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Functionalized Quinoxaline for Chromogenic and Fluorogenic Anion Sensing

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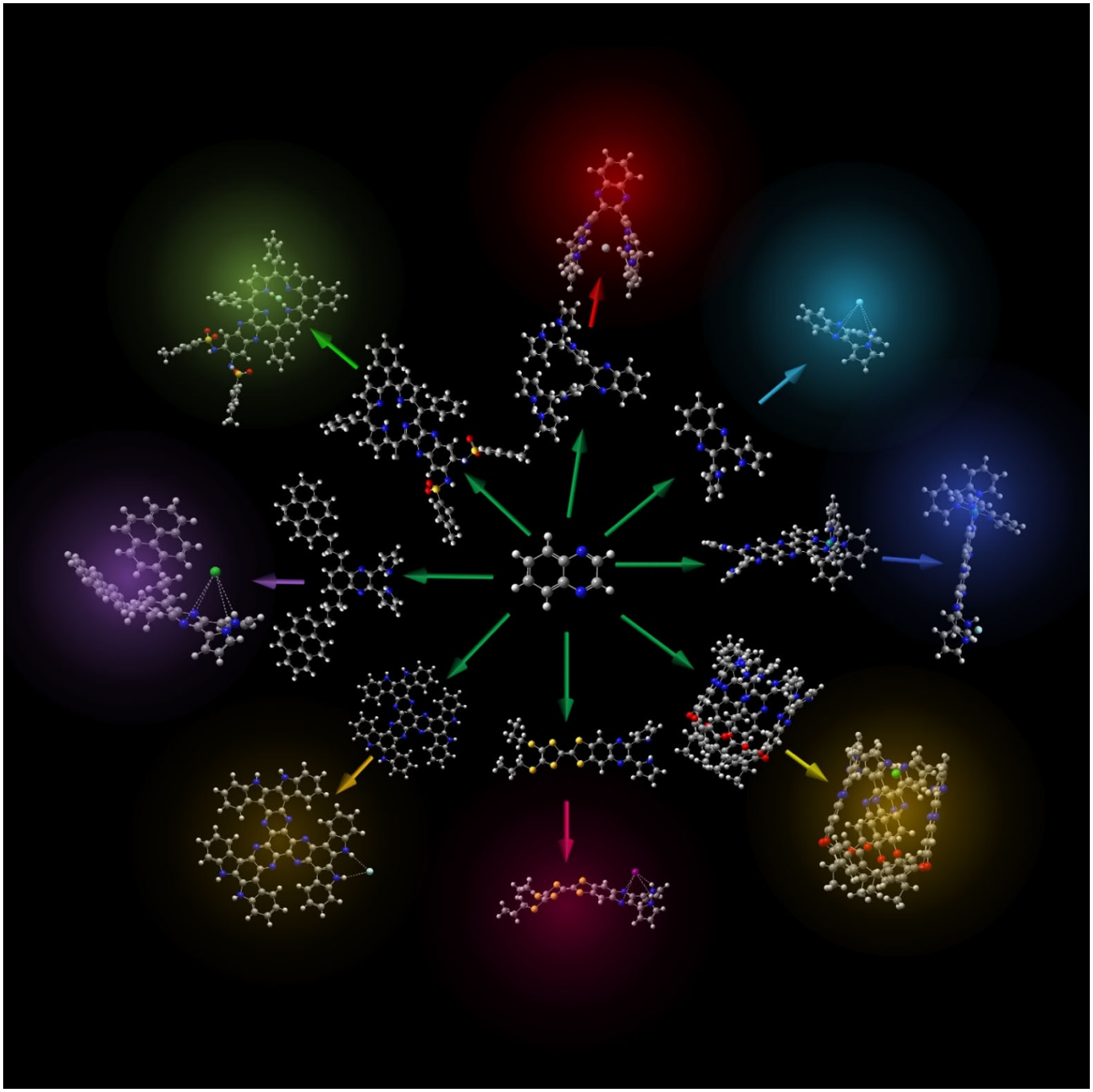

This Review article provides a comprehensive analysis of recent examples reported in the field of quinoxaline-based chromogenic and fluorogenic chemosensors for inorganic anions such as fluoride, cyanide, acetate, and phosphate, as well as their utility in biomolecular science. It commences with a discussion of the various structural motifs such as quinoxaline-based oligopyrroles, polymers, sulfonamides, cationic receptors, and miscellaneous receptors bearing mixed recognition sites in the same receptor. Advances are discussed in depth, where the focus of this review is to tackle mainly solution state anion sensing utilizing quinoxaline-based receptors using different spectroscopic techniques with reference to anion selectivity by colorimetric and fluorescence response. The various examples discussed in this Review illustrate how the integration of anion binding elements with the quinoxaline chromophore could result in anion responsive chemosensors. Over the years, it has been observed that structural modification of the quinoxaline moiety with different sets of signaling unit and recognition sites has resulted in a few anion specific chemosensors.

1. Introduction

Owing to their remarkable electronic and photophysical properties, quinoxaline and its derivatives have been widely employed as efficient building blocks for the synthesis of numerous organic molecules and polymeric materials appropriate for different applications.[1] The electron-deficient character of the conjugated quinoxaline ring is responsible for some interesting properties, such as distinctive absorption and emission spectra, charge transfer from an electron donor to the quinoxaline ring, high charge-carrier mobility, and a low reduction potential rendering the compound possible low energy band gap. Because of these interesting inherent properties, several quinoxaline-based conjugated materials have been synthesized in the past two decades and their applications in the field of light-emitting diodes (LEDs),[2] organic photovoltaics (OPVs),[3] dye-sensitized solar cells (DSSCs),[4] organic field-effect transistors (OFETs),[5] nonlinear optics,[6] and fluorescent optical chemosensors[7] have been widely explored.

The development of chromogenic and fluorogenic molecules for anion sensing has gained considerable research attention, owing to the fundamental roles that anions play in many biological, environmental, and chemical processes.[8] Inspired by the recognition tools exploited by nature in anion-binding proteins,[9] researchers have developed numerous synthetic receptors that employ hydrogen bonds offered by specific binding sites from amide, urea, pyrrole, indole, guanidinium, and imidazolium functionalities for the recognition and sensing of anionic species.[10] Chemosensors capable of representing an optical response upon receptor-anion interactions are viable, owing to the low cost and easy detection of anions in solution.

Chemosensors for anions generally involve the covalent linking of a chromophore/fluorophore signaling subunit capable of giving information about the anion binding event with the hydrogen bonding receptor subunit.[11] Whereas chemosensors commonly refer to systems that typically employ coordinative forces for anion binding, which in turn change the electronic properties of the receptor molecule, the term chemodosimeter (reactive sensors) is related to the use of specific irreversible reactions involving anions.[12] Boronic acid $-B(OH)_2$ functionalized fluorescent anion sensors are well documented in the literature as chemodosimeters for detecting and determining the concentration of fluoride in aqueous/semi-aqueous media.[13] In general, hydrogen-bond-induced π-electron delocalization, or anion-induced –NH or –OH deprotonation, are believed to be responsible for signaling the binding event in sensors that generally employ polarized –NH and –OH functions.[14] The ability to establish hydrogen bonds between the anion and receptors with –NH group(s) is usually determined by the degree of electron deficiency on the interacting –NH proton (or proton acidity) and the electronegativity of the anion (or anion basicity). Intense colorations with emergence of new bands in the optical spectral region can also be attributed to the strong anion–π charge transfer interactions involving π-acidic receptors, such as triazine, naphthalene diimide, and dinitrophenyl-functionalized receptors.[15] Currently, sensors based on anion-induced changes in luminescence properties are particularly attractive because of their potential for high selectivity and sensitivity at low substrate concentrations. The binding of anionic species leads to certain modification of the fluorescence emission behavior such as changes in emission intensity, wavelength, or lifetime of the of receptor molecules. Along this line, the design of ratiometric fluorescence chemosensors also provides the basis for the manipulation and advancement of various photophysical processes with the ultimate goal of selective and sensitive signaling of targeted anions.[16] The ratio of the emission intensities at two different wavelengths is sufficient to determine the analyte concentration independent of probe concentration or any instrument-related parameters.

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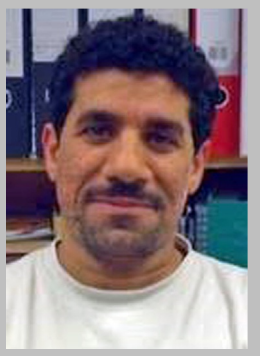

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Chromogenic and fluorogenic chemosensors are generally designed to combine the ability to recognize and respond to an external input with mediation of an internal charge transfer (ICT),[17] photoinduced electron transfer (PET),[18] excimer/exciplex emission,[19] excited-state intramolecular proton transfer (ESIPT),[20] enhancement/quenching of luminescence upon anion association,[21] or exciton–migration-induced signal amplification in polymer luminescence,[22] as a mode of signaling mechanism. Luminescent signaling of anion recognition has been achieved using a variety of conjugated chromophores including naphthalene, naphthalene (di)imide, anthracene, pyrene, and quinoxaline derivatives,[11,21,23] and also transition metal complexes such as, rhenium(I) and ruthenium(II) complexes.[24]

In spite of the large number of chromogenic and fluorogenic chemosensors for anions reported to date, there are only a few examples of highly selective chemosensor for a specific anion.[11,21,23,25] The main challenge for supramolecular and organic chemists working in the area of anion sensing and recognition is to achieve anion-specific chemosensor in aqueous medium. However, achieving both anion selectivity and water solubility of organic receptors may be quite challenging, which has perhaps limited the selective anion sensing studies mostly to organic media. High hydration enthalpy of some of the biologically and environmentally relevant anions like F^-, Cl^-, AcO^-, and PO_4^{3-} represents another obstacle towards anion recognition in water, owing to the formation of a hydration shell around the anions, which significantly limits the receptor anion interaction by hydrogen bonds at low analyte concentration. Several highly acknowledged reviews on chromogenic and/or fluorogenic chemosensors for anions can be noted in literature that have largely highlighted the use of nitrophenyl, naphthalene (di)imide, and polycyclic aromatic hydrocarbon based chemosensors.[11,21,23,25] However, functionalized quinoxaline-based anion sensors have not been well addressed anywhere, in spite of their frequent use in the development of chemosensors over the years.

This Review aims to deliver a comprehensive compilation of the examples reported to date related with the developments of quinoxaline-based chromogenic and fluorogenic chemosensors for inorganic anions such as, fluoride, cyanide, acetate, and phosphate. In this Review, based on the anion recognition motifs, quinoxaline-based anion sensors have been categorized into five different types: 1) quinoxaline oligopyrroles, 2) quinoxaline-based polymers, 3) quinoxaline sulfonamides, 4) quinoxaline-based cationic receptors, and 5) miscellaneous quinoxaline receptors with mixed recognition sites (e.g. amide and pyrrole in the same receptor). The focus remains primarily on the solution-state anion sensing properties of quinoxaline-based receptors using different spectroscopic techniques with reference to anion selectivity by colorimetric and fluorescence response.

2. Quinoxaline-Based Anion Sensors

2.1. Quinoxaline Oligopyrroles

Most of the quinoxaline-based receptors developed for the purpose of anion sensing have utilized 2,3-dipyrrolylquinoxaline (DPQ) derivatives, in which two pyrrole –NH groups could function as anion binding sites and the quinoxaline moiety can serve as a chromogenic and fluorogenic reporter of an anion binding event. The earliest contribution was made by Sessler and co-workers, who first reported the use of DPQ **1**, and nitro-DPQ **2** as efficient chromogenic and fluorogenic chemosensors for fluoride in dichloromethane (DCM) and dimethyl sulfoxide (DMSO) solutions.[26] They proposed that the DPQ system is expected to operate through a combination of electronic and conformational effects (Figure 1). Both the compounds display a remarkable F^--induced color change from yellow to orange (**1** + F^-) and yellow to purple (**2** + F^-), and their fluorescence emission are quenched to all extents in the presence of F^-. Sensing of F^- by DPQ was explained by the expected perturbation of the orbital overlap between the pyrrole and quinoxaline subunits, thereby changing the optical characteristics of the later. Owing to the greater electron deficiency, compound **2** displays an association constant ($K_a = 1.18 \times 10^5\ M^{-1}$ in DCM) that is significantly higher than that of **1** ($K_a = 1.82 \times 10^4\ M^{-1}$ in DCM) for 1:1 receptor–anion interaction, and also shows a remarkable selectivity for F^- over Cl^- and $H_2PO_4^-$ [K_a (F^-/Cl^-) > 1800, K_a ($F^-/H_2PO_4^-$) > 1400]. In contrast, the fluorinated receptor **3** exhibits a sharp color change from yellow to orange in the presence of both F^- and $H_2PO_4^-$ in DCM solutions, and its fluorescence emissions are also quenched in the presence of both F^- and $H_2PO_4^-$.[27] These maiden results of Sessler and co-workers illustrated how the anion sensing properties of DPQ can effectively be tuned by introducing different electron-withdrawing substituents on the quinoxaline or on the pyrrole subunits of the parent DPQ (Table 1). Based on these attractive spectroscopic features of DPQ and its derivatives, newer opportunities to synthesize variously substituted DPQs and related classes of motifs to develop anion sensors have been opened up.

