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Fluorescent and colorimetric ion probes based on conjugated oligopyrroles

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Metal ions and anions play important roles in many industrial and biochemical processes, and thus it is highly desired to detect them in the relevant systems. Small organic molecule based sensors for selective and sensitive detection of target ions show the advantages of low cost, high sensitivity and convenient implementation. In this area, pyrrole has incomparable advantages. It can be easily incorporated into linear and macrocyclic conjugated structures such as dipyrrins, porphyrins, and N-confused porphyrins, which may utilize the imino N and amino NH moieties for binding metal ions and anions, respectively. In this tutorial review, we focus on representative examples to describe the design, syntheses, sensing mechanisms, and applications of the conjugated oligopyrroles. These compounds could be used as colorimetric or fluorescent ion probes, with the advantages of vivid colour and fluorescence changes, easy structural modification and functionalization, and tunable emission wavelengths. Compared with normal porphyrins, simple di- and tripyrrins, as well as some porphyrinoids are more suitable for designing fluorescence "turn-on" metal probes, because they may exhibit flexible confirmations, and metal coordination will improve the rigidity, resulting in vivid fluorescence enhancement. It is noteworthy that the oligopyrrolic moieties may simultaneously act as the binding unit as well as the reporting moiety, which simplifies the design and syntheses of the probes.

Key learning points
(1) Fundamental knowledge of pyrrole chemistry and ion probe chemistry.
(2) Synthetic chemistry of linear and macrocyclic conjugated oligopyrroles.
(3) Advantages and characteristics of probes based on oligopyrroles.
(4) Design strategies for metal ion and anion probes.
(5) Unique ion sensing mechanisms of probes based on oligopyrroles.

1. Introduction

Ions play important roles in many industrial and biochemical processes. They may be either essential or toxic for human beings and animals, and thus it is highly desired to detect them in the relevant systems. Compared with the techniques based on expensive equipment, detection of target ions by small organic molecule-derived probes based on colour or fluorescence changes has the advantages of low cost, high sensitivity and convenient implementation. Upon addition of the target ion, a colorimetric probe will elicit colour changes which can be observed by the naked eyes. Similarly, fluorescent changes elicited by fluorescent probes can be detected using a fluorometer or even more conveniently under a portable UV lamp, showing higher sensitivity.[1] A common strategy for developing such a probe is to link a recognition unit to a signal reporting chromophore, such as rhodamine, anthracene, fluorescein, coumarin, boron-dipyrromethene (BODIPY), porphyrin, and cyanine dyes.[2,3] In most of such cases, complicated molecular design and multi-step syntheses are involved. To develop more conveniently accessible ion probes, it is feasible to employ a recognition unit, which can simultaneously act as the reporting moiety. In this respect, pyrrole is a promising building block.

Pyrrole is a naturally occurring five-membered heterocycle (Scheme 1). It can be easily incorporated into linear and macrocyclic conjugated structures such as dipyrrins, porphyrins, N-confused porphyrins,[4] and expanded porphyrins containing more than four pyrrole units, say, hexaphyrins (Scheme 1). These compounds may

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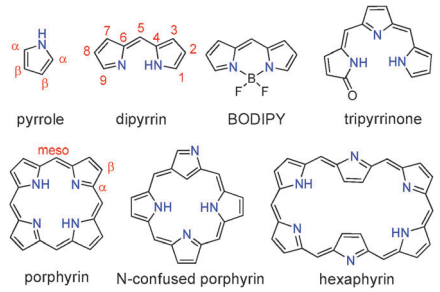


Scheme 1 Representative framework structures for conjugated oligopyrroles discussed in this tutorial review.

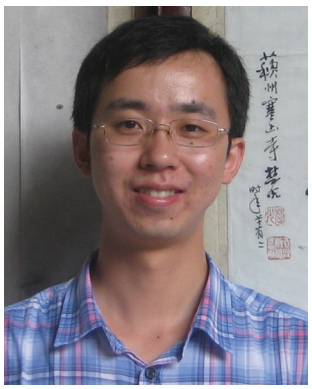
utilize imino N and amino NH moieties for binding metal ions and anions through metal coordination and hydrogen bonds, respectively. Meanwhile, they may also exhibit attractive and tunable colour and fluorescence changes.

This tutorial review is focused on the designing strategies, syntheses and ion sensing properties of colorimetric and fluorescent probes based on conjugated oligopyrroles. Herein, conjugated oligopyrroles refer to a class of compounds that bear two or more conjugated pyrrolic units as the central chromophore (Scheme 1), including linear ones such as dipyrrins, and tripyrrinones, as well as macrocyclic ones such as porphyrins and expanded porphyrins. In this respect, both cation and anion sensing using expanded porphyrins was first demonstrated by Sessler and coworkers.[5,6] Due to the limited length of this tutorial review, these early examples as well as non-conjugated pyrrole-based probes will not be described in detail, and previous reviews may be referred to ref. 7.

2. Metal ions sensing

2.1 Importance of metal ion sensing

The importance of metal ion sensing can never be overestimated. There are mainly two kinds of metal ions that are of special interest for detection. One is biologically essential, including Ca^{2+}, K^{+}, Na^{+}, Fe^{2+}, Zn^{2+}, *etc.* The concentrations of these ions should be maintained within a suitable range to guarantee their normal biochemical functions, and thus it is important to detect and quantify them.



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The other class is biologically toxic, such as Hg^{2+} and Pb^{2+}. These ions also need to be detected with high sensitivity both *in vivo* and *in vitro*.

2.2 Linear conjugated oligopyrroles for metal ion sensing

2.2.1 Fluorescence of dipyrrin complexes. The simplest linear conjugated oligoprroles are dipyrrins (Scheme 1), which can be synthesized by the 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of dipyrromethanes obtained from the acid-catalyzed condensation of pyrrole with suitable aldehydes. A typical dipyrrin has a planar dipyrrolic framework with two N atoms available for chelating metal ions or boron. Thus dipyrrins have been used as ligands for the construction of supramolecular coordination assemblies. Free dipyrrins usually emit very weak fluorescence. However, their boron complexes (BODIPYs, Scheme 1) are widely used as fluorescent dyes. In addition, some of their metal complexes also show intense fluorescence,[8] which provides the possibility of using dipyrrins as metal ion probes based on the fluorescence changes accompanied with the coordination to target metal ions.

The luminescent properties of dipyrrin metal complexes are influenced by many factors, such as the substituents, coordination modes, the metal ions, and the coordinated anions. In this section, the fluorescent behavior of dipyrrin complexes will be briefly described.

Bocian, Lindsey, Holten and co-workers found that introduction of a steric hindrance group into the 5-position of dipyrrins (Fig. 1) can enhance the fluorescence intensity of the zinc complexes.[9] Thus, complexes **1** and **2** show very weak fluorescence with a quantum yield (Φ_F) of 0.6–0.7% in toluene, while complex **3** is strongly fluorescent, showing a quantum yield of 36%. This observation may be ascribed to the fact that the bulky mesityl groups in **3** lead to steric constraints on intramolecular rotations, and thus dramatically suppress the nonradiative energy loss of the excited state, leading to the observed fluorescence "turn on".

Using a similar strategy, Boyle, Archibald, and co-workers also developed a fluorescent dipyrrin zinc complex **4** with a quantum yield of 5.7% (Fig. 1).[10] The 2-pyridyl group at the 5-position of the dipyrrin ligand is "locked" by coordination with zinc, leading to suppressed nonradiative energy loss and increased fluorescence.

