solubilises **45** under near physiological conditions above its critical micellar concentration by incorporating them in the micelle's wall.

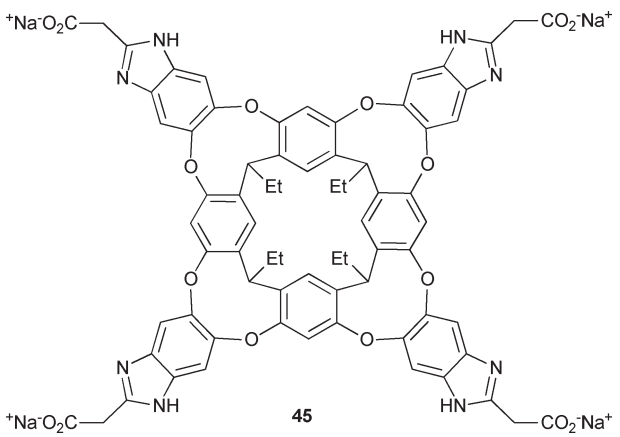



**Fig. 34** Tetrabenzimidazole cavitands with a hydrophobic inner surface and four carboxylates on the exterior promoting its water solubility.

Benzimidazole receptors have also been used for the recognition of neutral receptors as carboxylic acids, hydrogen bond donors, as urea or barbital, and *O*-methylated aminoacids. Neutral molecules are in general weakly bound and a better control of the complementarity between host and guest is then required. Moran and co-workers synthesized a receptor **46** for carboxylic acids that connects two benzimidazole units through a xanthene molecule in a tweezer-like structure (Fig. 35).[51] The cavity created between the two benzimidazole arms effectively binds methanol, DMSO or acetone in chloroform and the structure of the complexes was determined by single X-ray crystal diffraction. When carboxylic acids were studied, it was observed that the acid group protonates one of the nitrogen atoms present in the benzimidazole moieties while the other remains neutral and participates in the coordination of the resulting anion. When the acid used was anthracenecarboxylic acid, a strong decrease of the emission intensity was observed compared to the free acid. A PET mechanism has been pointed to as the reason for the quenching of fluorescence. The single crystal structure for the complex shows how the benzimidazole on the amide arm protonates while this NH and the other three NH groups coordinate the carboxylate moiety. A similar experiment with pyrene carboxylic acid showed no quenching of fluorescence emission in the presence of **46**.