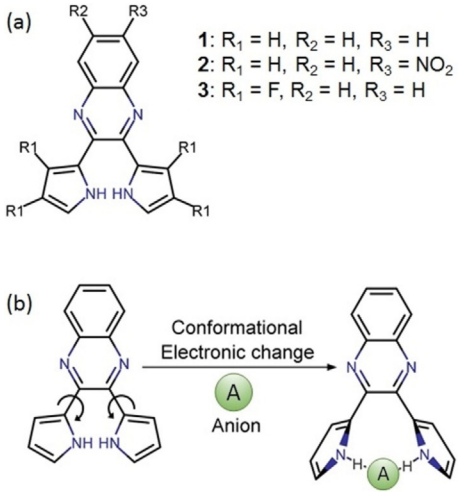


Figure 1. a) Dipyrrolylquinoxaline (DPQ, **1**) and its nitro and fluoro derivatives **2** and **3**, b) proposed mode of anion binding by DPQ.

Table 1. Association constants (K_a [M^{-1}]) of quinoxaline-based sensors with different anions. The absorption spectral change or fluorescence emission spectral change observed upon titration of a quinoxaline probe with anion was used to calculate the respective binding constants (× indicates that the association constant for the anion was not studied/determined).

Sensors	F^-	Cl^-	$H_2PO_4^-$	$H_2P_2O_7^{2-}$	AcO^-	CN^-
1	18200	50	60	×	×	×
2	118000	65	80	×	×	×
3	61600	180	17300	×	×	×
4	32000	550	4300	×	×	×
5	1000000	5800	300000	×	×	×
7a	2100	170	6800	×	×	×
7b	×	470	20000	×	×	×
8a	15531	514	9933	×	20602	×
8b	152535	821	78845	×	24452	×
9	8970000	10900	1130	×	×	×
10a	51300	< 100	< 200	93700	×	×
10b	24700	< 100	< 100	58900	×	×
10c	25600	< 100	< 100	57300	×	×
10d	27500	< 50	< 50	39000	×	×
10e	12200	< 100	< 100	30000	×	×
10f	10200	< 100	< 100	24300	×	×
11	17300	< 100	< 100	18000	×	×
12	19600	< 100	< 200	29500	×	×
13	16800	×	×	11200	×	×
14	482200	×	100	316000	1200	6630
15	150700	×	525	626000	3800	16800
17	60000	×	×	×	×	×
P3	70200	×	×	49300	×	×
P4	520000	×	×	380000	×	×
P5	616000	×	×	×	×	×
19	6500	×	2000	×	1100	×
20	255000	4400	70000	×	30000	×
21	25000	120	2300	×	13000	230000
21-Re	3100000	6500	28000	×	×	×
22	400000	210	19000	×	170000	×
22-Ru	1300000	1300	290000	×	1800000	×
23	140000	170	8800	×	670000	×
24	×	4200	×	×	1790000000	460000000
25	500000	×	×	×	×	×
26	440	×	×	×	×	×
26-Ru	12000	10	40	×	×	×
26-Co	54000	20	50	×	×	×
27	68000	500	1620	×	×	3450
27-Ru	640000	1700	14000	×	×	428000
31b	162000	×	×	×	187000	×
31c	×	×	×	×	764000	×
31d	758000	×	×	×	396000	×
32	19400	13400	21500	×	×	×
34	×	×	158500	5000	×	×
35a	50000000	60	250000	×	4000000	×
35b	×	60	631000	×	20000000	×
36	12000	110	23000	×	820000	×
37	×	×	×	×	2512000	×

Sessler and co-workers have also demonstrated that the inherent selectivity and anion binding affinities of DPQ can be modulated by introducing additional pyrrole groups to the α-pyrrolic positions of parent DPQ to give quinoxaline-oligopyrrole receptors **4** and **5**,[28] or by generating macrocyclic qui-

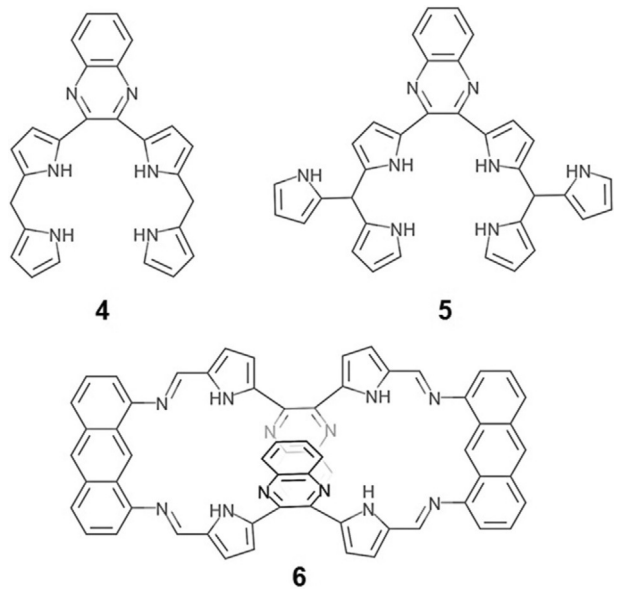


Figure 2. Quinoxaline–oligopyrrole receptors **4** and **5**, and macrocyclic quinoxaline-bridged porphyrinoids **6**.

noxaline-bridged porphyrinoids **6** (Figure 2).[29] Addition of fluoride to a dichloromethane solution of **4** results in a visible change in color from yellow to red, which can well be correlated with the UV/Vis spectral changes, which shows a decrease in the intensity of the original band (426 nm) and the appearance of a broad peak at higher wavelength (500–580 nm). The fluoride binding affinity of **4** having four pyrrole rings was found to be higher than the parent DPQ **1** (Table 1). On the other hand, receptor **5** with six pyrroles as hydrogen bond donors shows a 50-fold increase in binding constant value ($>10^6\,M^{-1}$) in comparison to **1** for the complexation of fluoride under similar conditions (Table 1). Because of the greater number of pyrrole –NH donors, receptor **5** shows a substantial increase in dihydrogenphosphate binding affinity and, from ^{1}H NMR spectral studies, it has been proposed to be hydrogen bonded with the receptor according to binding mode II (Figure 3). Larger fluoride-induced downfield shifts of the outer pyrrole –NH signals compared to the inner pyrrole –NH ($\Delta\delta =$ 3.80 vs. 2.05 ppm, respectively) suggest that the outer "claw-like" pyrrole subunits bind F^- more effectively. Unlike the acyclic derivatives of DPQ (**1**–**5**), macrocycle **6** contains *two* interconnected –NH binding cavities whose inward pointing cores can act as cooperative anion binding sites. Both F^- (20 equiv) and $H_2PO_4^-$ (300 equiv) can induce a colorimetric response

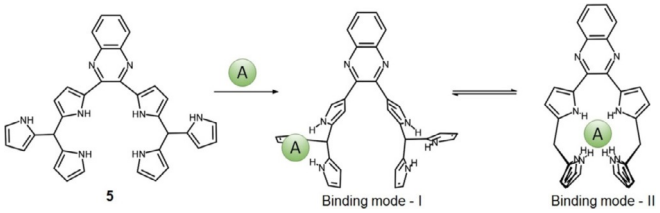


Figure 3. Proposed anion binding modes of receptor **5**.

from yellow to orange in 10% DMSO/DCM solutions of **6**. However, such color changes are not observed, even upon the addition of more than 300 molar equivalents of Cl^-, Br^-, NO_3^-, or HSO_4^- to the individual solutions of **6**, likely owing to the lower charge density present on these anions relative to those on F^- and $H_2PO_4^-$. UV/Vis spectrophotometric titrations showed the origin of two new bands at 329 and 480 nm at the expense of the original bands observed at 367 and 427 nm upon titration with F^- and $H_2PO_4^-$, respectively, in DCM. The UV/Vis titration curves and ab initio calculations, carried out at the HF/3-21G level for **6** and its possible fluoride complexes with different binding modes, led to the conclusion of positive homotropic allosteric binding behavior (Figure 4). That is, once a fluoride ion is captured in one cavity, the other cavity "shrinks" to the point where its size is better optimized for fluoride binding. The fluoride complexes, inner(**6**–F^-) and inner(**6**–2F^-) with inward binding modes are more stable by 15.73 and 24.20 kcal mol^{-1}, respectively, than outer(**6**–F^-) and outer(**6**–2F^-), wherein the fluoride anion is bound outside the macrocycle.

Sessler and co-workers have also explored the anion recognition properties of 2,3-diindolyl quinoxaline (DIQ) **7a** and its mono-nitro derivative **7b** (nitro-DIQ) by performing UV/Vis titration experiments in DCM (Figure 5).[30] The nitro-DIQ receptor **7b** displays a significant colorimetric response from yellow to orange when exposed to fluoride and dihydrogenphosphate, and the resulting titrations revealed several isosbestic points expected for a 1:1 binding stoichiometry. For both the receptors, the greatest affinity has been displayed for $H_2PO_4^-$, unlike their DPQ analogues, which showed the greatest affinity for F^- (Table 1). However, a reliable binding constant could not be determined from the spectrophotometric titration of **7b** with F^- anion, owing to the observation of biphasic behavior. The higher $H_2PO_4^-$ selectivity of DIQs [K_a(**7a**)/K_a(**1**) = 113, and K_a(**7b**)/K_a(**2**) = 250] can be ascribed to the β-connectivity that links the two indole recognition motifs to the quinoxaline core and, thereby, provides a more open cavity expected to favor the binding of larger anionic substrate like dihydrogenphosphate.

Yan and co-workers have further oxidized compounds **7a** and **7b** with DDQ in TFA to afford the corresponding indolocarbazole quinoxalines **8a** and **8b** (Figure 5).[31] Both the receptors showed high binding affinity for fluoride, acetate, and dihydrogen phosphate, as determined by UV/Vis–fluorescence titration in DMSO (Table 1). However, **8a** showed selective colorimetric response only in the presence of fluoride, whereas **8b** showed colorimetric response for F^- and AcO^-. The X-ray crystal structures of chloride and acetate complexes of **8b** showed that the indolocarbazole quinoxaline has a highly flat rigid conjugated structure and an anion is hydrogen bonded with the –NH groups of the carbazole unit. A similar strategy was utilized by Liu et al. to produce polydentate conjugate molecules based on a rigid quinoxaline plane surrounded by six indole –NH groups, that is, **7c** and **8c**.[32] Both **7c** and **8c** (Figure 5) showed selectivity for fluoride ions. The interaction of receptor **7c** and **8c** with F^- was investigated by suing UV/Vis and fluorescence spectroscopic titration. Compared to **7c**,

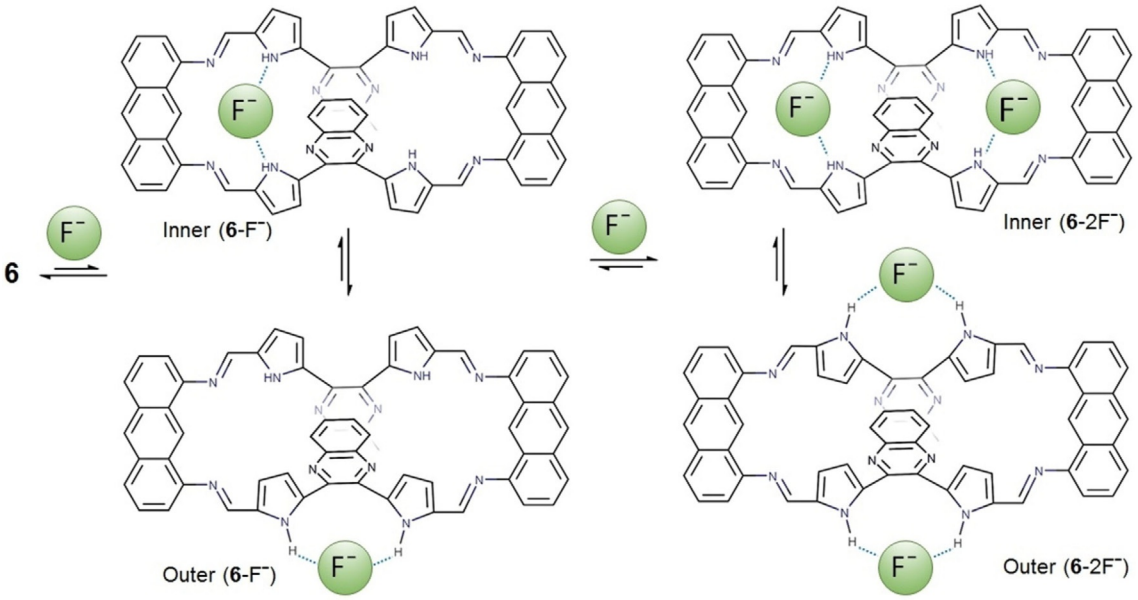


Figure 4. Possible anion binding modes of macrocyclic receptor **6**.