By changing the metal coordination mode, Cheprakov, Vinogradov, and co-workers discovered that the fluorescence of

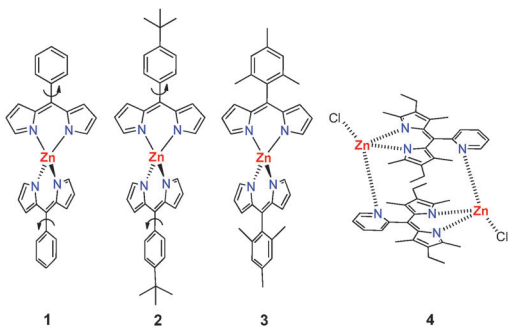

Fig. 1 Chemical structures of dipyrrin Zn(II) complexes **1–4**.

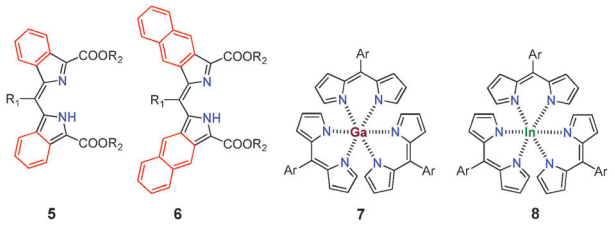

Fig. 2 Chemical structures of dipyrrins **5** and **6**, and Ga(III) and In(III) complexes **7**, and **8**. R_1 = 4-methoxycarbonylphenyl, R_2 = *t*-Bu, Ar = 2,4,6-trimethylphenyl.

zinc complexes of π-extended dipyrrins (Fig. 2) can be reversibly modulated.[11] Free dipyrrins **5** and **6** do not fluoresce. Addition of $Zn(OAc)_2$ to an acetone solution of dipyrrin **5** resulted in immediate vivid fluorescence enhancement with a quantum yield of 70%. Then precipitation formed in a few hours, accompanied with disappearance of the fluorescence. The "off–on–off" fluorescent behavior could be ascribed to the initial formation of heteroleptic zinc complexes in the form of MLX (M = Zn^{2+}, L = dipyrrin ligand, X = OAc^-, fluorescence on), followed by the formation of homoleptic complexes in the form of ML_2 (fluorescence off) due to the presence of excess dipyrrins. And the homoleptic complexes can be converted back to the heteroleptic ones by reacting with excess Zn^{2+} in pyridine. In addition to the influence induced by the different metal coordination modes, the π-conjugation size also showed an important influence on the fluorescent properties of the dipyrrin complexes. Compared with **5**, dipyrrin **6** has a larger π-conjugation system, and thus its Zn^{2+} complex showed red-shifted fluorescence in the near infrared (NIR) region around 761 nm, which is favorable for potential biomedical applications (*vide infra*).

In addition to the influence of different substituents and metal coordination modes, the types of coordinated metal ions are also very important for modulating the fluorescence of dipyrrin complexes. Cohen, Magde and co-workers found that Ga^{3+} and In^{3+} complexes of 5-mesityl dipyrrin are also fluorescent (Fig. 2).[12] Complexes **7** and **8** display green fluorescence in hexanes with quantum yields of 2.4% and 7.4%, respectively. These values are much lower than that of 36% for the corresponding Zn^{2+} complex **3**, which may be ascribed to ligand-centered lowest energy transition and existence of dominant nonradiative decay pathways in complexes **7** and **8**.

Fluorescence of dipyrrin complexes can also be modulated by the coordinated anions, as demonstrated by Kawashima, Kobayashi, and coworkers.[13] They synthesized a tin complex **9** by the reaction of a lithium dipyrrinate with $SnCl_2$, and found that its fluorescence can be enhanced by 10-fold upon reacting with AgOTf in toluene to generate complex **10** (Fig. 3), which shows green fluorescence with a high quantum yield of 42%. The fluorescence enhancement may be ascribed to the formation of cationic tin species with a substantially decreased energy level of the lone-pair orbital of the tin atom.[13]

As described above, the fluorescence of dipyrrins may be drastically enhanced upon coordination to certain metal ions, such as Zn^{2+}. Hence, dipyrrins may be used as fluorescence

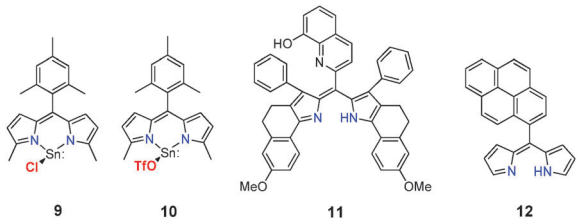

Fig. 3 Chemical structures of compounds **9–12**.

"turn-on" Zn^{2+} probes. In the following section, we will focus on the fluorescence "turn-on" Zn^{2+} probes based on dipyrrins and their tripyrrolic analogues.

2.2.2 Dipyrrins and their tripyrrolic analogues for Zn^{2+} sensing. Zn^{2+} is a biologically essential element, which should be maintained within a suitable concentration range in living systems. Thus, the detection of Zn^{2+} with high sensitivity and selectivity using readily synthesized probes has attracted extensive attention. Fortunately, dipyrrins and their tripyrrolic analogues can be developed as fluorescent probes for Zn^{2+} with advantages of tunable emission wavelengths, high selectivity, high sensitivity, and good cell-permeability.

Dipyrrins and tripyrrinones. Bentley *et al.* reported a ratiometric fluorescent probe **11** for Zn^{2+} based on the intramolecular charge transfer (ICT) mechanism (Fig. 3).[14] The dipyrrin and the 8-hydroxyquinoline moieties act as the electron-donating and withdrawing groups, respectively. When probe **11** interacts with Zn^{2+} in acetonitrile, a 1 : 2 (M : L) type of zinc complex was formed, resulting in weakened ICT and thus its fluorescence emission wavelength was blue shifted from 672 nm to 616 nm. By measuring the ratio of fluorescence intensities at these two wavelengths, a ratiometric probe can be developed, and the influences from probe concentration and instrumental factors can be eliminated, thus affording more reliable quantitative detection. In continuation of this work, the same group further developed a sensitive and selective Zn^{2+} probe **12** (Fig. 3) that can image Zn^{2+} concentration in neuronal vesicles,[15] with a remarkable 84-fold increase of fluorescence in a CH_3CN/HEPES buffer (1 : 1, v/v) solution upon addition of Zn^{2+}, and the fluorescence intensity was found to be linearly dependent upon the Zn^{2+} concentrations in a range of 5–50 μM, with negligible interference from other common metal ions.

Considering the fact that fluorescence wavelengths are highly dependent on the π-conjugation size of the fluorophores, Xie *et al.* reported four di- and tripyrrin based fluorescent Zn^{2+} probes, **13–16** (Fig. 4), based on the chelation enhanced fluorescence (CHEF).[16] Upon addition of Zn^{2+}, zinc complexes formed with a metal/ligand stoichiometry of 1 : 2 for dipyrrins **13–15**. In contrast, a 1 : 1 type of complex was formed for the tripyrrinone **16**. Vivid fluorescence "turn on" was observed accompanying with Zn^{2+} coordination, which could be ascribed to the CHEF effect associated with the improved rigidity and planarity of the ligands in the metal complexes, as evidenced by the single crystal structures. As expected, **13–16** show tunable emission colours varying from green (514 nm) to red (637 nm)

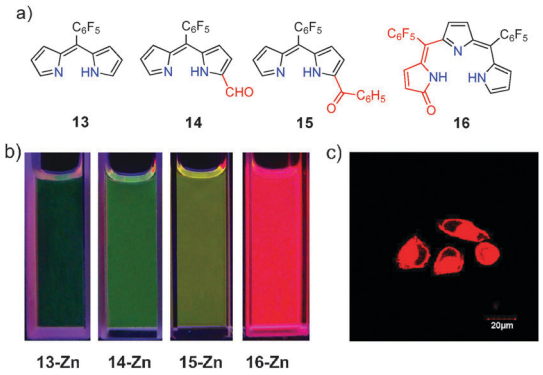

Fig. 4 (a) Chemical structures of dipyrrins **13–15** and tripyrrinone **16**; (b) images of probes **13–16** upon addition of Zn^{2+} under a portable UV lamp; (c) Zn^{2+} imaging in living KB cells using probe **16**. Reprinted with permission from ref. 16, copyright (2011) Royal Society of Chemistry.