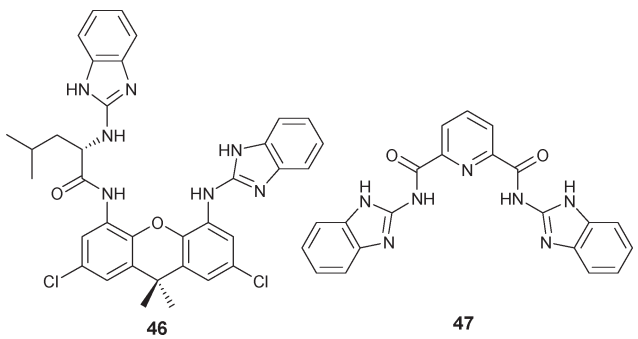



**Fig. 35** Tweezers-like receptors bearing two benzimidazole rings.

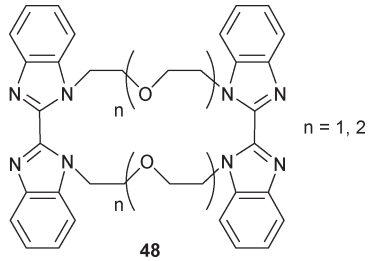



**Fig. 36** Macrocyclic receptors connecting two 2,2′-bis(benzimidazole) subunits.

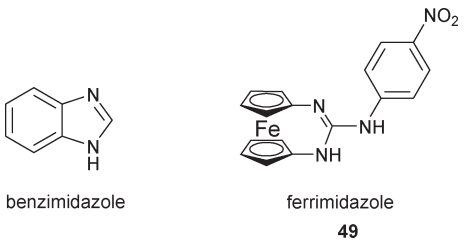



**Fig. 37** Structural analogies between benzimidazole and 1,3-diaza[3] ferrocenophane (*ferrimidazole*).

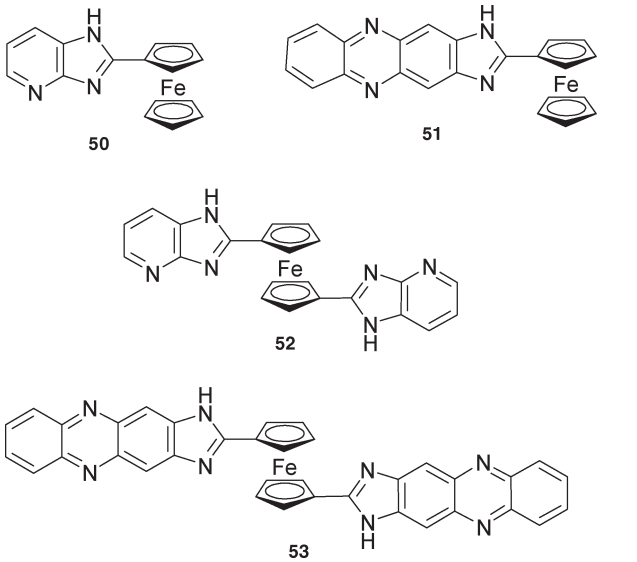



**Fig. 38** Ferrocenyl-containing imidazopyridine and imidazophenazine receptors.

Gale and co-workers prepared a simple tweezer-like receptor **47** connecting two benzimidazole units through a 2,6-pyridinedicarboxylic amide.[52] Receptor **47** binds preferentially with barbital over the structurally related urea, thiourea or imidazolinone in DMSO/$MeNO_2$. In the crystal structure of the complex a good complementarity is observed that leads to the formation of four hydrogen bonds.

Other examples of the use of benzimidazole in molecular recognition are the two related macrocycles with the general structure **48** in which these heterocycles are connected through polyether alkyl chains (Fig. 36).[53] These compounds have been used for the recognition of *O*-methylated α-aminoacids in chloroform. In the study it has been observed how the length of the macrocyclic arms influences the selectivity due to the complementarity of hydrogen bonds and π–π stacking.

The guanidine unit, in the guise of 2-aminoimidazole, present in the new structural motif **49** acts as a binding site for anions (Fig. 37). The calculated nucleus-independent shifts (NICs) gave rise to values between 0 and 2 ppm indicating that the ferrimidazole ring is not aromatic and resembles more imidazolines than imidazoles. Because of the amphoteric nature of the guanidine unit, it displays an interesting pH-dependent redox behaviour. Moreover, it allows the sensing of acetate, benzoate, $F^-$, $Cl^-$ and $Br^-$ anions through an unusual redox ratiometric fashion and spectroscopic measurements. Its monoprotonated form is able to selectively sense the less basic $Cl^-$, $Br^-$ and $NO_3^-$ anions: the oxidation redox peak is then cathodically shifted and the low energy band of the absorption spectrum is red-shifted upon complexation. In addition, the signals due to the NH protons in the $^1H$ NMR spectrum are remarkably downfield shifted once the recognition event has taken place.[54]

## Fused imidazole receptors

The realisation that imidazole and benzimidazole derivatives can function as selective and effective ion receptors has also led to work on studying the ability of some other systems in which the imidazole moiety is fused to other cyclic or heterocyclic systems.