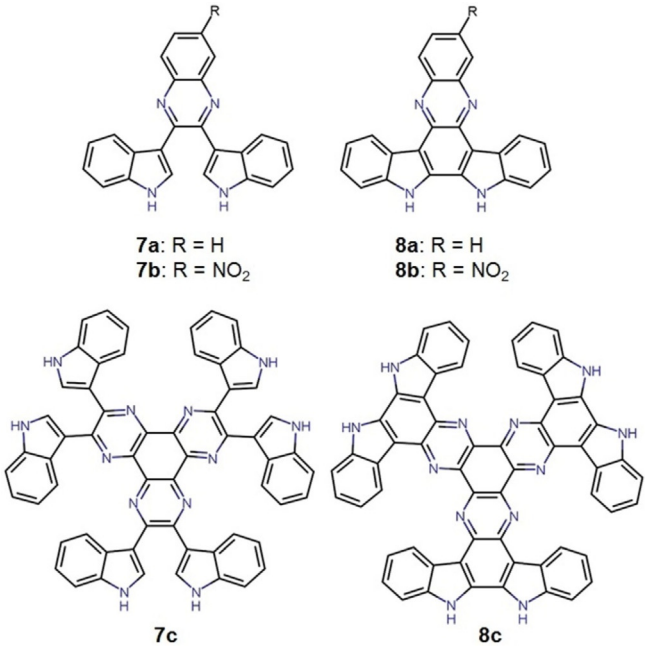


Figure 5. Diindolyl quinoxalines (DIQs) **7a–c** and corresponding indolocarbazole quinoxalines **8a–c**.

receptor **8c**, with the same ligating sites and chemical environment but with structure that is more rigid and no conformational flexibility, resulted in different sensing behavior. The ability of **8c** to detect F^- was shown by ratiometric fluorescence measurements, as shown in Figures 6A and 6B.

To further enhance the selectivity and sensitivity of quinoxaline oligopyrroles for inorganic anions, Sessler and co-workers developed a new class of calix[4]pyrrole receptor **9** (Figure 7) bearing 6-nitro-2,3-dipyrrolylquinoxaline (**2**) as strapping elements that would allow the anion binding event to be followed rather easily.[33] The receptor displays a significant colori-

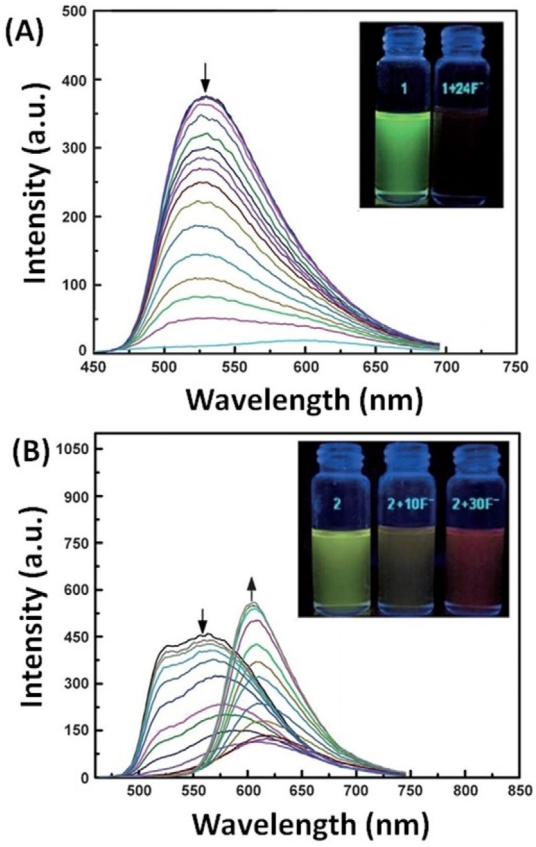


Figure 6. Fluorescence titration of A) receptor **7c** with F^- (as a TBAF salt from 0 to 30 equiv) in DMSO (λ_{ex} = 420 nm) and B) receptor **8c** with F^- (as a TBAF salt from 0 to 100 equiv) in DMSO (λ_{ex} = 440 nm); the insets in (A) and (B) show fluorescence emission color changes of the receptor **7c** and **8c** solution upon addition of F^-. Reprinted from Ref. [32] with permission. Copyright (2012) Wiley-VCH.

metric response from orange to blue/purple when exposed to fluoride and dihydrogenphosphate in CH_3CN/DMSO (97:3 v/v)

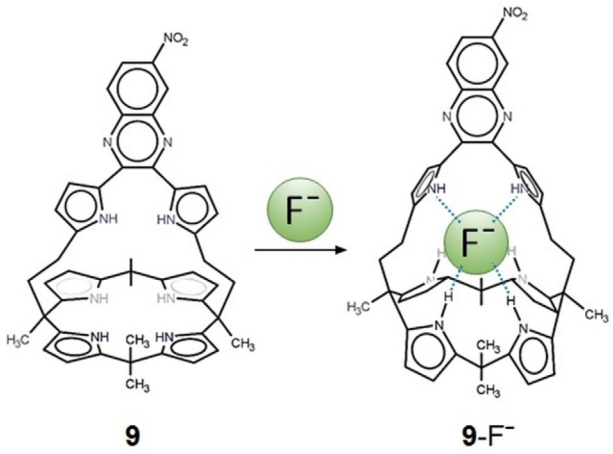


Figure 7. Quinoxaline calix[4]pyrrole receptor **9** and its proposed binding mode with fluoride.

solutions, and an enhanced anion affinity as compared to **1** and **2** (Table 1). A visible color change can also be observed in the presence of acetate anion. In the ^{1}H NMR titration with fluoride ($CD_3CN/[D_6]DMSO$, 9:1 v/v), a significant downfield shift of the calix[4]pyrrole –NH signals ($\Delta\delta = 4.85$ ppm) compared to the pyrrole –NH signals on the nitro-DPQ ($\Delta\delta =$ 0.42 ppm), and a rather unusual downfield shift of the β-pyrrolic –CH protons on the nitro-DPQ strap, led to the conclusion that a fluoride ion is hydrogen bonded to the calix[4]pyrrole core and is also involved in anion–π interaction with the pyrrole rings of the nitro-DPQ strap. The association constants obtained from the UV/Vis titration experiments have further been verified by isothermal calorimetric (ITC) titration experiments performed in CH_3CN/DMSO (97:3 v/v).

Towards systematic modulation of electronic density in the quinoxaline chromophore, Anzenbacher and co-workers introduced a range of aryl substituents to the 5- and 8-positions of the quinoxaline ring of DPQ (Figure 8).[34] The extended aryl substituents of varying electronic nature served to enhance

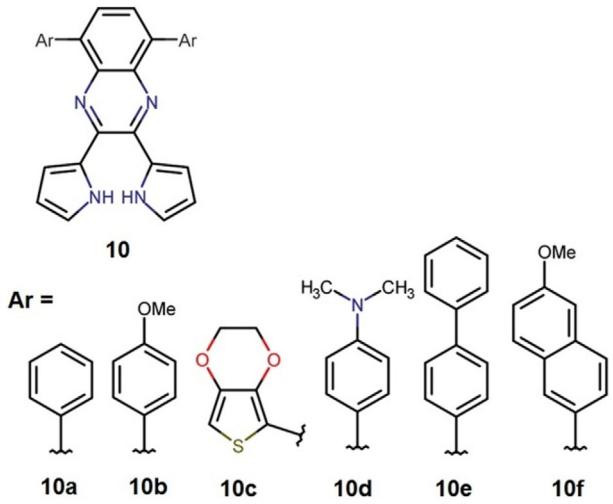


Figure 8. Aryl substituted DPQs **10a**–**10f**.

the sensor emissivity by expanding the conjugated quinoxaline chromophore, and to tune the output emission wavelength as well as the anion binding affinity of the receptors through substituent effects. When observed under an UV lamp ($\lambda_{ex} =$ 360 nm), sensors **10a**–**10f** can well respond to the presence of fluoride and pyrophosphate anions, as observed by a dramatic decrease in their fluorescence emission in aprotic solvents such as acetonitrile, dichloromethane, and DMSO. Fluorescence titration experiments revealed more than 95% quenching of the emission intensity in all cases upon addition of fluoride and pyrophosphate to the dichloromethane solutions of the receptors. Whereas other anions, such as chloride, bromide, hydrogensulfate/sulfate, cyanide, and dihydrogenphosphate, are unable to induce any observable changes in the fluorescence emission and absorption spectra of the receptor solutions. In UV/Vis experiments, the addition of fluoride and pyrophosphate to the individual dichloromethane solutions of **10a**–**10f** results in the decrease of the absorption intensity at 400–450 nm, together with the appearance of a strong band centered at 500–550 nm, which is responsible for the intense color of the solutions. The high affinity of receptors **10a**–**10f** for fluoride and pyrophosphate is a result of high surface charge density of fluoride anion and pyrophosphate dianion and is evident from their binding constant values summarized in Table 1. Notably, receptor **10a** show considerably increased affinity for fluoride and pyrophosphate compared to the parent DPQ (**1**) sensor.

Furthermore, to improve the performance of luminescence-based anion sensors, Anzenbacher and co-workers reported two novel ways of upgrading the DPQ sensor by attaching a pyrene antenna capable of resonance energy transfer (RET) to the parent DPQ or by excited-state delocalization in the conjugated system through acetylene bridges.[35] Visual inspection under UV light ($\lambda_{ex} = 365$ nm) showed remarkably enhanced emission for sensors **11** and **12** (Figure 9) in DCM solutions compared to the parent DPQ. The fluorescence emission of sensor **11** is observed at 495 nm and, for sensor **12**, the emission is shifted to 550 nm, and this amplification get even stronger in polar solvents such as DMSO that strongly quench the DPQ emission ($\lambda_{max} = 495$ nm). Addition of fluoride and pyrophosphate results in significant quenching of their emission intensity and can be observed visibly under a UV lamp. The emission-data-derived binding constants revealed that sensor **12** displays a twofold increase in binding affinity for pyrophosphate compared to the parent DPQ (Table 1).

Motivated by the increasing appreciation of quinoxaline-based chemosensors, Wu et al. synthesized receptor **13** (Figure 10) to understand the mechanism of anion sensing by DPQ with extended conjugation.[36] The absorption spectral changes and fluorescence quenching in DPQ-based anion sensors was previously attributed to the formation of hydrogen bonding between an anion and pyrrole –NH protons. However, it seems to be unlikely to bring about such large electronic perturbation (typical bathochromic shift of ca. 5000 cm^{-1} upon addition of fluoride anions) by simple hydrogen bonding interactions. Identical to the majority of DPQ-based anion sensors, receptor **13** also experienced a colorimetric response and fluo-

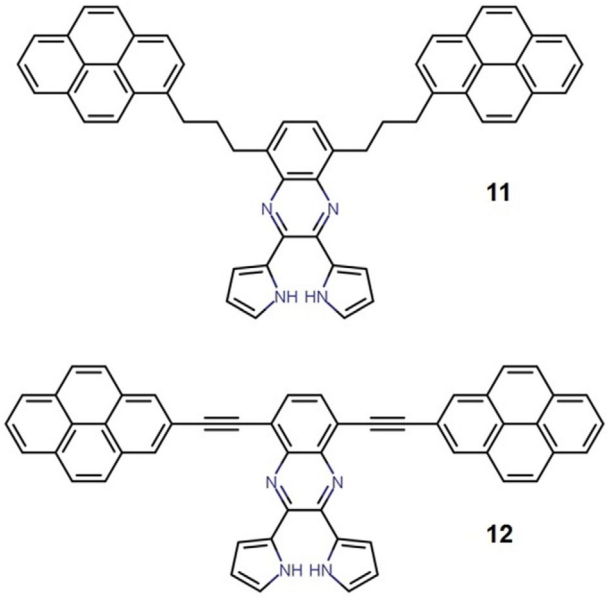


Figure 9. Pyrene functionalized DPQs **11**–**12**.

rescence quenching upon addition of fluoride and pyrophosphate anions in DCM solutions. The ^{1}H NMR titration experiments in [D_6]DMSO solution revealed the deprotonation of one of the pyrrole –NH protons in presence of excess fluoride or pyrophosphate anions (5 equiv), and the formation of a hydrogen-bonded complex between deprotonated receptor and the anion (Figure 10). The ^{1}H NMR experiments also indicated that the receptor **13** could be fully recovered by adding equivalent amounts of trifluoroacetic acid to the anion-containing solution.