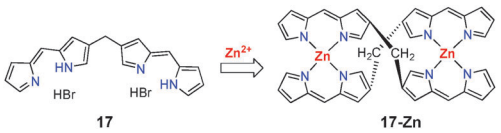

Fig. 5 Proposed Zn^{2+} sensing mechanism using the 3,3′-bis(dipyrrin) salt **17**.

while detecting Zn^{2+} (Fig. 4b). Among these probes, **16** shows the highest sensitivity with a detection limit of 4.6×10^{-8} M and the longest emission wavelength at 637 nm, enabling its practical application for Zn^{2+} imaging in living cells (Fig. 4c).

Recently, Dudina *et al.* reported the HBr salt of a 3,3′-bis(dipyrrin) **17** (Fig. 5), which can be applied as a highly selective fluorescence "turn on" probe for Zn^{2+}.[17] Addition of Zn^{2+} to a chloroform solution of **17** resulted in fluorescence enhancement by ~60-fold, which can be ascribed to the CHEF mechanism due to the formation of the 2 : 2 zinc complex.

Dipyrrins with unique substitution modes and 5-OH substituents. The α-positions of normal, unfunctionalized and sterically unhindered pyrroles are more susceptible to electrophiles than the β-positions, due to the formation of more stable cationic intermediates.[18] However, acylation of 5-pentafluorophenyldipyrromethane with *p*-anisoyl chloride afforded three products, *i.e.*, α-monoacylated and α,β′- and α,α′-diacylated. Subsequent oxidation afforded the corresponding dipyrrins **18–20** in high yields (Fig. 6).[19]

18–20 can coordinate with Zn^{2+} with vividly enhanced fluorescence. The applications of **18–20** as Zn^{2+} probes were demonstrated to be highly sensitive, selective, fast and applicable in a large pH range. The good selectivity towards Zn^{2+} may be related to the coordination preference and suitable size of Zn^{2+}. The observed fluorescence enhancement can also be ascribed to the CHEF effect. Emission wavelengths of zinc complexes of **18–20** vary from 549 to 588 nm, due to the different numbers and acylation positions of the *p*-anisoyl substituents. Impressively, the unique α,β′-diacylated dipyrrin **19** shows the highest sensitivity of 4.4×10^{-8} M.

Later, the Xie group systematically investigated the electronic effect on the acylation positions.[20] Acylation of 5-*p*-cyanophenyl

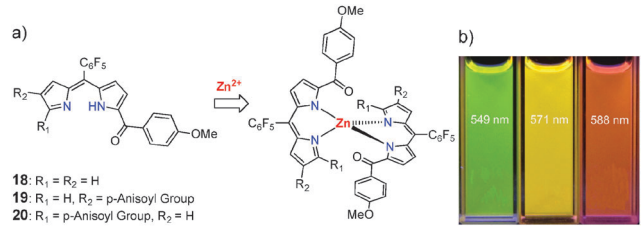

Fig. 6 (a) Proposed Zn^{2+} sensing mechanism for **18–20**; (b) images of **18–20** (from left to right) upon addition of Zn^{2+} under a portable UV lamp. Reprinted with permission from ref. 19, copyright (2013) American Chemical Society.

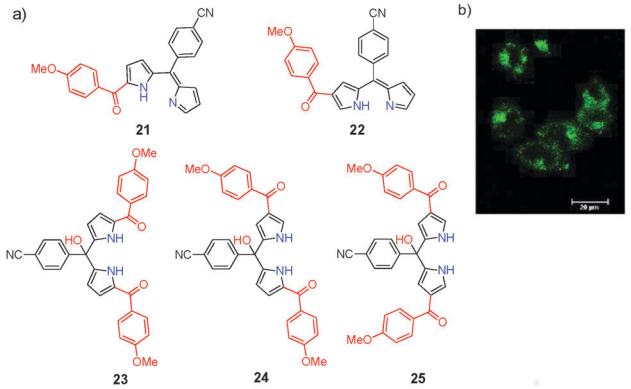

Fig. 7 (a) Chemical structures of dipyrrins **21** and **22**, and 5-OH substituted dipyrromethanes **23**, **24**, and **25**; (b) Zn^{2+} imaging in living HeLa cells using probe **24**. Reprinted with permission from ref. 20, copyright (2015) Elsevier.

dipyrromethane with *p*-anisoyl chloride afforded two mono- and three di-acylated products, *i.e.*, α- and β-mono-acylated, and α,α′-, α,β′- and β,β′-diacylated. Interestingly, only the α- and β-monoacylated dipyrromethanes can be oxidized to the corresponding dipyrrin products **21** and **22** (Fig. 7). In contrast, oxidization of the diacylated dipyrromethanes afforded corresponding 5-hydroxyl substituted products **23–25**. Similar to their previous work, **21–25** can be applied as fluorescence "turn on" Zn^{2+} probes. It is noteworthy that **23–25** has no background fluorescence due to the interruption of the conjugated framework by the sp^3 carbon atom between the two pyrrolic units. Upon addition of Zn^{2+}, these nonconjugated compounds can be oxidized to the conjugated dipyrrins, accompanied with Zn^{2+} coordination. Thus, **23–25** act as fluorescence "turn on" Zn^{2+} probes, demonstrating a high signal-to-noise ratio and high sensitivity without background fluorescence. As a result, among **21–25**, compound **24** shows the best Zn^{2+} sensitivity with a detection limit of 1.5×10^{-8} M, and it can be applied for Zn^{2+} imaging in living HeLa cells.

Xie *et al.* also developed three additional 5-OH substituted dipyrromethanes **26–28** (Fig. 8), which also showed fluorescence "turn-on" sensing of Zn^{2+} with high sensitivity and no background fluorescence.[21]

Prodigiosin derivative. Aforementioned results clearly demonstrated that dipyrrins and 5-OH substituted dipyrromethanes can be used as fluorescence "turn-on" Zn^{2+} probes with high

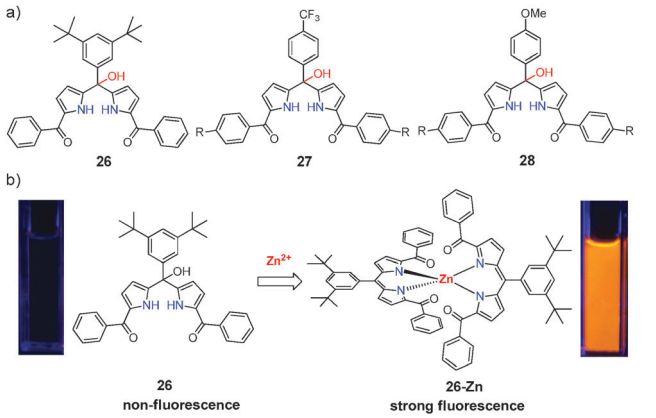

Fig. 8 (a) Chemical structures of *meso*-OH substituted dipyrromethanes **26–28**. R = OCH_3; (b) the proposed sensing mechanism of probe **26**, and images of probes **26** upon addition of Zn^{2+} under a portable UV lamp. Reprinted with permission from ref. 21, copyright (2013) Royal Society of Chemistry.

selectivity and sensitivity. Higher sensitivity would be favorable for practical applications. To further improve the sensitivity, probes with stronger Zn^{2+} binding affinities are desired. One effective way for improving the binding affinity is to develop probes with more chelating atoms. Consistent with this expectation, the tripyrrinone **16** (*vide supra*) indeed demonstrated higher sensitivity as compared with its dipyrrin analogues **13–15**.