In this context, a study has been carried out regarding how the binding properties of the benzimidazole core can be not only modulated but also changed either by introduction of an additional heterocycle nitrogen atom at an appropriate position in the six-membered ring, or by linear annelation to aza-heterocycles leading to expanded benzimidazole derivatives bearing several binding sites. Thus, new simple and easily synthesized mono- and two-armed molecules **50–53** (Fig. 38) were prepared through short synthetic sequences from commercial starting materials. These ferrocenyl derivatives **50–53**, not only display a strong interaction between the aza-heterocycle ring and Pb(II) ions, but also distinguishes this metal ion, using electrochemical and spectroscopic (absorption, emission and $^1H$ NMR) techniques, from other metal ions, including the strong competitors Ca(II), Cd(II), and Hg(II). As a consequence, **50–53** represent the first examples of Pb(II) multichannel chemosensor molecules, which combine redox detection ($\Delta E_{1/2}$ = 110–180 mV), and the sensitivity of fluorescence (detection limit of **50** = 2.7 $\mu gL^{-1}$) with the convenience of colorimetric assays, which allow for the potential of "naked eye" detection.[55]

Recently, Pandey and co-workers described a ferrocenylimidazoquinazoline derivative which selectively senses $Hg^{2+}$ and $Pb^{2+}$ in an aqueous environment.[56]

Examples of imidazole containing adjacently fused anthraquinone units have also been described in the field of chemosensors for anions. Thus, phenyl-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **54a** and its derivatives **54b** and **54c** (Fig. 39) have been reported as new colorimetric and ratiometric fluorescent chemosensors for $F^-$. These properties are ascribed to an anion-induced proton transfer process. By changing the electron properties of substituents on the phenyl *para* position, the sensor–$F^-$ interaction mechanism, the $F^-$ selectivity, and the fluorescence response can be finely tuned.[57]

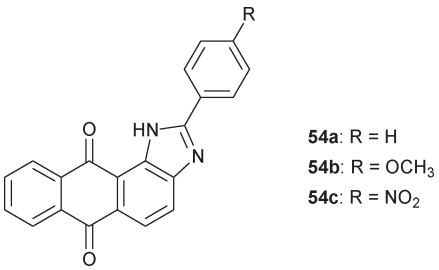



**Fig. 39** Anthra[1,2-*d*]imidazole-6,10 dione receptors.

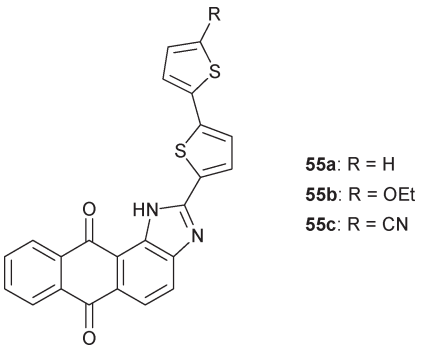



**Fig. 40** Bithienyl-imidazo-anthraquinone receptors.

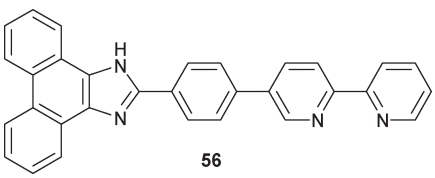



**Fig. 41** Phenanthroimidazole receptor.

Closely related to this structure are the novel bithienyl-imidazo-antraquinone derivatives **55a–c** (Fig. 40). These compounds, undergo deprotonation of the imidazole NH upon addition of $F^-$ anions and the resulting deprotonated species have been proved to be efficient sensors for metal ions such as Zn(II), Hg(II) and Cu(II).[58]

Receptor **56** (Fig. 41), which consists of a phenanthroimidazole chromophore connected to a bipyridyl group has also been prepared.[59] Interestingly, upon treatment with Fe(III) this receptor displayed a ratiometric fluorescent response with enhancement of the ratios of emission intensities at 440 and 500 nm from 0.36 to 3.24. In addition, the sensor showed good selectivity to Fe(III) over other metal ions tested.

Diruthenium(II) complex **57** (Fig. 42) which contains two metallolumophores and a two receptor system acts as an "off-on-off" luminescent pH sensor through protonation and deprotonation in MeOH-$H_2O$ (1 : 1 v/v) solution at room temperature.[60]

Until quite recently, no examples of ferrocenyl substituted imidazole had been published as multichannel chemosensors with high selectivity and sensitivity not only for metal cations but also for anions. However, during the last few years significant studies have been reported by our group, within this research area.