In quest of electro-optical sensors for inorganic anions, Wong et al.[37] and Anzenbacher et al.[38] have synthesized a series of sensors **14**–**16** (Figure 11), which utilize a DPQ-like moiety for anion binding and a redox-active quinone moiety to generate strong colorimetric and electrochemical signals. Sensor **16** could be obtained only in trace amount by the condensation of dipyrrolylethane-1,2-dione with tetraamino-1,4-benzoquinone, owing to polymerization and, thus, its synthesis and anion sensing properties were not pursued further.[38] Sensors **14** and **15** showed a dramatic change in color in the presence of fluoride, cyanide, pyrophosphate ($HP_2O_7^{3-}$), and acetate in MeCN solution, whereas the addition of dihydrogenphosphate ($H_2PO_4^-$), benzoate, or chloride did not result in any appreciable change in color. Association constants calculated

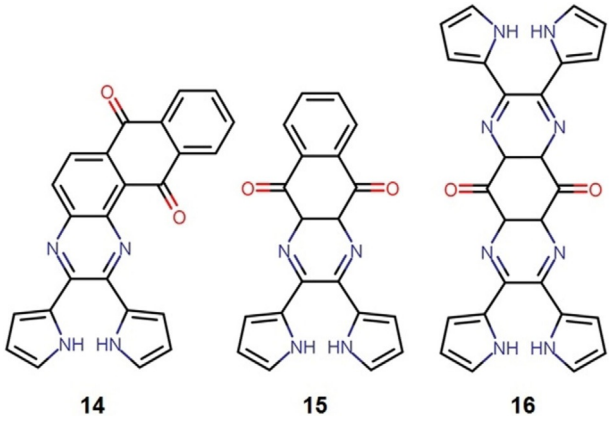


Figure 11. Redox active quinone-based dipyrrolyl pyrazine receptors **14**–**16**.

by monitoring the changes in the UV/Vis titration curves of sensors **14** and **15** in presence of anions revealed that sensor **14** has a much higher affinity for fluoride followed by pyrophosphate, whereas sensor **15** has a fourfold higher affinity for pyrophosphate than fluoride (Table 1). The anion affinity of sensors **14** and **15** was also investigated by using cyclic (CV) and square-wave voltammetry (SWV).[38] Both methods confirmed that the anion binding is accompanied by an anion-specific change in redox potential and decrease in current, a behavior attributed to the formation of the receptor–anion complex with a lower diffusion coefficient. SWV titrations show measurable changes in peak current and reduction potential even in the case of anions that induce only a weak color change that is insufficient for reliable determination by absorption spectroscopy (e.g. $H_2PO_4^-$).

It is to be noted that the majority of the above discussed DPQ-based sensors were not anion specific in the sense that they showed optical signaling in the presence of fluoride and also in the presence of acetate or phosphates (dihydrogenphosphate/pyrophosphate). Thus, their selectivity is limited to at least two anions or even more, as observed in the cases of **14** and **15**. In our work with DPQ-based sensors, we have observed that the anion selectivity can be specifically tuned for fluoride only by functionalization of DPQ-like recognition sites with tetrathiafulvalene (TTF), **17** (Figure 12).[39]

The receptor showed optical color changes from orange to pink only in the presence of F^-, whereas no color changes have been observed in the presence of Cl^-, Br^-, AcO^-, HSO_4^-, or $H_2PO_4^-$ in DCM solutions (Figure 12). UV/Vis titration of **17** with F^- in DCM showed a notable redshift of the original ab-

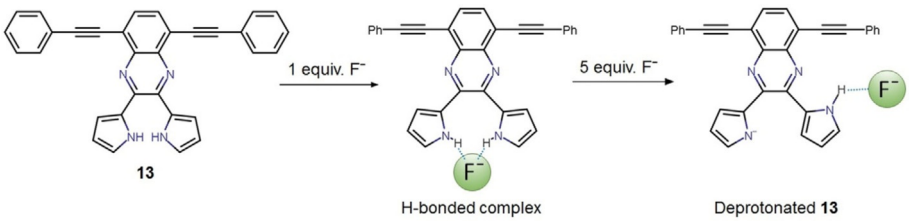
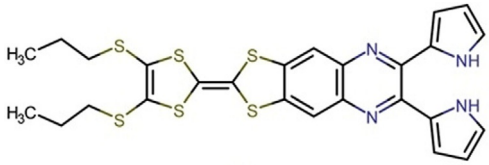


Figure 10. Formation of H-bonded fluoride complex and subsequent deprotonation of phenyl conjugated DPQ, **13**.

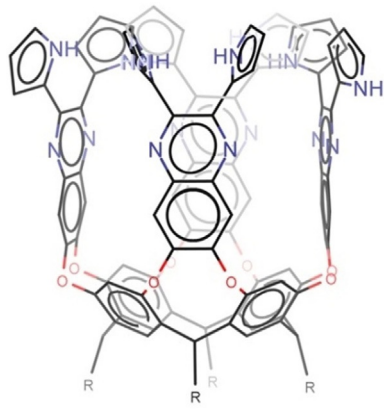


17

Figure 12. TTF-functionalized DPQ, **17** for selective fluoride sensing. Fluoride selective color changes observed for **17** in CH_2Cl_2. Reprinted from Ref. [39] with permission. Copyright (2012) Royal Society of Chemistry.

sorption bands with three clear isosbestic points. Furthermore, the emission intensity of **17** was significantly enhanced upon addition of F^- and an association constant value of $6\times10^4\ M^{-1}$ was obtained by fitting the changes in the emission data to a 1:1 binding stoichiometry. Based on H NMR spectroscopy, which showed the disappearance of pyrrole –NH and broadening of pyrrole –CH protons upon addition of F^-, we have suggested that anion-induced deprotonation of –NH is responsible for the selective sensing of fluoride. Finally, the material may be easily electrodeposited from solution by scanning the potential to the second oxidation process, which eventually produces a stable modified electrode that is electrochemically active in contact with aqueous sodium fluoride (NaF) solution.

A deep cavitand **18** bearing four DPQ moieties has been reported by Rebek and co-workers for anion recognition (Figure 13).[40] From NMR spectroscopy, it has been suggested that the cavitand **18** exists as a vase-like structure in solution. This DPQ-functionalized cavitand showed a color change from yellow to red in the presence of fluoride and acetate anions in acetone/dichloromethane. UV/Vis spectroscopic analysis showed the disappearance of the original band at 420 nm and the appearance of two new bands at 350 and 490 nm upon addition of fluoride or acetate. Broadening of H NMR signals for all groups of protons were observed upon the addition of fluoride and acetate in [D_6]acetone. Interestingly, no anion binding was observed to occur in deuterated aromatic solvents.



18 R = $(CH_2)_{10}CH_3$

Figure 13. Cavitand **18** with DPQ recognition sites.

2.2. Quinoxaline-Based Polymers

Aldakov and Anzenbacher have also presented a materials chemistry approach for anion sensing by employing two DPQ-based conductive polymers **P1** and **P2** (Figure 14), which are able to undergo an adjustable degree of p-doping, owing to the presence of thiophene moieties in the polymeric backbone.[41] Thus, two independent modes of signal transduction can be obtained in the chromogenic sensory materials, increasing the overall reliability of the sensing process. Spectroelectrochemical analysis of **P1** and **P2** films has enabled the investigation of the polymer electronic structure and determination of the polymer band gaps. The anion sensing ability of the polymers were tested by titration of the polymer films at a constant potential of 0.00 V with different anions (5.0 mM, pH ≈6.5) in aqueous solution, whereas Vis–NIR spectra were recorded concurrently. Gradual absorption spectral changes have been observed upon addition of fluoride and pyrophosphate anions into the individual cells containing the sensor films of **P1** and **P2**. Changes were also observed upon addition of phosphate into a cell containing **P2** film. The low level of p-doping at 0.70 V and a corresponding positive charge in the polymers resulted in a dramatic increase of their anion affinity. For example, the association constant of **P1** for pyrophosphate recorded at 0.70 V was calculated as $K_{PP}(0.70\ V) = 260\,000\ M^{-1}$, whereas the constant recorded at 0.00 V was $K_{PP}(0.0\ V) = 61\,100\ M^{-1}$. **P2** displays a stronger binding and higher association constants compared to **P1** due to the increased acidity of –NH protons of the chlorinated pyrrole.

Wu et al. synthesized two alkylated conductive polymers, **P3** ($n=7$) and **P4** ($n=110$) to understand the mechanism of anion sensing by DPQ-based polymers (Figure 14).[36] The absorption and emission spectra are not very sensitive to the degrees of polymerization, but do show some redshift with a higher degree of polymerization. Both polymers exhibited very bright fluorescence, but are sensitive to the presence of proton donors such as water and acetic acid in solution. As expected, colorimetric responses were observed upon addition of fluoride or pyrophosphate anions to **P3** and **P4** solutions, which could be attributed to the anion-induced deprotonation of –NH proton(s). Furthermore, the sensitivity of anion-induced fluorescence quenching of **P3** and **P4** was significantly enhanced over the corresponding monomeric sensor **13** (Table 1). The anion-induced deprotonation generates low-energy, non-fluorescent trapping sites and is responsible for the signal amplification, where the quenching of the excited state occurs from the deprotonated DPQ site in the network by rapid exciton migration along the polymeric backbone. Again, the fluorescence lifetimes of the polymer solution do not vary with the concentrations of the anion, indicating that a

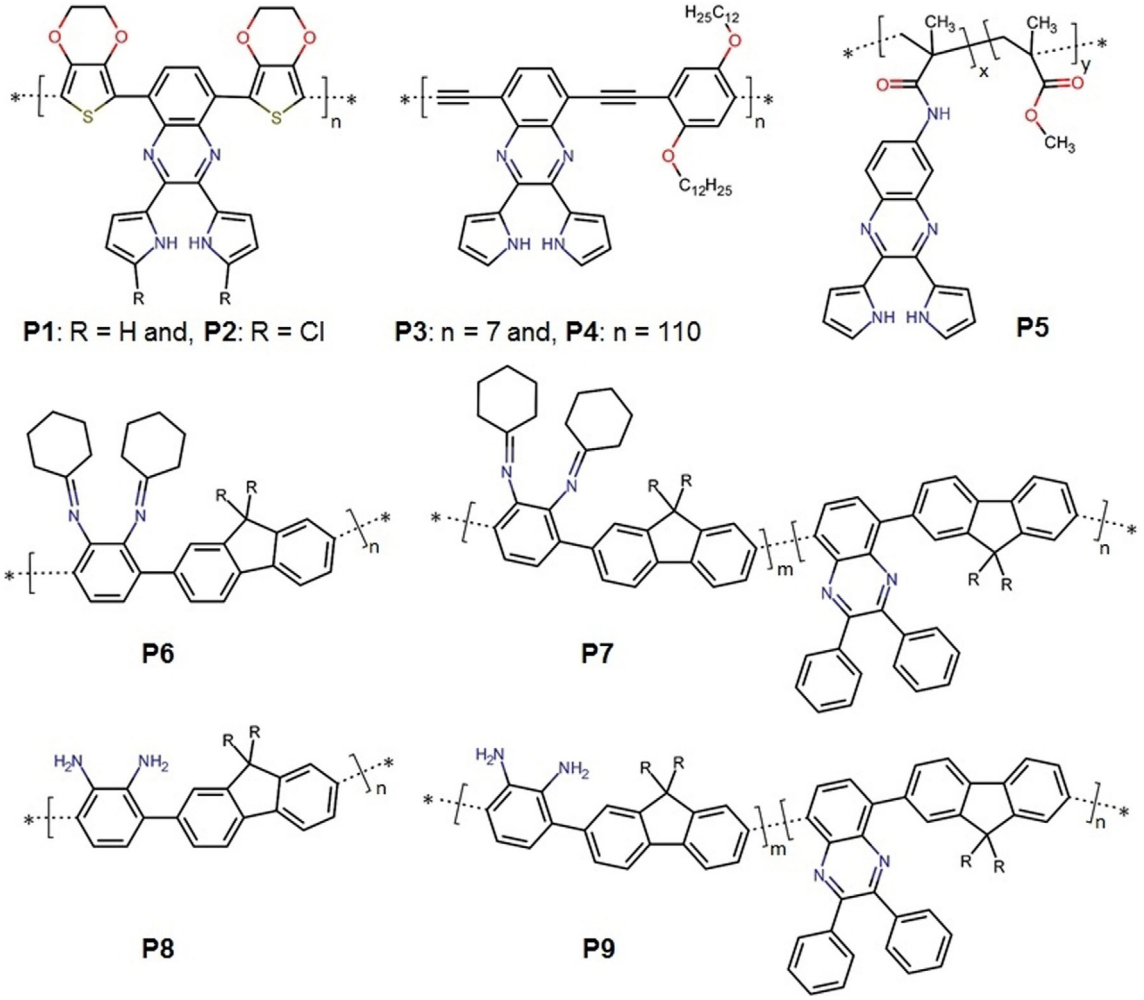


Figure 14. DPQ-based polymers, **P1–P5**, the azomethine-containing conjugated polymers linked with fluorene and/or quinoxaline units **P6** and **P7**, and the poly(*ortho*-diaminophenylene) derivatives containing fluorene and/or quinoxaline moieties **P8** and **P9**.

statically quenched polymer–anion complex dominates the fluorescence quenching mechanism in these systems.