Based on this background, the Xie group further developed a novel tripyrrolic prodigiosin derivative. Thus, 2,2′-bipyrrole was acylated with pentafluorobenzoyl chloride. Interestingly, they separated six acylated products with rich substitution modes, *i.e.*, α-, β-, and β_1-monoacylated and α,α′-, α,β′-, and α,β_1′-diacylated (**29–34**, Fig. 9).[22] Then, the α,α′-diacylated compound, **32**, was used for further reactions to synthesize a prodigiosin derivative **35**, which shows very weak fluorescence with an extremely low quantum yield of 0.4% in DMF. However, addition of Zn^{2+} drastically enhanced its fluorescence at 622 nm with the quantum yield increased to 9.5%. As expected, **35** indeed demonstrated very high sensitivity towards Zn^{2+}, with a detection limit of 1.1×10^{-8} M.

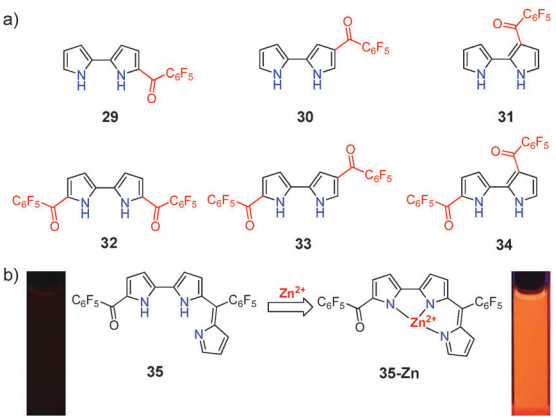

Fig. 9 (a) Synthesis of acylated bipyrroles **29–34** and the prodigiosin derivative **35**; (b) proposed Zn^{2+} sensing mechanism using **35** as the probe. Reprinted with permission from ref. 22, copyright (2014) Royal Society of Chemistry.

These examples demonstrated that linear conjugated oligopyrroles, such as dipyrrins, tripyrrinones, and prodigiosins, can be developed as promising fluorescence "turn-on" probes for detecting Zn^{2+} based on the so-called chelation-enhanced fluorescence (CHEF), which is related to the suppression of nonradiative energy loss by chelation enhanced rigidity of the molecules. From the representative examples discussed above, we could briefly summarize the main points for designing fluorescence "turn-on" Zn^{2+} probes based on linear conjugated oligopyrroles: (1) variation in the pyrrolic unit number and the substitution modes are effective in improving the sensitivity; (2) incorporation of an OH group at the 5-position of a dipyrromethane is an effective way to obtain probes with no background fluorescence; and (3) π-conjugation frameworks of the oligopyrroles may be enlarged to red shift the emissions to the NIR wavelength range, and thus to eliminate biological damage and the interference from biological autofluorescence, which will enable the applications in biochemical analysis.

2.3 Macrocyclic conjugated oligopyrroles for metal ion sensing

Since the pioneering work of sensing dioxo actinide cation with expanded porphyrins was reported by Sessler and coworkers,[5] macrocyclic conjugated oligopyrroles, including porphyrins and their analogues, have also been employed to detect metal ions such as Zn^{2+}, Mg^{2+}, Cu^{2+}, Hg^{2+}, and Ag^{+}. In this section, we will briefly describe recent progresses in this respect.

Porphyrins for Zn^{2+} sensing. Porphyrins and their derivatives widely occur in natural and artificial optoelectronic systems. A porphyrin molecule contains four pyrrole units interconnected *via* *meso*-methine bridges (=CH–) at their α-positions (Scheme 1). It contains an 18-π conjugation framework, showing intense absorption in the visible region and red fluorescence with emission wavelengths longer than 600 nm. Unlike linear conjugated oligopyrroles, the macrocyclic framework is rather rigid, and metal coordination cannot significantly improve the rigidity. Consequently, its fluorescence cannot be drastically enhanced upon coordination to metal ions, say Zn^{2+}. Therefore, the porphyrin macrocycle cannot be used simultaneously as the binding moiety as well as the reporting moiety for the design of fluorescence "turn-on" Zn^{2+} probes. Fortunately, its *meso*-positions can be readily functionalized, and thus Lippard *et al.* developed Zn^{2+} probes by introducing dipicolylamine (DPA) moieties as the binding motifs.[23]

DPA is a typical Zn^{2+} selective binding group, which has been widely used for designing fluorescent Zn^{2+} probes. By introducing a DPA unit as the Zn^{2+} binding site and three sulfonatophenyl groups to improve the water solubility, Lippard *et al.* synthesized compound **36** and its manganese complex **36–Mn** for Zn^{2+} sensing in living HEK-293 cells (Fig. 10).[23]

Upon addition of Zn^{2+} to a buffer solution of **36**, vivid red fluorescence "turn on" can be detected at 648 nm and 715 nm based on a photoinduced electron transfer (PET) mechanism. A large Stokes shift of 230 nm was observed, accompanied with more than 10-fold fluorescence enhancement. Probe **36** is selective for zinc with only little interference from Cd^{2+} and

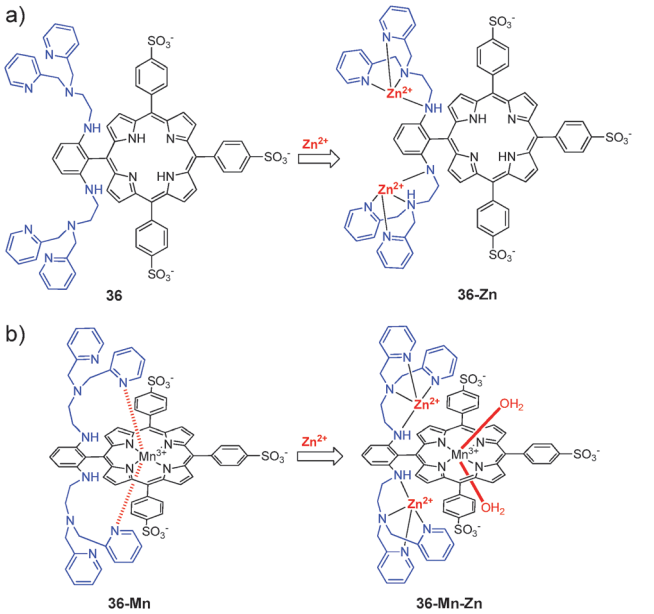

Fig. 10 Fluorescence and MRI Zn^{2+} sensing using porphyrin **36** and its manganese complex **36–Mn**.

Hg^{2+}, and it works well in a large pH range from 4.5 to 10.1. Interestingly, its manganese complex, **36–Mn**, can be applied as an MRI contrast agent for imaging Zn^{2+} in living HEK-293 cells. The MR signal in both the T1- and T2-weighted images decreased drastically upon interaction with Zn^{2+}, with the T1 and T2 relaxation rates decreased and increased, respectively.

Wang, Lv and co-workers developed a ratiometric fluorescent Zn^{2+} probe **37** by combining a triamino Zn^{2+} chelating unit with a porphyrin fluorophore (Fig. 11).[24] The triamino unit showed good Zn^{2+} affinity and improved water solubility of the probe. Addition of Zn^{2+} to an aqueous solution of **37** induced vivid ratiometric fluorescence changes. The fluorescence emission at 650 nm was decreased, and a new peak developed at 610 nm, which could be ascribed to the variation of the ICT effect due to the formation of a zinc complex with a 1 : 1 ligand/metal ratio. Application of **37** as a ratiometric Zn^{2+} probe works well in the physiological pH range and shows the advantages of

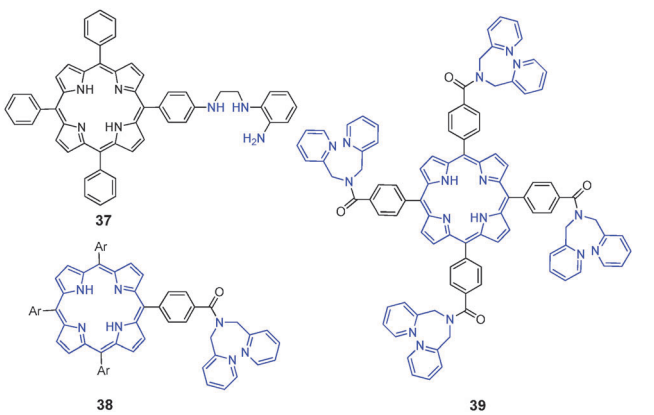

Fig. 11 Chemical structures of probes **37–39**, Ar = 4-*tert*-butylphenyl.

fast response, excellent reproducibility and high selectivity, with a detection limit of 1.8 μM.