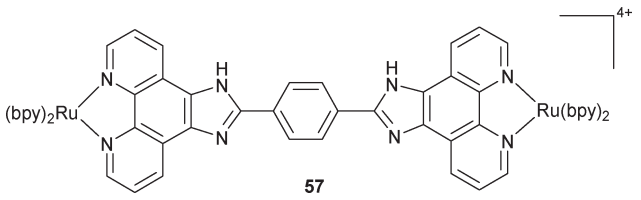



**Fig. 42** Receptors based on bipyridil Ru(II) complexes of bis(imidazophenanthroline).

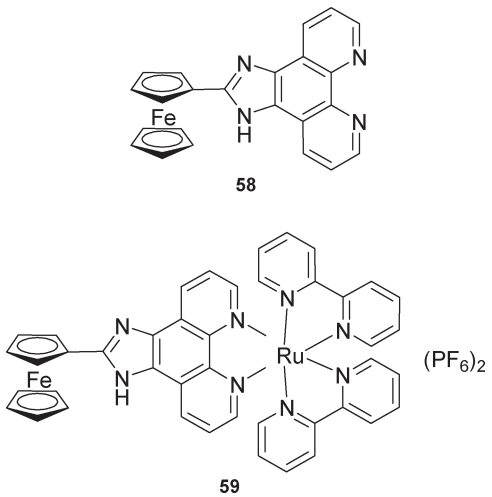



**Fig. 43** Receptors based on a ferrocenyl-imidazophenantroline dyad and its corresponding Ru(II)bipyridyl complex.

Studies carried out on the ferrocene-imidazophenanthroline dyad **58** (Fig. 43) demonstrated that it can be used to effectively recognize aqueous hydrogenpyrophosphate and the organic anions ADP and ATP through three different channels: electrochemical, colorimetric and fluorescent. It is worth mentioning that the changes observed in the absorption spectra are accompanied by colour changes from pale yellow to pink, which allows the "naked-eye"detection of these ions. On the basis of $^1H$ and $^{31}P$ NMR studies as well as DFT calculations, information about the molecular sites involved in bonding was also reported. On the other hand, reaction of **58** with *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate followed by treatment with $NH_4PF_6$ gave rise to the heterobimetallic ligand **59** which selectively senses the $Cl^-$ anion over other anions examined through two channels: electrochemical and fluorescent. Thus, a cathodic redox shift of the Fe(II)/Fe(III) redox couple, keeping the oxidation wave of the Ru(II) center unchanged, and a significant red emission enhancement (30 fold) were observed when the recognition process took place.[61]

The synthesis and properties of ferrocene-based heteroditopic receptors in which the ferrocene moiety is attached to an imidazo[4,5-f]quinoxaline unit have also been reported. These nitrogen-rich ferrocene derivatives show remarkable ion-sensing properties because of the presence of the redox active ferrocene unit and the polyazaheteroaromatic ring system which act as a dual binding site for anions and metal cations. Thus, receptor **60a**[62] displays an anodic shift (up to 150 mV) of the oxidation wave upon complexation with metal cations such as Zn(II),



Cd(II), Hg(II) and Pb(II), and a strong cathodic shift in the presence of $F^-$ anion, as a consequence of a deprotonation process of the free receptor. Moreover, the low energy band present in the free receptor also undergoes an increase in intensity upon binding to those metal cations. This change in the absorption spectra is accompanied by a dramatic colour change which allows the potential for "naked eye" detection. Similarly, the ferrocene-imidazoquinoxaline dyad **60b** behaves as a highly selective redox, chromogenic and fluorescent chemosensor molecule for Pb(II) in acetonitrile solutions while **60c**, bearing two additional pyridine rings as substituents has shown its ability for sensing Hg(II) cations through the above mentioned three different channels (Fig. 44).[63]