Sessler and co-workers developed a DPQ-based copolymer **P5** (Figure 14), which is responsive to hydrofluoric acid (HF) vapors in the state of polymeric materials, such as films.[42] Thin films of **P5** on glass slides, which were prepared by both drop-casting and spin-coating methods, were examined for their ability to detect HF in vapor form and in solution when used as a dipstick. Upon exposure to vapors of 12.5% HF solutions, by weight, the initially bright yellow thin films changed to a distinct red color. This color change was both rapidly reversible upon exposure to vapors of concentrated ammonium hydroxide and slowly reversible under ambient conditions. Similarly, a dipstick test that was performed by submerging the end of a slide covered with the thin film into an aqueous solution of HF provided an even stronger response, with a change from yellow to purple. The association constant of **P5** for F^- in DCM was estimated to be $6.16\times10^5\ M^{-1}$ for each DPQ unit.

Kim et al. compared the sensing capabilities azomethine-containing conjugated polymers linked with fluorene and/or quinoxaline units **P6** and **P7** (Figure 14).[43] These two polymers are highly responsive and reversible to proton in the solid state, making them promising materials for acid gas sensory. Based on this, reversible chromatic switching behavior was accomplished through pH control of the solution. Protonation of **P6** and **P7** allowed for naked-eye colorimetric detection of iodide and acetate anions. A structure modification strategy for these two polymers is suggested to tune the ion-detecting properties by colorimetric change (Figure 15). In another report, Kim et al.[44] described the synthesis of poly(*ortho*-diaminophenylene) derivatives containing fluorene and/or quinoxaline moieties **P8** and **P9**. They explored the colorimetric and fluorometric anion sensing capabilities of these materials and found that the color of the polymer solution was altered dramatically upon the addition of fluoride anions without noticeable absorption change in UV/Vis spectrum. The fluorescence was ratiometrically quenched with a linear relationship between fluorescence intensity and fluoride anion concentration, implying static quenching mechanism.

2.3. Quinoxaline Sulfonamides

In addition to functionalized DPQs, several quinoxaline bis(sulfonamide)-based receptors have been synthesized and applied

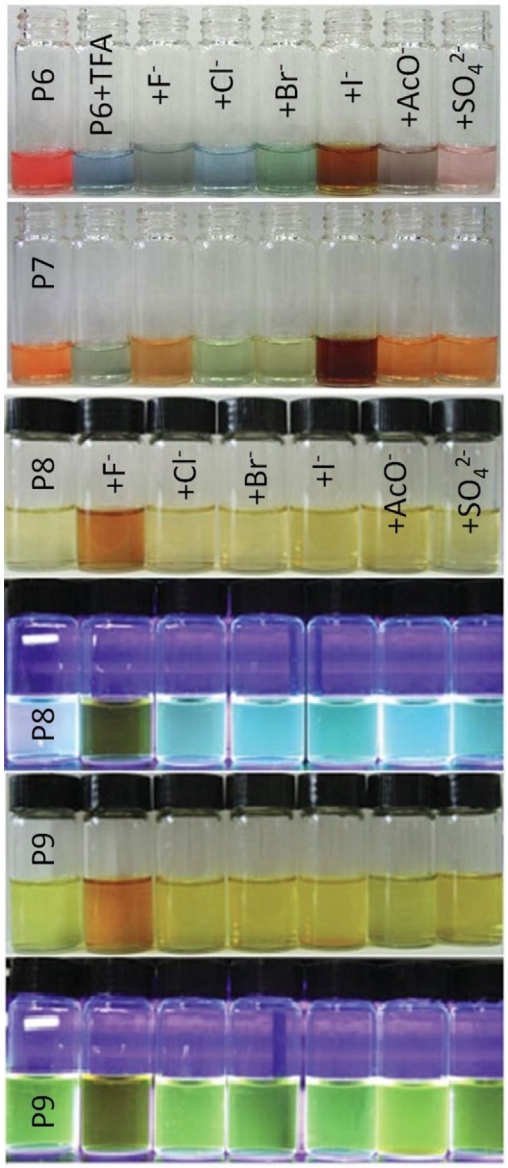


Figure 15. Color change of **P6** and **P7** in chloroform solutions upon addition of 100 equivalents of anions as their tetrabutylammonium salts (from left to right: polymer, polymer + TFA, polymer + TFA + F^-, polymer + TFA + Cl^-, polymer + TFA + Br^-, polymer + TFA + I^-, polymer + TFA + AcO^-, polymer + TFA + SO_4^{2-}), **P8** and **P9** in THF solutions gave fluoride selective color and fluorescence change by addition of 100 equivalenta of the anion as compared to other anions in the bottom four rows. Reprinted from Ref. [43] with permission (top). Copyright (2008) Elsevier. Reprinted from Ref. [44] with permission (bottom). Copyright (2007) John Wiley & Sons.

in anion sensing studies by different research groups, including us. In our effort to study the anion binding capabilities of DPQ and quinoxaline bis(sulfonamide), we synthesized a dipyrrole-bis-sulfonamide-based receptor **19** with two sulfonamide groups on the DPQ unit (Figure 16).[45] This receptor showed strong colorimetric and fluorescent responses for fluoride, dihydrogen phosphate, and acetate in chloroform [colorless to red (F^-)/yellow ($H_2PO_4^-$/AcO^-)]. The fluorescence intensity of **19** was enhanced upon addition of F^-, $H_2PO_4^-$, and AcO^- in chloroform. ^{1}H NMR titration of **19** with F^- revealed that the

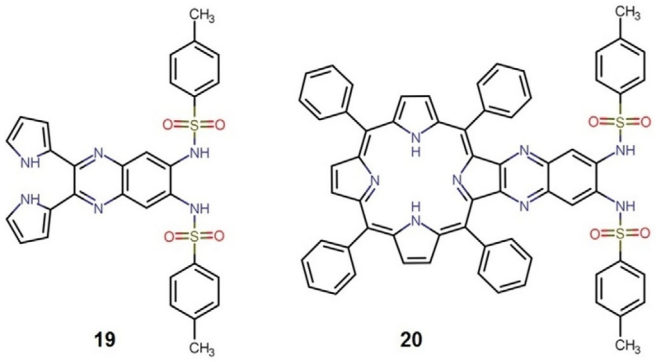


Figure 16. Dipyrrolylquinoxaline-bis(sulfonamide) receptor **19** and quinoxaline-bridged bis(sulfonamide) porphyrin receptor **20**.

sulfonamide –NH proton may be deprotonated while the pyrrole –NH protons are engaged in hydrogen bonding interactions with fluoride. Thus, the colorimetric and fluorometric signaling of F^-, $H_2PO_4^-$, and AcO^- by **19** could be assigned, owing to the deprotonation of sulfonamide –NH complemented by pyrrole –NH hydrogen bonds.

Starnes et al. synthesized a quinoxaline-bridged bis(sulfonamide) porphyrin receptor **20** (Figure 16), whose anion binding capability has been detected from the perturbation of the porphyrin Soret and Q bands in the UV/Vis spectrophotometry.[46] The Soret band of **20** at 422 nm was red-shifted by 12–16 nm and a clean isosbestic point was observed in each spectrophotometric titration with different anions, carried out in dichloromethane. The receptor showed highest binding affinity for F^- followed by $H_2PO_4^-$, AcO^-, and Cl^- (Table 1). The recognition properties of **20** were also investigated by using ^{1}H NMR spectroscopy for F^- and Cl^- binding.

Sun and co-workers synthesized a series of quinoxaline bis(sulfonamide)-based receptors **21**–**23** (Figure 17), capable of recognizing F^-, AcO^-, CN^-, and $H_2PO_4^-$ with different sensitivities.[47] The anion binding properties of **21**–**23** have been investigated by UV/Vis and fluorescence spectroscopy, and binding

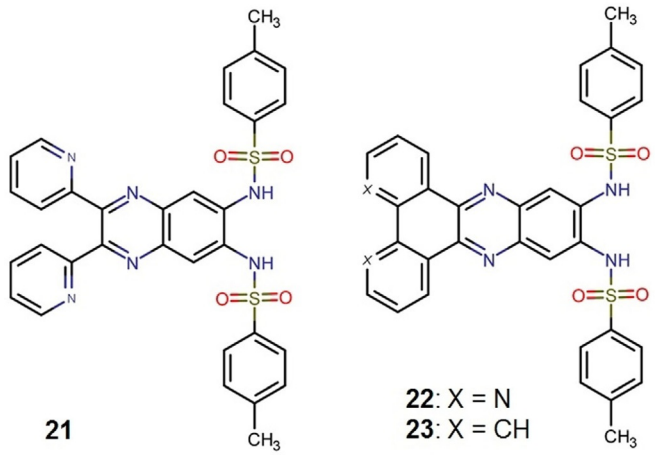


Figure 17. Pyridine, phenanthroline, and phenanthrene functionalized quinoxaline-bis(sulfonamide) receptors, **21**, **22**, and **23**, respectively.

constants are calculated from the changes in the UV/Vis spectra (Table 1). The results from ^{1}H NMR spectroscopic experiments provide further evidence for identifying the receptor–anion interaction processes. Sensor **21** has the weakest acidic sulfonamide –NH protons and, therefore, simply forms hydrogen-bonding complexes with F^-, AcO^-, CN^-, and $H_2PO_4^-$ in acetonitrile (CH_3CN) solutions. Notably, the emission intensity (λ_{em}) of **21** at 530 nm shows an enhancement upon the addition of F^-, AcO^-, CN^-, or $H_2PO_4^-$, unlike the DPQ-based anion sensors that experience fluorescence quenching upon addition of fluoride or pyrophosphate. Sensor **22** undergoes a stepwise process with the addition of F^- and AcO^- anions, namely formation of hydrogen bonded complex followed by sulfonamide –NH deprotonation in DMSO solutions. Direct sulfonamide –NH deprotonation occurs upon the addition of CN^-, but only a hydrogen-bonded complex forms with $H_2PO_4^-$ in DMSO solutions of **22**. Similar receptor-to-anion interactions have also been detected for **23** with the addition of F^-, CN^-, and $H_2PO_4^-$. However, only a genuine hydrogen-bonded complex forms in the presence of the AcO^- in a DMSO solution of **23**, because of the subtle difference in the *p*Ka values of sulfonamide –NH protons when probes **22** and **23** are compared. The degrees of receptor–anion interactions can be easily visualized by naked-eye colorimetric or luminescent responses.

A dithieno[3,2-*a*:2′,3′-*c*]phenazine-based bis(sulfonamide) receptor **24** (Figure 18) for anion detection has been reported by Kaafarani and co-workers.[48] Anion binding studies using fluorescence and ^{1}H NMR titration experiments revealed strong binding of **24** with cyanide, carboxylate (acetate and benzoate), and dihydrogenphosphate. Fluorescence titration of **24** ($CHCl_3$) with any of these anions resulted in an enhancement of the emission intensity of the probe with concomitant blue shift from 620 to 560 nm. In ^{1}H NMR titration ($CDCl_3$), the sulfonamide –NH proton disappeared, owing to hydrogen bonding with anion; however, a significant downfield shift of the thiophene –CH proton has been observed because of the electrostatic interaction of the tetrabutylammonium cation with dithieno moieties coupled with the delocalization of electron density on the extended aromatic systems and the electron withdrawing effect of the sulfur atoms. Halides were unable to induce any significant changes in the fluorescence emission intensity of **24** as compared to cyanide and carboxylates.