Porphyrins for Pb^{2+} and Cu^{2+} sensing. As mentioned above, DPA is a typical Zn^{2+} selective binding moiety. Occasionally, it can also be used to detect ions other than Zn^{2+}. Jiang *et al.* synthesized two DPA-modified porphyrin derivatives, **38** and **39**, for sensing Pb^{2+} and Cu^{2+} (Fig. 11).[25] Different from compounds **36** and **36–Mn**, the porphyrin core in **38** and **39** acts simultaneously as the signal reporting unit and the metal recognition site. Addition of Pb^{2+} to **38** and **39** induced vivid ratiometric changes in solution colour and fluorescence, while addition of Cu^{2+} quenched the fluorescence. The binding stoichiometry between **38** and Pb^{2+} was 1 : 1.5, while its binding with Cu^{2+} is stronger, showing a ligand/metal ratio of 1 : 2. Thus, addition of Cu^{2+} to the solution of **38**–Pb^{2+} can displace Pb^{2+} to form the **38**–Cu^{2+} complex. Compound **39** showed sensing behaviour similar to that of **38**, but the binding modes are different. It binds Pb^{2+} in a stoichiometry of 1 : 3 to form a coordination network, and it may bind Cu^{2+} with a ligand/metal ratio of 1 : 5.

Using a zinc porphyrin as the fluorophore and 2,2′-dipyridylamine (dpa) as the binding site, Ye *et al.* developed two fluorescent Cu^{2+} probes, **40** and **41** (Fig. 12).[26,27] In $CHCl_3$, probes **40** and **41** emit red fluorescence at 610 and 608 nm, with quantum yields of 3.6% and 5.8%, respectively. Only in the presence of Cu^{2+}, the fluorescence can be effectively quenched, and the quenched fluorescence can be recovered by adding EDTA. The quenching process could be ascribed to the formation of corresponding copper complexes with stoichiometry of 1 : 2 and 1 : 1 (probe : Cu^{2+}), respectively. The Cu^{2+} detection limits were estimated to be 3.3×10^{-7} M and 1.5×10^{-6} M for probes **40** and **41**, respectively.

Porphyrins for Hg^{2+} sensing. In general, ICT and FRET (Förster resonance energy transfer) mechanisms are commonly used in designing ratiometric fluorescent probes, but the ICT based fluorescent probes often suffer from overlapped emission spectra, and FRET based fluorescent probes are relatively difficult to design and synthesize. Another strategy for designing ratiometric probes is to synthesize a probe molecule bearing two independent recognition units for one target analyte.

As an example, Zhang *et al.* reported a ratiometric fluorescent Hg^{2+} probe **42** by linking two independent Hg^{2+} sensitive

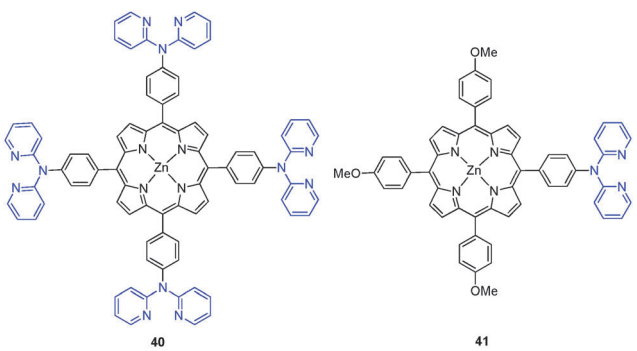

Fig. 12 Chemical structures of probes **40** and **41**.

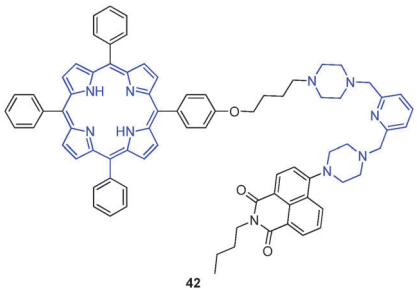

Fig. 13 Chemical structure of probe **42**.

moieties (Fig. 13).[28] In **42**, the porphyrin and naphthalimide fluorophores share the same excitation wavelength and emit fluorescence at 650 and 525, respectively, with a 125 nm gap between these two emission peaks. Upon addition of Hg^{2+}, the emissions at 650 nm decreased accompanied with an increase at 525 nm, indicative of a ratiometric response of **42** to Hg^{2+}. NMR spectroscopy reveals that both the pyridine–piperazine moiety and the porphyrin core in **42** can bind Hg^{2+}. Thus **42** coordinates with Hg^{2+} in a ligand/metal ratio of 1 : 2, with Hg^{2+} binding constants of 4.26×10^5 M^{-1} and 6.31×10^5 M^{-1} for the pyridine–piperazine moiety and the porphyrin core, respectively. Probe **42** shows high selectivity towards Hg^{2+}, and the binding was found to be fast, reversible and only slightly affected within a wide pH range between 4.0 and 8.0. The dynamic range for Hg^{2+} detection lies within 1×10^{-7} M ~ 5×10^{-5} M, and the detection limit was found to be 2×10^{-8} M, indicative of its high sensitivity. It is noteworthy that probe **42** can be applied in living HeLa cells.

Porphyrin analogues with a N_3C cavity for Zn^{2+} sensing. Replacing one of the pyrrole units with a 1,3-phenylene moiety is an effective approach for synthesizing porphyrin analogues. Hung *et al.* reported such an oligopyrrole as an NIR fluorescent probe for detecting Zn^{2+}.[29] Thus, compound **43** was synthesized in one pot with a yield of 27%, which showed no apparent fluorescence in acetonitrile due to the presence of a relatively flexible conjugation framework. Upon addition of Zn^{2+}, the fluorescence at 672 nm was sharply enhanced (Fig. 14). The probe shows acceptable selectivity towards Zn^{2+}, with noticeable

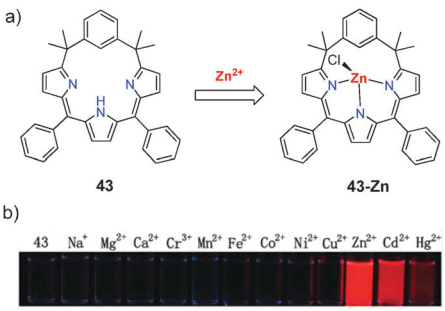

Fig. 14 (a) Proposed sensing mechanism of probe **43** for detecting Zn^{2+}; (b) images of probe **43** upon addition of various metal ions under a portable UV lamp. Reprinted with permission from ref. 29, copyright (2008) Royal Society of Chemistry.

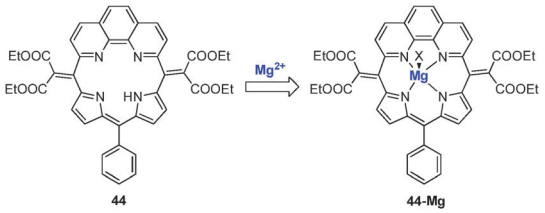

Fig. 15 Proposed sensing mechanism of probe **44** for detecting Mg^{2+}.

interference only from Cd^{2+} and Hg^{2+}. The Zn^{2+} sensing process was studied by NMR, mass spectrum, Job's plot and X-ray analysis, which unambiguously indicated the formation of a zinc complex of **43** with a Zn^{2+}/**43** stoichiometry of 1 : 1 (Fig. 14).