The heteroditopic receptor **61**, with a 2,1,3-benzothiadiazole ring fused to the imidazo moiety, also behaves as a highly selective dual-redox and chromogenic chemosensor not only for Pb(II) cations but also for $HP_2O_7^{3-}$ anions.[62]

More recently, the synthesis and sensing behaviour of the structurally related ferrocenyl imidazo[4,5-*h*]phenazines containing fused aromatic or heteroaromatic groups have also been described (Fig. 45).[64] It is worth mentioning that the binding events are strongly affected by the nature of the aromatic ring fused to this ring system. Dyad **62a** behaves as a highly selective redox/chromogenic/fluorescent chemosensor molecule for Pb(II) cations in $CH_3CN/H_2O$ (9 : 1). In addition, dyad **62a** also exhibited a redox induced complexation/decomplexation type signalling patterns that can be used for the construction of more elaborate supramolecular switching systems. Dyad **62b**, bearing two fused pyridine rings, displays the same type of sensing properties but now toward Hg(II) cations. The changes in the absorption spectra are accompanied by a color change from yellow to orange which allows the potential for "naked eye" detection. On the other hand, electrochemical data suggest that the interaction between receptors **62a** and **62b** with $AcO^-$ and $H_2PO_4^-$ anions involve both formation of hydrogen-bonded complex and deprotonation. However, $HP_2O_7^{3-}$ and $F^-$ anions induced deprotonation. The electrochemical study shows its ability for detecting the formation of the ion-pair [**62a**·$Pb(H_2PO_4)_2$] and [**62b**·$Hg(AcO)_2$] complexes, which were also detected by electrospray mass spectrometry.

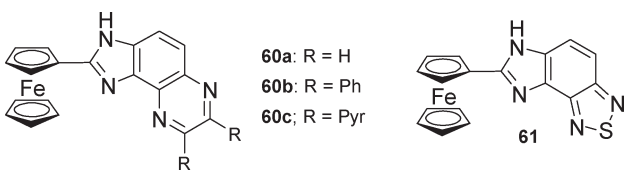



**Fig. 44** Imidazo-quinoxaline and imidazo-benzothiadiazole receptors.

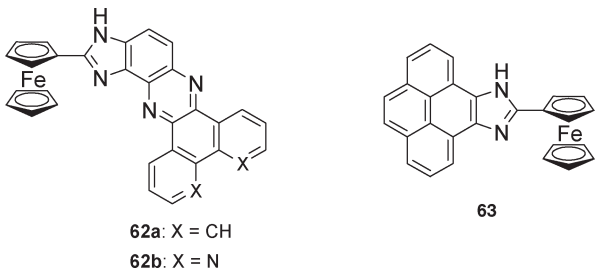



**Fig. 45** Receptors based on imidazo-phenazine and ferrocene-imidazopyrene dyads.

Simpler receptors can also function as very effective host-separated ion pair receptors. Such is the case of the ferrocene-imidazopyrene dyad **63**,[65] bearing the imidazole ring as the only receptor site. This species acts as a redox and optical molecular sensor for ion pairs exhibiting an easily detectable signal change in the redox potential of the ferrocene/ferrocenium redox couple and a remarkable perturbation of the emission spectrum. Interestingly, the perturbation of the emission spectrum follows the order Pb(II) > Hg(II) > Zn(II) for cations and $H_2PO_4^-$ > $AcO^-$ for anions.

## Conclusions

The important progress achieved in the development of imidazole based receptors can be exemplified by the number of systems that have recently been described in this field. In most cases, such receptors are able to recognize either cations or anions. However, relevant examples in which the imidazole unit displays its dual behaviour, that is the simultaneous sensing of both cations and anions, through different channels (redox, colorimetric, fluorescent, spectroscopic) have also been reported. Moreover, noteworthy examples of imidazole-based receptors for relevant organic molecules, such as aminoacids and carbohydrates as well as a host-separated ion-pair receptor, have also been described. As a consequence of this background, we thus predict that this topic constitutes an area of supramolecular chemistry that is ripe for future growth.

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