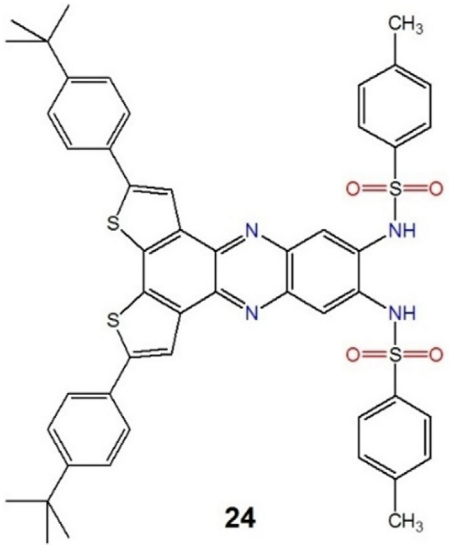


Figure 18. Dithienophenazine based bis(sulfonamide) receptor **24**.

Unlike the above-discussed quinoxaline bis(sulfonamide) receptors, which lack selectivity for a specific anion, our work on naphthalene diimide-functionalized dihydroquinoxaline bis(sulfonamide) receptor **25** (Figure 19) showed selective optical signaling and fluorescence quenching only in the presence of fluoride among other tested anions (Cl^-, Br^-, I^-, AcO^-, HSO_4^-, and $H_2PO_4^-$).[49] Receptor **25** showed selective colorimetric response from blue to green for F^- in chloroform or in DMSO solution (Figure 19). Significant quenching (ca. 97%) of the emission intensity of **25** was observed upon addition of three equivalents of fluoride to a chloroform solution, whereas other anions produced negligible quenching under similar conditions. ^{1}H NMR spectroscopy and single-crystal X-ray structure analysis confirmed the deprotonation of a sulfonamide –NH group in the presence of fluoride. A distinctive bathochromic shift (ca. 100 nm) of the original absorption bands of **25** with a clear isosbestic point has been observed in the UV/Vis titration with fluoride in DMSO. Based on the UV/Vis titration data, the association constant was calculated to be $0.5\times10^6\ M^{-1}$, for 1:1 binding.

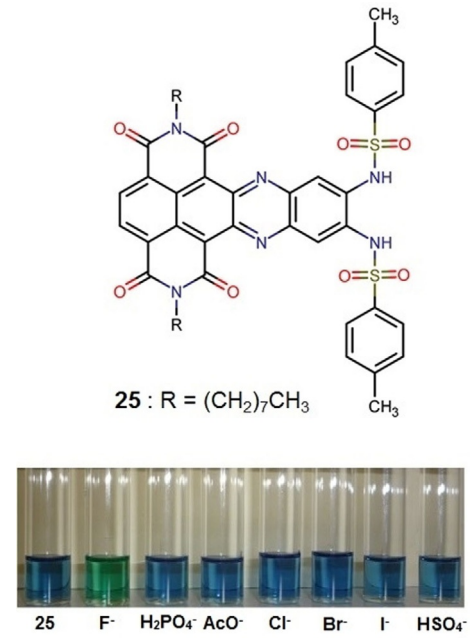


Figure 19. Naphthalene-diimide-functionalized dihydroquinoxaline bis(sulfonamide) receptor **25** and color changes observed in the presence of different anions. Reprinted from Ref. [49] with permission. Copyright (2009) American Chemical Society.

2.4. Metal Complexes of Quinoxaline-Based Sensors

Synthetic modification of DPQs and other quinoxaline-based anion receptors through the strategic incorporation of cation binding elements onto the receptor backbone to yield metal complexes to be employed as anion sensors has also resulted in significant enhancement in the anion binding affinity particularly towards fluoride and pyrophosphate. The first contribution in this field was made by Sessler and co-workers, who demonstrated the fluoride recognition properties of the ruthenium(II) and cobalt (III) complexes of a pyrazino-phenanthroline fused dipyrrolylquinoxaline derivative, **26** (Figure 20). In complexes **26-Ru^{II}** and **26-Co^{III}**, the electron-withdrawing effects that would render the pyrrole –NH protons more acidic take place efficiently through the quinoxaline backbone and lead to enhanced anion binding affinities.[50] In UV/Vis spectroscopy, the addition of F^- to a DMSO solution the cobalt (III) complex resulted in the emergence of a new peak at higher wavelength (650 nm) with a concomitant change in color from pink to purple, whereas the absorbance of the original absorption bands (323 and 525 nm) significantly decreased.

The proposal of adding cationic charges to a DPQ-based sensor can indeed be employed to increase the anion affinities, as evidenced by the evaluated binding constants of **26**, **26-Ru^{II}**, and **26-Co^{III}** with F^-, Cl^-, and $H_2PO_4^-$, based on their absorption spectral changes (Table 1). The **26-Co^{III}** complex with greater charge displayed a much higher affinity for F^- anion, as compared to **26** and **26-Ru^{II}**. The free receptor **26** displayed a rather low F^- affinity, presumably because of the additional electron density donated to the DPQ functionality from the phenanthroline moiety. In the differential pulse voltammetry (DPV) studies, the addition of F^- to a DMSO solution of **26-Co^{III}** resulted in a complete disappearance of the sharp Co^{III}/Co^{II} reduction signal, suggesting a redox-inactive nature in the complex formed. Furthermore, the fact that the Co^{III}/Co^{II} signal can be restored upon the addition of small amount of water indicates that the complexation between **26-Co^{III}** and F^- is reversible.

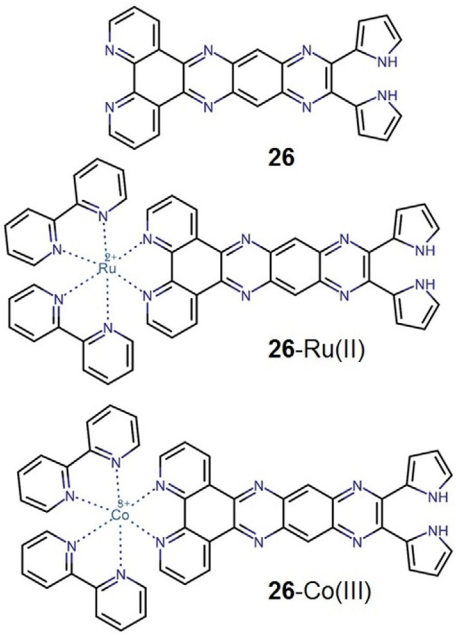


Figure 20. Pyrazine–phenanthroline-fused dipyrrolylquinoxaline **26** and its Ru^{II} and Co^{III} complexes **26-Ru^{II}** and **26-Co^{III}**.

Anzenbacher et al. reported an example of luminescence lifetime-based anion sensing by employing a Ru^{II} metal complex of phenanthroline-fused dipyrrolylpyrazine, **27** (Figure 21).

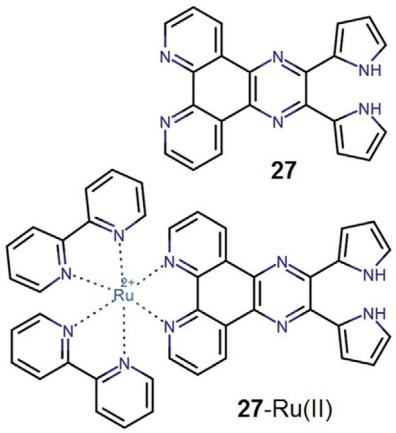


Figure 21. Phenanthroline fused dipyrrolylpyrazine, **27** and its Ru^{II} complex **27-Ru^{II}**.

Preliminary investigations revealed that the addition of fluoride, cyanide, and phosphate to the DCM/MeCN (98:2 v/v) solutions of **27** and **27-Ru^{II}** caused significant changes in their absorption and emission properties.[51] The emission spectrum of **27-Ru^{II}** is significantly quenched and red-shifted ($\lambda_{ex}=493$ nm) with increasing CN^- concentration, indicating a lowering in energy of the excited state and enhancement of non-radiative decay. In all cases, the emission-data-derived binding constants are substantially enhanced in **27-Ru^{II}** relative to **27**, owing to the electron-withdrawing effects caused by the Ru^{II} center (Table 1). In absence of an anion, **27-Ru^{II}** exhibited a single-exponential lifetime of $\tau=377(\pm 20$ ns) and, with increasing cyanide concentration, the intensity decays exhibited complex kinetics that adequately fit a sum of two exponentials (long $\tau=$ 320–370 ns and short $\tau=13$–17 ns). These emission lifetime data suggest that there are at least two distinct luminescent species, consisting of anion-bound **27-Ru^{II}** (short τ) and free **27-Ru^{II}** (long τ), the sum of which results in the observed lifetime quenching.

In an effort to increase the sensitivity of receptors **21** and **22**, metal complex probes **21-Re^{I}** and **22-Ru^{II}** have been synthesized upon metal coordination with the pyridylquinoxaline moiety of **21** and the phenanthroline moiety of **22**, respectively (Figure 22).[47,52] As a consequence of metal coordination, the sulfonamide –NH protons become increasingly acidic, thereby facilitating proton transfer from the probe molecules to basic anions. A two-step equilibrium phenomenon was observed in the UV/Vis titration of **21-Re^{I}** with F^- in DMSO solution. The stepwise process observed can be described by the formation of a hydrogen-bonded complex with sulfonamide –NH protons

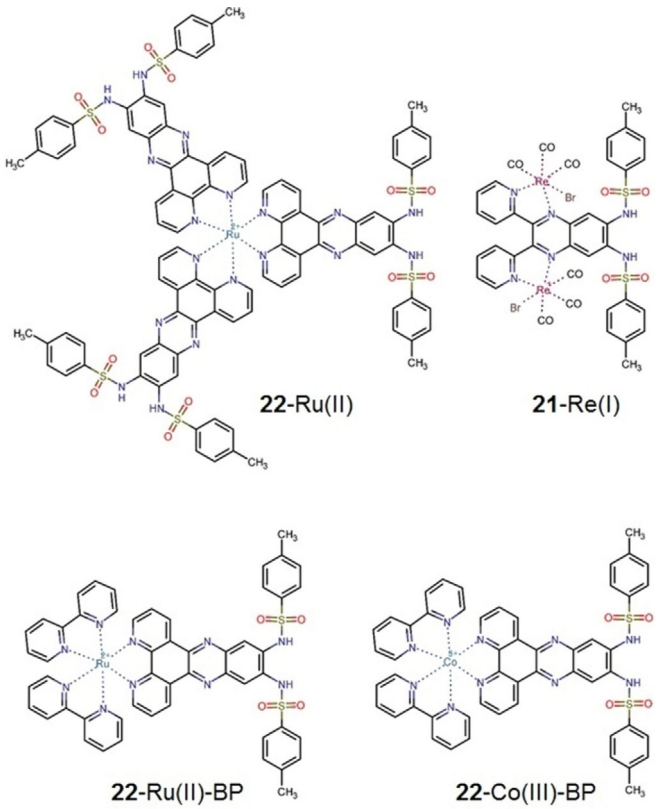


Figure 22. Rhenium(I) complex of pyridine-functionalized quinoxaline bis(sulfonamide), **21-Re^{I}** and ruthenium(II) complex of phenanthroline-fused quinoxaline bis(sulfonamide) **22-Ru^{II}** and 2,2′-biyridine ruthenium(II) and cobalt(III) complexes of phenanthroline-fused quinoxaline bis(sulfonamide) **22-Ru^{II}-BP** and **22-Co^{III}-BP** (BP = bipyridine).

followed by deprotonation of a sulfonamide –NH proton to form mono-deprotonated probe **21-Re^{I}** and HF_2^-. In the cases of CN^- and AcO^-, the spectrophotometric responses are attributed to a stepwise double deprotonation, which was further confirmed by titration of **21-Re^{I}** with OH^- ions and ^1H NMR experiments. However, spectrophotometric titrations with Cl^- and $H_2PO_4^-$ showed the formation of a 1:1 hydrogen bonding complexes for both anions, further confirmed by ^1H NMR experiments. A two-step process corresponding to the formation of a hydrogen-bonded complex followed by deprotonation has also been observed in the spectrophotometric titration of **22-Ru^{II}** with F^- in DMSO solution. Similar spectral responses were also observed for AcO^- and $H_2PO_4^-$, albeit with less sensitivity. However, the two-step absorption spectral isotherms obtained with the addition of CN^- are ascribed to a double deprotonation process, which is different from the single proton-transfer process observed in **22**. The 1:2 stoichiometry for receptor–anion interactions together with a two-step process observed in the spectrophotometric titrations of **22-Ru^{II}** with basic anions implies that only one sulfonamide ligand is in action with the incoming anions. Thus, it was speculated that the coordination of a Ru^{II} metal center to ligand **22** greatly facilitates the sulfonamide –NH proton dissociation in a polar DMSO solution. As a result, **22-Ru^{II}** tends to become a neutral molecule with two –NH protons dissociated at two different ligands, leaving only one intact sulfonamide ligand available for anion interaction.