Porphyrin analogues with a N_4 cavity for Mg^{2+} sensing. Mg^{2+} is one of the most abundant and essential metal ions in living systems. It plays important roles in manipulating important biological polyphosphate compounds and enzyme functions. The detection of Mg^{2+} using porphyrin analogues was achieved by Naruta *et al.*[30,31] Compound **44** has a suitable central cavity size for selective detection of Mg^{2+} over Na^+, K^+, and Ca^{2+}, showing a binding constant of 37.3 M^{-1} in the presence of water (Fig. 15). In addition, there is only one proton-bearing nitrogen atom in the central cavity, which can minimize its metal ion coordination steps. Free compound **44** showed very weak fluorescence at 572 nm with a quantum yield of 0.3%. NMR and MS spectral measurements revealed that addition of $MgCl_2$ to the solution of **44** in acetonitrile generated its Mg^{2+} complex, leading to vivid absorption spectral changes and 16-fold fluorescence enhancement with an emission wavelength at 639 nm and a quantum yield of 1.5%. Similar fluorescence response upon addition of Mg^{2+} was also observed in the HEPES buffer. Thus, **44** can be used as a fluorescent Mg^{2+} probe. Further studies revealed that fluorescence behavior of the Mg^{2+} complex of **44** is partially related to the effect of donor-excited photo-induced electron transfer (d-PET) processes from the dipyrrin subunit to the 1,10-phenanthroline moiety.[31]

Expanded porphyrins for Zn^{2+} sensing. Expanded porphyrins contain more than four pyrrolic subunits. Furan, thiophene, or even benzene could be used in place of the pyrrolic units. Applications of these compounds for sensing potentially hazardous materials have been reviewed by Sessler *et al.*[32] These compounds usually have larger internal cavities than porphyrins, and they demonstrate unique spectral and electronic features, thus extending their applications as photosensitizers, MRI contrast agents, ion probes and transporters, and enzyme models. Interestingly, they may coordinate to metal ions with relatively large radius or even more than one metal ion in the large cavity. On the other hand, expanded porphyrins usually demonstrate better conformational flexibility than porphyrins due to the presence of the larger conjugation framework, and thus their molecular rigidity will be drastically improved upon metal coordination, which may result in enhanced fluorescence. Hence, they may be used as fluorescence "turn-on" metal probes. In addition, their fluorescence may occur in the NIR range due to their large conjugated framework, thus enabling them to be promising candidates for

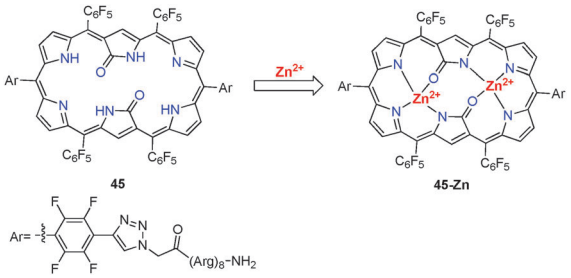

Fig. 16 Proposed sensing mechanism of probe **45** for detecting Zn^{2+}.

applications as NIR fluorescent metal ion probes. In this respect, Furuta *et al.* developed a fluorescent Zn^{2+} probe **45** with an emission wavelength of 1050 nm using a doubly N-confused hexaphyrin (Fig. 16).[33] Two highly hydrophilic octa-arginine peptides were incorporated into the probe to ensure its water solubility. Upon addition of excessive Zn^{2+} to the probe in water, a sharp fluorescence "turn on" was observed at 1050 nm, with the quantum yield enhanced by 14-fold due to the formation of a zinc complex with a Zn^{2+}/**45** ratio of 2 : 1. In addition, it was demonstrated that probe **45** can be used to detect Zn^{2+} at neutral to weakly alkaline pH values.

Another example of using an expanded porphyrin as the fluorescent Zn^{2+} probe was reported by Xie and Furuta *et al.*[34] The pyrrolyl norrole **46** adopts a nonplanar and flexible conformation, and thus its quantum yield was found to be as low as 0.16% in CH_2Cl_2, while its zinc complex **46–Zn** showed much stronger fluorescence with a quantum yield of 9.9% in CH_2Cl_2 (Fig. 17), due to the improved molecular rigidity upon coordination. Thus, addition of Zn^{2+} to the methanol soultion of **46** resulted in drastic fluorescence enhancement by 31-fold, with an emission wavelength of 736 nm in the NIR region.

Expanded porphyrins for Hg^{2+} and Ag^+ sensing. Mercury ions are among the most toxic pollutants to the environment and human beings, thus the effective detection of mercury ions and other mercuric compounds has attracted extensive attention. In this respect, Wong and co-workers synthesized a [26]hexaphyrin-(1.1.1.1.1.0) **47** for selective and sensitive detection of Hg^{2+} (Fig. 18).[35] It shows an intense NIR fluorescence with the wavelength higher than 900 nm. Upon addition of Hg^{2+}, the fluorescence was quenched distinctly. Addition of Hg^{2+} to a methanol solution of **47** resulted in the formation of a mercury complex with an Hg^{2+}/**47** ratio of 2 : 1, and the binding constant

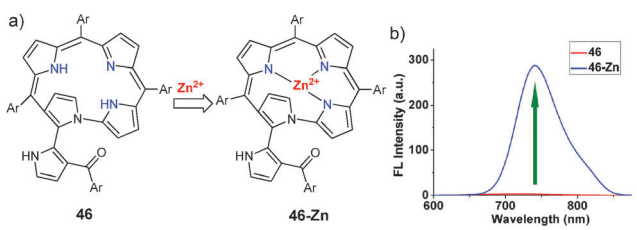

Fig. 17 (a) Proposed sensing mechanism of probe **46** for detecting Zn^{2+} (Ar = C_6F_5). (b) Fluorescence spectra of **46** and **46–Zn** (10 μM) in CH_2Cl_2. Reprinted with permission from ref. 34, copyright (2013) American Chemical Society.

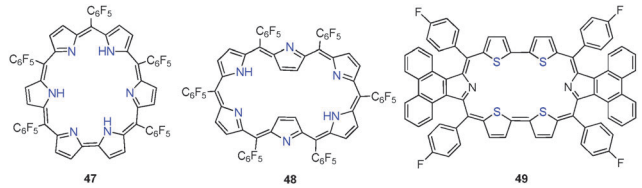

Fig. 18 Chemical structures of probes **47–49**.

was calculated to be 1.62×10^9 M^{-2}. Selectivity measurements confirmed that the presence of completing cations such as Li^+, Na^+, K^+, Rb^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} did not obviously interfere with the detection of Hg^{2+}, and the Hg^{2+} detection limit was found to be 10^{-7} M. Similarly, a fluorescent Ag^+ probe based on [26]hexaphyrin(1.1.1.1.1.1), **48**, was also reported by the Wong group (Fig. 18).[36]

Another expanded porphyrin based Hg^{2+} probe was reported by Rurack, You, Shen and co-workers.[37] The authors envisioned that expanded porphyrins with "soft" donor sites may show higher affinity towards "soft" metal ions such as Hg^{2+}, and thus they synthesized a rubyrin derivative, **49** (Fig. 18). Although it is insoluble in water, limiting its Hg^{2+} sensing application in practical systems, the authors incorporated it into a polyurethane hydrogel to improve its sensing performance in aqueous solutions. Thus, they achieved a satisfactory Hg^{2+} detection limit of *ca.* 1 ppm.