Shang et al. compared ruthenium(II) and cobalt(III) sulfonamide–quinoxaline complexes as electrochemical sensors (Figure 22).[53] Spectrophotometric results indicate that **22-Ru^{II}-BP** and **23-Co^{III}-BP** have strong affinities for F^- or AcO^-, and moderate affinities for $H_2PO_4^-$ or OH^-. The interaction of these artificial receptors with F^- and AcO^- causes visible color changes, which make the receptors colorimetric sensors that can be ascribed to the hydrogen-bond formation with strong effects on the quinoxaline group. By changing the substitution site on the phenyl ring, for example, from *para* to *ortho*, the selectivity between fluoride and acetate may be finely tuned. The correlations between the electronic properties of the substituent and the affinity, as well as the selectivity and the configuration of receptor, will be a very useful guide to design more selective chemosensors to recognize F^- or AcO^-.

Xu et al.[54] designed a novel NIR-emitting cationic Ir^{III} complex with CN ligands containing dimesitylboryl groups and an extended NN ligand, **28-Ir^{III}** (Figure 23). Upon photoexcitation, the complex shows NIR phosphorescent emission around 680 nm. Interestingly, the complex can be excited with long wavelength around 610 nm, which can reduce the background emission interference and improve the signal-to-noise ratio. Through the selective binding between boron centers and F^-, an ON–OFF-type NIR phosphorescent probe was realized.

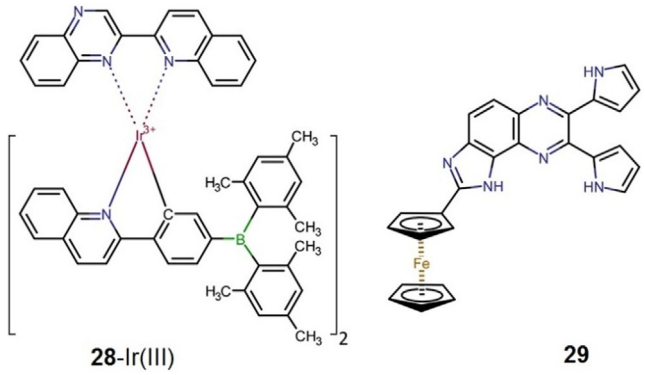


Figure 23. The chemical structures of Ir^{III} complex $[Ir(Bpq)_2(quqo)]PF_6$ **28-Ir^{III}** and ferrocene–imidazole–quinoxaline triad **29**.

Alfonso et al.[55] reported a nitrogen-rich ferrocene–imidazole–quinoxaline triad **29** decorated with two pyrrole rings (Figure 23), which, owing to its ditopic nature behaves as an ion-pair receptor for Ni^{2+}/Hg^{2+} cations and AcO^- anions. Although no affinity for acetate has been observed in UV/Vis study, fluorescence spectrophotometric titrations revealed enhancement of the emission spectrum in the presence of AcO^- and $H_2PO_4^-$. Cyclic voltammetry titration studies also showed selectivity for AcO^- and $H_2PO_4^-$, where the wave corresponding to the neutral receptor disappears when 2.5 equivalents of AcO^- is added in acetonitrile medium. It also displays the rare property consistent with the cooperative and recognition of ion pairs.

Balamurugan and Velmathi used a quinoxaline-based copper complex in a redox process toward the sensing of iodide ions.[56] They synthesized quinoxaline-based azine derivatives **30a** and **30b**, which showed a highly selective color change from orange and yellow to violet and blue, respectively, in the presence of copper ions. The iodide ions selectively regenerated the receptors **30a** and **30b** from their copper complexes. The receptors showed good binding constants and micromolar detection limit with 1:2 stoichiometric ratio of copper(II) and 1:4 of iodide ions (Figure 24).

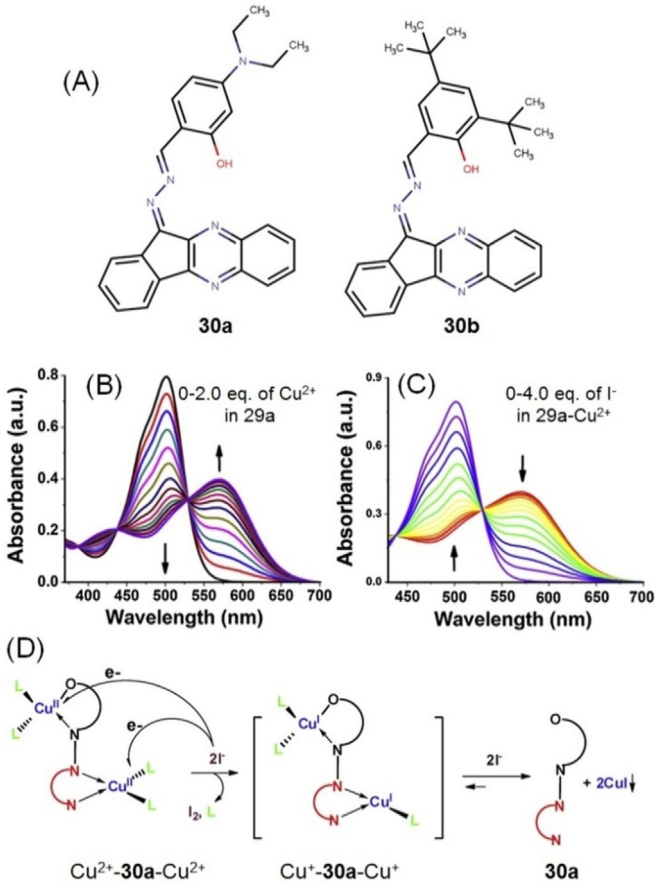


Figure 24. Chemical structures of **30a** and **30b** ligands (A), UV/Vis titration of **30a** with Cu^{2+} (B), UV/Vis titration of **30a**-Cu^{2+} with I^- anion (C), and redox process regenerating **30a** from **30a**-Cu^{2+} using iodide anion (D). Reprinted from Ref. [56] with permission. Copyright (2016) Elsevier.

2.5. Quinoxaline-Based Cationic Receptors

A wide variety of hydrogen-bond donor cationic systems containing ammonium, guanidinium, pyridinium, and imidazolium moieties exist, which can behave as anion sensors through a combined effect of hydrogen bonding and electrostatic interactions.

In their contribution, Kim and co-workers reported a series of four quinoxaline-based imidazolium receptors **31a**–**31d** (Figure 25), which are able to display an anion-induced excimer formation or charge-transfer phenomenon in organic media,[57] defining its uniqueness and exclusivity among the quinoxaline-based anion sensors. The anion binding affinities of these systems have been studied by using fluorescence and ^{1}H NMR titration techniques. In the fluorescence study of the compounds in the presence of excess anions (100 equiv), the anion-induced excimer formation (ca. 430 nm) has been observed with almost all anions, except $HP_2O_7^{3-}$ and AcO^-, which induce unique charge-transfer fluorescent responses in **31a** and **31b**, respectively. The anion-induced intermolecular π–π stacking between two quinoxaline rings is responsible for the excimer-state band. Whereas, the deprotonation of **31a**/**31b** in the presence of pyrophosphate or acetate can be correlated with the appearance of a distinct fluorescent peak at higher wavelength (500 nm), owing to the rapid charge-transfer phenomena from quinoxaline to deprotonated imidazolium ring.

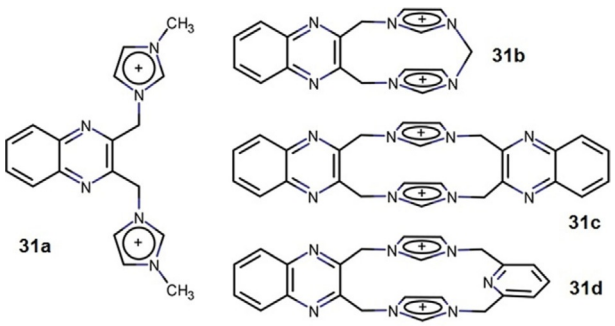


Figure 25. Quinoxaline-based imidazolium receptors **31a**–**31d**.

Kruger et al. have shown that the protonation of 2,3-dipyridylquinoxaline **32** results in a significant change in the absorption and emission properties of the molecule, owing to the alteration (flattening) of the molecular conformation. Protonated 2,3-dipyridylquinoxaline (Figure 26) behaves as luminescence anion sensor, showing some degree of selectivity for dihydrogenphosphate, chloride, and fluoride over other anions.[58]

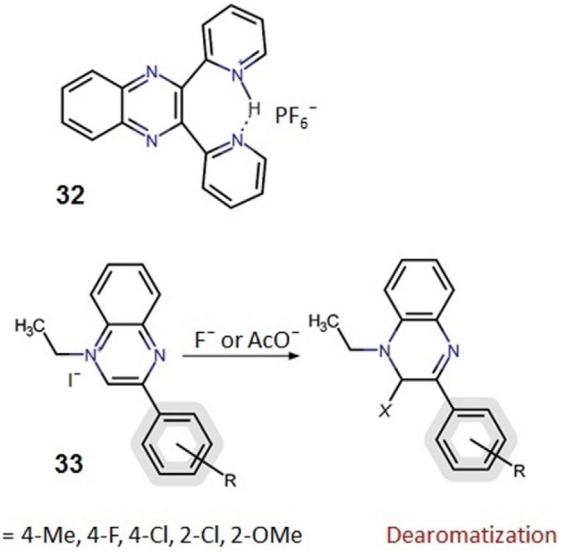


Figure 26. a) Protonated 2,3-dipyridylquinoxaline **32** and b) nucleophilic addition of fluoride/acetate at the C2 position of the substituted phenyl quinoxalinium cation **33**.

Fluoride and dihydrogenphosphate quenched the emission intensity (at 454 nm) by 50 and 60%, respectively. However, deprotonation of the protonated receptor was observed at very high concentrations of fluoride and dihydrogenphosphate, providing the parent molecule, as evidenced both by absorption and luminescence spectroscopy.

Recently, phenyl quinoxalinium salts **33** (Figure 26) have been recognized as chemosensors for fluoride and acetate, owing to the nucleophilic addition of these anions at the electron deficient C2 position of the quinoxalinium cation.[59] Nucleophilic addition of fluoride/acetate leads to the de-aromatization of the quinoxalinium cation, resulting in fluorescence quenching and decolorization of the quinoxalinium salt solution, as reflected in the absorption spectroscopic studies, where a significant decrease in the intensity of the absorbance bands was observed upon incremental addition of anion solution. In a representative ^{1}H NMR experiment, addition of 1 equivalent of fluoride to **33** (R = F) resulted in the disappearance of a singlet peak for the quinoxaline proton (adjacent to the positively charged N) at $\delta = 9.71$ ppm with the concomitant appearance of a new peak at $\delta = 5.99$ ppm that confirms the nucleophilic addition of anion. Similar ^{1}H NMR spectral changes were observed upon addition of 5 equivalents of acetate to **33** (R = F). Unlike F^- and AcO^-, ascorbate (large anion) quenches fluorescence through a photoinduced electron transfer (PET) mechanism, owing to the formation of a host–guest complex, and no peak shifting was observed in ^{1}H NMR spectroscopy.

The selective binding of monophosphate over diphosphate and triphosphate by receptor **34**, composed of two [9]aneN$_3$ units separated by a 2,3-dimethylenequinoxaline spacer (Figure 27), has been studied by means of potentiometric titrations as well as ^{1}H and ^{31}P NMR experiments in aqueous solutions by Bazzicalupi et al.[60] In aqueous solution, the amine groups of the macrocycle can easily become protonated to give charged polyammonium receptor **34**. The selective binding of monophosphate by **34** is determined by the distance between the two macrocyclic [9]aneN$_3$ units imposed by the dimethylenequinoxaline spacer that gives rise to a cleft of appropriate dimension for $H_2PO_4^-$ anion. Two similar receptors composed of two [9]aneN$_3$ units separated by 2,6-dimethylenepyridine and 2,9-dimethylene-1,10-phenanthroline showed preferential binding for diphosphate and triphosphate, respectively. ^{1}H and ^{31}P NMR experiments revealed that the complexes are essentially stabilized by electrostatic and hydrogen bonding interactions between the phosphate anion and the protonated amine groups of the macrocyclic subunits of the receptors.