3. Anion sensing

3.1 Background research on anion sensing

Compared with metal ions, most anions have larger size and lower charge density, thus the electrostatic interactions between anions and the host molecules are generally weaker than metal coordination bonds. Hence, it is more difficult to detect target anions in complicated environments as compared with the metal ions.[38] In spite of these difficulties, the development of anion probes has received extensive attention, which may be ascribed to the fact that anions play important roles in chemical and biological systems.[39] Sessler, Gale and co-workers systematically demonstrated that pyrrolic, especially oligopyrrolic compounds, are promising agents for anion recognition and transport.[7,40] Different from non-conjugated oligopyrroles, the conjugated ones usually display vivid colour and fluorescence signals, which make the sensing processes more convenient and visible. Thus, in this section of the review, anion sensing behavior of conjugated oligopyrroles will be described. The readers are also referred to excellent reviews about anion responsive properties and anion-driven discrete assemblies of pyrrole-based molecules.[41]

3.2 Conjugated oligopyrroles for F^- sensing

Fluoride is a micronutrient for human health, which can prevent dental cavities and promote healthy bone growth, and its intake should be kept in a reasonable amount. Excessive intake may result in serious toxicity, because excess fluoride will bind calcium ions to form insoluble CaF_2 in the blood, which may even be fatal. Thus, the selective detection and quantification of fluoride anions are highly desired.

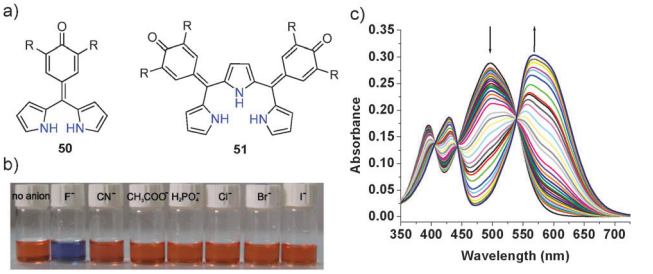

Fig. 19 (a) Chemical structures of probes **50** and **51**. Ar = *t*-Bu; (b) A photograph showing the colour changes of **50** (25 mM) upon addition of 40 equiv. of various anions in DMSO; (c) UV-vis spectral changes of **50** (10 μM) observed upon the addition of 0–180 equiv. F^- in DMSO. Reprinted with permission from ref. 42, copyright (2010) Royal Society of Chemistry.

Considering that the NH moiety in pyrrole can be used as the binding site for fluoride detection. Xie *et al.* synthesized two pyrrole-hemiquinone compounds **50** and **51** that can be applied as colorimetric fluoride probes in DMSO (Fig. 19).[42] Upon addition of F^- to a DMSO solution of **50**, the solution colour changed from orange to bright blue, with high selectivity for F^- over competing anions such as CN^-, CH_3COO^-, $H_2PO_4^-$, Cl^-, Br^-, and I^- due to the extremely strong hydrogen bonding ability of F^-. Vivid UV-Vis spectral changes with several isosbestic points were observed during gradual addition of F^-, and the NMR measurements revealed that the mechanism for the colour changes can be ascribed to F^- induced deprotonation of the N–H moiety in **50**. Interestingly, the NH protons in compound **51** showed two-step deprotonation processes upon addition of F^-. Whereas, only one-step deprotonation was observed upon addition of CN^-, CH_3COO^-, and $H_2PO_4^-$, and no deprotonation was observed for Cl^-, Br^-, and I^-. It is also noteworthy that in less polar solvents, such as CH_2Cl_2, the F^- sensing process was accompanied with tautomerism shifts, which provide additional means of modulating the sensing behavior.

Later, the Xie group developed a macrocyclic tetrapyrrole **52** that shows controllable and reversible tautomerism in chloroform upon alternate addition of F^- and H^+ (Fig. 20).[43] Two sets of isosbestic points could be observed in the UV-Vis spectra when F^- was gradually added to **52**, which can be ascribed to the hydrogen binding between **52** and F^- as well as a further deprotonation process. It is noteworthy that the macrocyclic compound **52** shows quantitative tautomeric conversion in

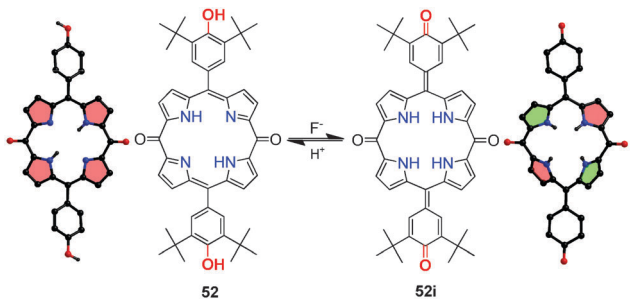

Fig. 20 Illustration of F^- and H^+ promoted interconversion between **52** and **52i**, with the corresponding crystal structures shown adjacent to the molecular structures.

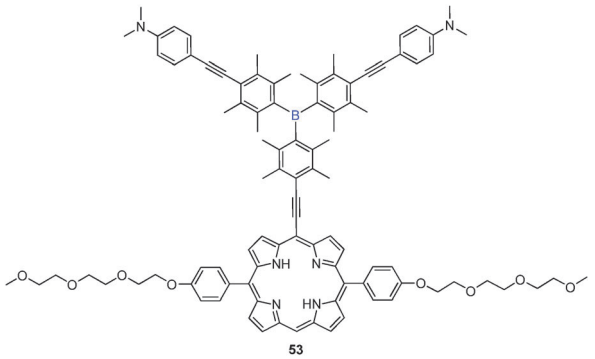

Fig. 21 Chemical structure of the F^- probe **53**.

different solvents, while the linear one **50** (*vide supra*) exists as a mixture of two isomers in chloroform.

Using triarylborane as both the recognition and energy donor unit, Shinkai and Takeuchi, *et al.* reported a colorimetric and fluorescent probe **53** for selective detection of F^- (Fig. 21).[44] NMR spectroscopy revealed that addition of F^- to the solution of **53** led to the formation of the corresponding **53**–F^- complex, with F^- coordinated at the boron centre of the triarylborane unit. UV-Vis measurements suggested a binding ratio of 1 : 1 between **53** and F^-, with an association constant of 99 700 M^{-1}. Interestingly, the addition of F^- induced increased fluorescence at 356 and 692 nm, accompanied with decreased fluorescence at 670 nm. These observations could be ascribed to perturbation of the π conjugation and the energy transfer between the triarylborane donor and the porphyrin acceptor in **53** by forming the **53**–F^- complex.

3.3 Conjugated oligopyrroles for CN^- sensing

Cyanide is an inhibitor of cytochrome *c* oxidase, and it is extremely toxic to living organisms. Selective and sensitive detection of cyanide is an important research topic. Conjugated oligopyrroles have found applications in this respect.

By introducing a carbonyl group to the α-position of the dipyrrin chromophore, Xie and co-workers developed three highly selective colorimetric CN^- probes **54** (Fig. 22), **14** and **15** (Fig. 4).[45] In dichloromethane, they showed colour changes from light yellow to orange or pink upon addition of F^- and CN^-, respectively. Other investigated competing anions, including CH_3COO^-, $H_2PO_4^-$, Cl^-, Br^-, and I^-, could not induce obvious spectral or colour

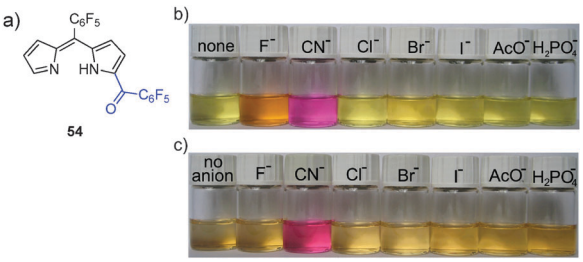

Fig. 22 (a) Chemical structure of CN^- probe **54**; (b) and (c) photographs showing the colour changes of probe **54** upon addition of various anions, (b) in CH_2Cl_2; (c) in DMSO–H_2O. Reprinted with permission from ref. 45, copyright (2012) Royal Society of Chemistry.

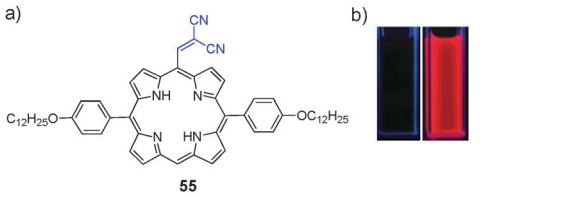

Fig. 23 (a) Chemical structure of CN^- probe **55**; (b) images of probe **55** before (left) and after (right) addition of CN^- under a portable UV lamp. Reprinted with permission from ref. 46, copyright (2013) Royal Society of Chemistry.

changes. The vivid colour changes induced by F^- and CN^- indicated that these compounds may be applied as colorimetric probes for both F^- and CN^-. Moreover, in aqueous solutions, only the addition of CN^- changed the solution colour from light yellow to pink, while F^- did not induce any noticeable colour changes, which could be ascribed to the different interactions for F^- and CN^-. F^- forms hydrogen bonds with the NH moieties, which can be displaced by water molecules in aqueous solutions. In addition to the hydrogen bonding interactions, the nucleophilic addition reactions between CN^- and the probes resulted in the formation of corresponding dipyrrin adducts, and the reaction may proceed smoothly in aqueous solutions. Hence, the probes work well for sensing CN^- even in the aqueous systems. The detection limits were found to be 3.6×10^{-6}, 7.1×10^{-6}, and 4.2×10^{-6} M, for **54**, **14** and **15**, respectively.

In addition to the carbonyl group, the dicyanovinyl (DCV) unit is also widely employed in the design of CN^- probes because of its electron deficient character and susceptibility to nucleophilic attack by the CN^- anion. However, the fluorescence intensity of the probes may be either increased or decreased upon interaction with CN^-, showing insufficient predictability. With the purpose to develop a general strategy for rational design of fluorescence "turn-on" CN^- probes, the Xie group developed a series of such probes using DCV as the recognition unit.[46] It was found that when DCV was introduced into a sterically demanding framework, fluorescence of the fluorophore can be quenched *via* a twisted intramolecular charge transfer (TICT) effect or just simple distortion of the π conjugation framework. One of such examples is compound **55**, whose quantum yield is as low as 0.53% in CH_2Cl_2 (Fig. 23). After nucleophilic attack by CN^- at the DCV moiety, vivid red fluorescence "turn-on" was observed.

3.4 Sensing of other anions

Sensing of halides. N-confused porphyrins usually show unique properties different from normal porphyrins. Xie and Furuta *et al.* found that N-confused oxoporphyrin **56** showed unique axial binding towards halides (Fig. 24).[47] Generally, N-confused porphyrins and their metal complexes can bind halide anions at the outer NH moiety. Whereas, addition of Cl^- to the dichloromethane solution of **56** led to the formation of complex **57**, in which an additional Sn^{IV}–Cl^- bond was formed at one of the axial positions. The axial binding resulted in better rigidity and planarity of the complex, leading to vivid fluorescence enhancement in the NIR region. The axial binding of **56** with Br^- and I^- also enhanced its fluorescence, but the binding constants are smaller. Thus, complex **56** can be used as a fluorescence "turn-on" halide probe.

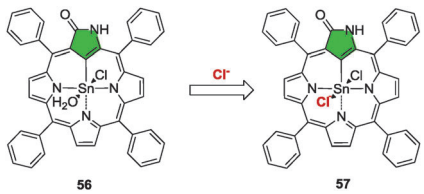

Fig. 24 Proposed Cl^- binding mode of probe **56**.

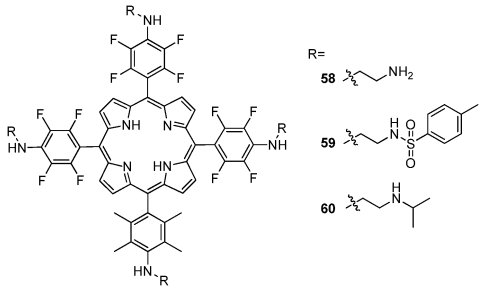

Fig. 25 Chemical structures of probes **58–60**.

Sensing of phosphate anions. Phosphates are biologically important anions that exist in DNA and RNA and in the form of adenosine phosphates. Application of water soluble sapphyrins as fluorescent probes for phosphate anions was reported by Sessler *et al.* in 2003.[6] Very recently, Tomé and Sessler *et al.* further constructed optical probes for phosphate anions by combining a porphyrin chromophore with diamino derivatives.[48] UV-Vis measurements in $CHCl_3$ revealed that **58–60** showed selective absorption spectral changes upon addition of $H_2PO_4^-$ (Fig. 25). Compounds **58–60** are insoluble in water. However, through incorporation into a piezoelectric sensor, these probes are highly selective for HPO_4^{2-} in the aqueous media.

Sensing of sulfate anions. Sulfates are widely used in industry, and they can be pollutants to the environment, so that the detection is needed. Beer *et al.* reported that imidazolium and triazolium modified zinc porphyrins **61** and **62** can be applied as probes for sulfate anions in aqueous solutions (Fig. 26).[49,50] In DMSO, **61** can bind Cl^-, $H_2PO_4^-$ and HSO_4^-, while in a mixed solvent of water–DMSO (5 : 95), its interactions with HSO_4^- and SO_4^{2-} are much stronger than other tested anions. Similarly, only the addition of SO_4^{2-} changed the solution colour of probe **62** in 15% water–acetone, with an association constant of $2.5 \times 10^4\ M^{-1}$.

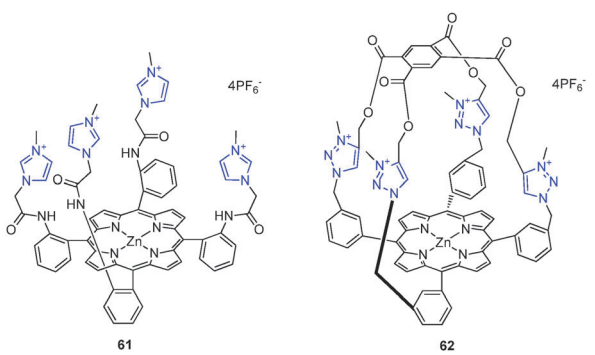

Fig. 26 Chemical structures of probes **61** and **62**.

4. Conclusions and future outlook

In this tutorial review, we briefly described recent progresses on colorimetric and fluorescent probes based on conjugated oligopyrroles for sensing metal ions and anions. The design strategies, sensing mechanisms, and ion sensing behavior of linear and macrocyclic conjugated oligopyrroles are briefly described. The representative examples indicated that conjugated oligopyrroles could be applied as colorimetric or fluorescent ion probes, with the advantages of vivid colour and fluorescence changes, easy structural modification and functionalization, and tunable emission wavelengths. The obtained probes with NIR emissions may be suitable for biochemical applications. It is noteworthy that the simple di- and tripyrrins, as well as some porphyrinoids, demonstrate flexible conformations, and metal coordination will improve the rigidity, which may result in vivid fluorescence enhancement. Therefore, these compounds are suitable for developing fluorescence "turn-on" probes for metal ions with large signal-to-noise ratios and high sensitivity. In these probes, the oligopyrrolic moieties may simultaneously act as the binding unit as well as the reporting moiety, which simplifies the design and synthesis of the probes.

Despite these successful examples, research on ion probes based on conjugated oligopyrroles is still in the beginning stage. There is still a long way to go in the future. For example, water solubility of the probes needs to be improved for real applications. Besides, the metal ion probes based on metal coordination may suffer from interference of competing ions. Thus, probes based on other interactions, such as specific reactions, need to be developed. In addition, more research studies are highly desired in developing practical anion probes based on conjugated oligopyrroles.

In conclusion, successful metal ion and anion probes based on conjugated oligopyrroles with unique advantages have been developed. More research studies are desired for developing probes suitable for real applications in environmental and biochemical analyses.

Acknowledgements

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