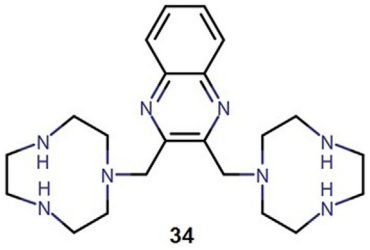


Figure 27. Dimethylquinoxaline-bridged macrocyclic polyamine receptor **34**.

2.6. Miscellaneous Quinoxaline-Based Sensors

Further towards the development of highly sensitive chromogenic and fluorescent anion sensors with polarized –NH functions, Sun and co-workers established that quinoxaline-based receptors **35 a** and **35 b** (Figure 28) featuring the combination

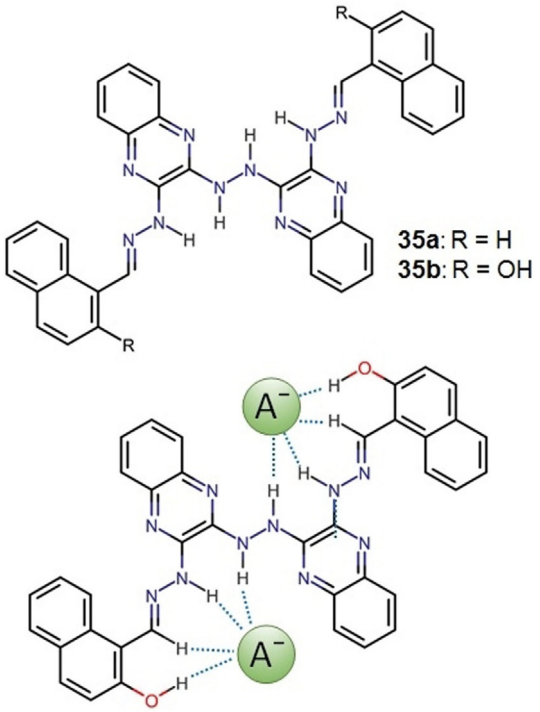


Figure 28. a) Hydrazine and hydrazone functionalized quinoxaline derivatives **35 a**,**b** and b) proposed 1:2 receptor–anion binding mode of **35 b**.

of hydrazine, hydrazone, imine, and hydroxyl functions can serve as efficient optical sensors for F^-, AcO^-, and $H_2PO_4^-$ in DMSO solutions.[61] The involvement of hydroxyl groups in anion binding resulted in stronger binding affinity of **35 b** than **35 a**, as established from the ^{1}H NMR titration experiments in [D$_6$]DMSO, and energy-minimized molecular models derived from semi-empirical MOPAC/AM1 method. Owing to their structural flexibility, receptors **35 a** and **35 b** could adopt a conformation to accommodate strongly interacting anions such as F^-, AcO^-, and $H_2PO_4^-$ and to compensate the energy required to "twist" the structural framework by forming multiple hydrogen bonds. Two potential anion binding pockets within the receptor structure result in a 1:2 binding stoichiometry with F^-, AcO^-, and $H_2PO_4^-$ in case of **35 a**; whereas, for **35 b**, a 1:2 binding stoichiometry was observed only with AcO^- and $H_2PO_4^-$, and the binding isotherm with F^- was found to be complicated with multiple equilibria occurring in solution. The formation of an aggregated [2+2] supramolecular complex has been proposed to rationalize the observed absorption and emissive responses of **35 b** upon addition of F^- (both titration spectra ex-

hibited two distinct conversion steps with increasing concentration of F^- anion), and is also supported by electrospray ionization (ESI) mass spectrometry and pulsed-field gradient NMR spectroscopy. The association of a first F^- anion to form a dimeric aggregate via a combination of multiple hydrazine/hydrazone/imine/hydroxyl anion hydrogen bonding and π–π stacking interactions allows for the association of a second F^- anion within the preorganized hydrogen bonding pocket and could, therefore, exert homotropic cooperativity effect.

Sun and co-workers also reported a biphenyl quinoxaline-based receptor **36**, featuring the dipyrrole–carboxamide anion recognition motifs (Figure 29).[62] The compound showed high selectivity for cyanide over a range of common inorganic anions in semi-aqueous environment (CH_3CN/H_2O, 9:1, v/v), owing to the formation of cyanohydrin derivative. Selective cyanide sensing is expressed by a colorimetric response from colorless to yellow accompanied through a change in fluorescence from blue to green. In the UV/Vis titration, three new bands appeared at the expense of the original bands and isosbestic points indicated a clean conversion throughout the titration process. Based on absorption spectral changes, the binding constant was calculated to be $\log K = 5.91\ M^{-1}$ for a 1:2 receptor–cyanide stoichiometry. Based on the ^1H NMR spectral changes upon addition of cyanide in [D_6]DMSO solution of **36**, the formation of a cyanohydrin adduct has been proposed and was also confirmed by ESI mass spectrometry and ^{13}C NMR spectroscopy.

However, F^- and AcO^- anion-induced deprotonation of receptor **36** has been proposed from ^1H NMR experiments. The amide and pyrrole –NH signals of **36** shifted downfield and became broad upon addition of even less than 1 equivalent of AcO^-, indicative of a dynamic process occurring at a rate comparable to the ^1H NMR spectroscopic timescale.[63] The quinoxaline –CH proton signal also shifted downfield and the rest of the aromatic proton signals displayed upfield shifts. These observations suggest the initial formation of a hydrogen-bonding complex between **36** and AcO^-, followed by an intramolecular proton transfer from one of the amide –NH protons to an acetate anion (Figure 29). The titration of F^- against a [D_6]DMSO solution of **36** resulted in a downfield shift and peak broadening of the amide and pyrrole –NH signals, indicating the formation of a typical hydrogen-bonding complex upon addition of 1 equivalent of F^-. The amide –NH signals gradually disappeared upon further addition of F^- and the quinoxaline –CH peak get slightly upfield shifted, suggesting the neat deprotonation of an amide -NH group to form the HF_2^- anion.[62]

Duke and Gunnlaugsson reported a bis-quinoxaline amidothiourea-based supramolecular cleft, **37** (Figure 30), for the fluorescent sensing of anions in organic media.[64] Both the ground and excited states of **37** were considerably affected upon recognition of acetate by the individual amidothiourea

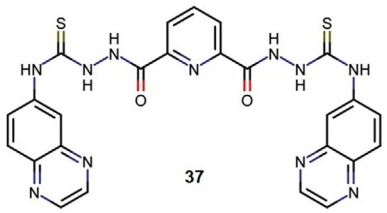


Figure 30. Bis-quinoxaline amidothiourea based supramolecular cleft **37**.

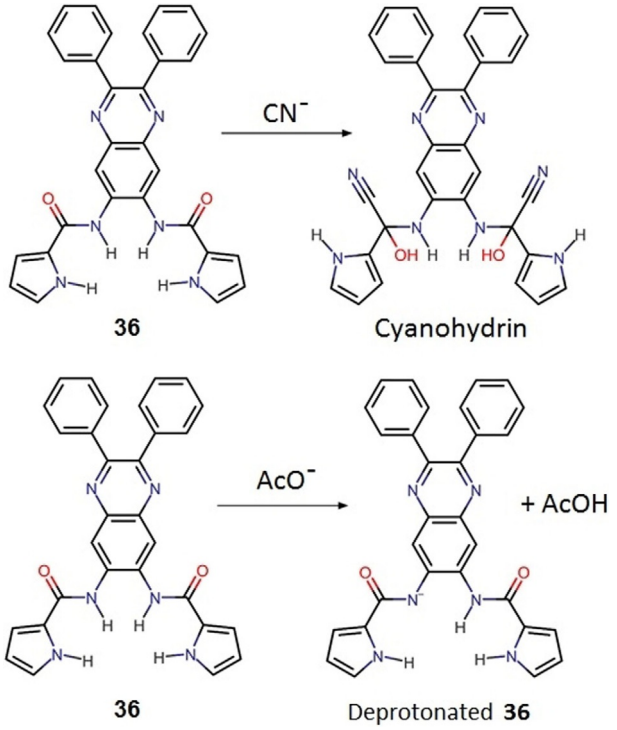


Figure 29. a) Formation of cyanohydrin derivative upon addition of cyanide to a solution of **36** and b) deprotonation of **36** upon addition of acetate.

functions. The emission intensity at 464 nm was quenched by approximately 62% after the addition of 2 equivalents of AcO^- in acetonitrile (MeCN) solution. The absorption spectral changes upon titration with AcO^- were best fitted to a three-component binding model using the non-linear regression analysis programme SPECFIT, and two binding constants were determined for the 1:1 and 1:2 receptor–anion interactions ($\log K_{1:1} = \log K_{1:2} = 6.4$). This clearly indicates that both amidothiourea functions are acting independently and a mixture of both the 1:1 and 1:2 complexes are formed in an almost equal amounts. Similar changes in the absorption and emission spectra were observed in the presence of hydroxide ions, indicating the anion-induced deprotonation of the receptor is responsible for the sensing of acetate anion and were also confirmed by carrying out ^1H NMR titrations in [D_6]DMSO.

3. Conclusions

In this Review, we have given a comprehensive account of quinoxaline-based chromogenic and fluorogenic chemosensors and reagents for inorganic anions. The concept of anion coordination chemistry coupled with optical signal generation by hydrogen-bond-induced changes in the electronic properties or deprotonation of the sensory probe is the primary approach

employed in most of the reports. The examples discussed in this Review illustrate how the integration of anion binding elements with the quinoxaline chromophore could result in anion responsive chemosensors. One aspect that has been observed in common for these chemosensors is that they all showed colorimetric response for fluoride, and very often for acetate and phosphate as well, owing to their high basicity as compared to other halides and oxyanions. Only quinoxaline receptors **7c**, **8a**, **8c**, **17**, and **24** as well as polymers **P8** and **P9** showed highly selective colorimetric and fluorescence response towards fluoride, and **35** showed optical selectivity only for cyanide by cyanohydrin formation. Thus, over the years we see that structural modification of the quinoxaline moiety with different sets of signaling unit and recognition sites has resulted in a few anion selective receptors. Based on the reports on several functionalized DPQ systems, it is evident that the anion binding affinities can be significantly enhanced by incorporation of electron-withdrawing functions on DPQ or by introducing aromatic functions on to the quinoxaline ring or by metal complexation.

However, there are very few single-crystal X-ray structures showing the receptor anion hydrogen bonding interactions for quinoxaline-based receptors. Amongst the neutral receptors, dihydrogenphosphate complex of **7b** and chloride/acetate complexes of **8b** are the only three examples where hydrogen bonding between pyrrole –NH and anion (spherical chloride, trigonal acetate and tetrahedral dihydrogenphosphate) can be observed in the respective crystal structures. Then again, no deprotonated receptor molecule (with tetrabutylammonium counter cation) has been structurally characterized although pyrrole –NH deprotonation in the presence of basic anions suggested being responsible for colorimetric sensing in several receptors based on spectroscopy results. Amongst the cationic receptors, hydrogen bonding between a chloride anion with the imidazolium –CH protons of receptors **30a** and **30d** has been established by crystallography.

Thus, it can be concluded that the anion sensing by quinoxaline-based receptors are limited to only basic anions in organic medium, and no effort has been made to date towards the sensing of some other environmentally and biologically toxic anions such as arsenate or selenate. It is important to mention here that the detection and determination of anions in real wastewater samples have not been pursued with any of these quinoxaline-based receptors, possibly owing to their poor solubility in water. However, innovative design and synthesis of quinoxaline-based molecules and materials by considering their stabilities, optimal geometries for hydrogen bonding interactions, optoelectronic properties, and water solubility should make it possible to obtain attractive sensory systems for anions in aqueous medium, which will contribute greatly to the academic foundation and practical applications of anion recognition chemistry.

We hope that this Review article will help new researchers to take up research in the emerging field of anion sensing and develop highly selective and sensitive anion sensors in water, which could find practical applications in chemical science and technology.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: anions · chromogenic chemosensors · fluorogenic chemosensors · quinoxaline · sensors

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