Recognition of Iodide Ion by Artificial Receptors

Indrajit Saha, Assistant Professor, Department of Chemistry, Ramakrishna Mission Residential College, Narendrapur, Kolkata, India, indra_ku@yahoo.co.in

Abstract: Anion recognition is one of the major thrust areas of contemporary research due to their wide role in biological, chemical and industrial sciences. Among several anions, iodide I⁻ ions play a vital role in human biological activities. In it's molecular form, iodine is utilized for several industrial applications such a syntheses of medicines, fabric dyes, food additives, solar cell electrolytes, catalysts, and agrochemicals. Either the excess or deficiency of I⁻ ions in the human body and environmental samples has certain consequences. Therefore, the selective and sensitive detection of I⁻ ions in the human body and environment is important for monitoring their overall profile. However, in comparision to other halides, iodide anion is difficult to bind using artificial receptor due to its weak hydrogen bonding capability. Therefore, number of receptors for iodide is very less in number. This review highlights the some selected work on iodide recognition by abiotic receptors.

I. INTRODUCTION

Iodide is an important anion of significant physiological importance because of its essential role in the normal growth, development and functioning of the brain and body [1]. Any deficiency of iodide can give rise to serious diseases such as enlargement of goitres or mental retardation. Iodine is a biologically essential element in seawater, where it exists predominantly as the iodide species and some organic iodine compounds. So far, numerous analytical methods have been developed for iodide analysis in various samples such as seawater, drinking water, milk, seaweed, and salts [1].

Therefore, the determination of iodide anion is important in a variety of fields such as food [2], clinical, biological sciences [3, 4], and also in environmental and industrial applications [5, 6]. Till date, a number of analytical methods, such as chemiluminescence [4], diffuse reflectance spectroscopy [2], ion chromatography [5], ICP-MS [6], pulse stripping analysis [7], inductively coupled plasma-atomic emission spectrometry [8], flow-injection analysis [9], gas chromatography- mass spectrometry [10] have been proposed for the direct determination of trace iodide. However, all of them involve long analysis time and considerable volume samples.

After the pioneering work of Czarnik [11] in the detection of analytes by using fluorescent chemosensors [12], anion sensing by anion-responsive optical sensors has been developed during the last decade [13]. With regard to the iodide ion only a few reports dealing with fluorescent sensors are found in the literature.

II. RECEPTORS FOR IODIDE

Kang *et al*. designed and synthesized fluorescent anion receptor **1**, bearing two methylene bridged bis-imidazolium unit on 1, 8-positions of naphthalene. Anion binding studies carried out using fluorescence spectroscopy and ¹H NMR revealed that receptor **1** displayed selective affinity for iodide ion [14].

Latter, Jang *et al*. reported benzimidazole-based tripodal receptor **2** which showed fluorescence intensity only with I⁻ in CH_3CN/H_2O (9:1, v/v). Interestingly, it did not show any significant change in emission upon addition of other anions such as F⁻, Cl⁻, Br⁻, HSO_4^-, NO_3^-, AcO⁻ and $H_2PO_4^-$ [15].
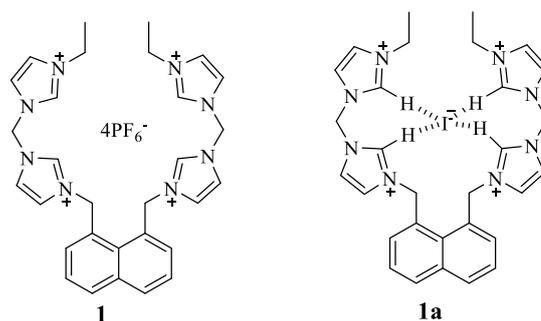

Figure 1: Structure of receptor 1 and its iodide complex

Similarly, a Cu (II) complex of a tripodal receptor **3** bearing an anthracene moiety on one pod as a fluorophore has recently been synthesized. The receptor **3** provided a preorganised anion-binding site that selectively sensed iodide at the micromolar level in the presence of other anions in aqueous CH_3CN without any interference [16].
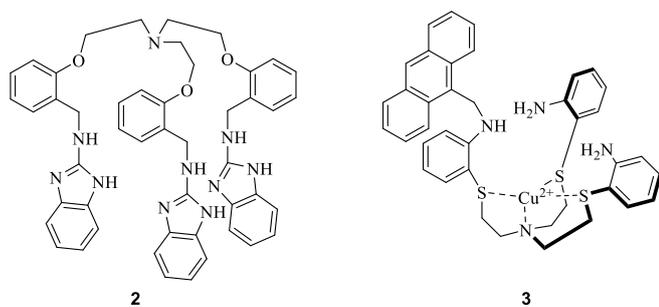
Figure 2: Structures of receptors 2 and 3.

A quaternary ammonium salt **4** bearing a pyrene fluorophore was grafted onto the surface of a delaminated zeolite and used as a selective chemosensor for iodide [17]. For all of the halides studied, only iodide is capable of quenching the emission intensity of pyrene fluorophore centered at 375 nm (λ_{ex} = 338 nm) by exhaustive ion exchange of the PF_6^- by the iodide anion. The emission quenching was probably due to a heavy atom effect or to a single electron transfer from the iodide atom to the pyrene induced by the interaction of the iodide with the ammonium cation present in **4**.
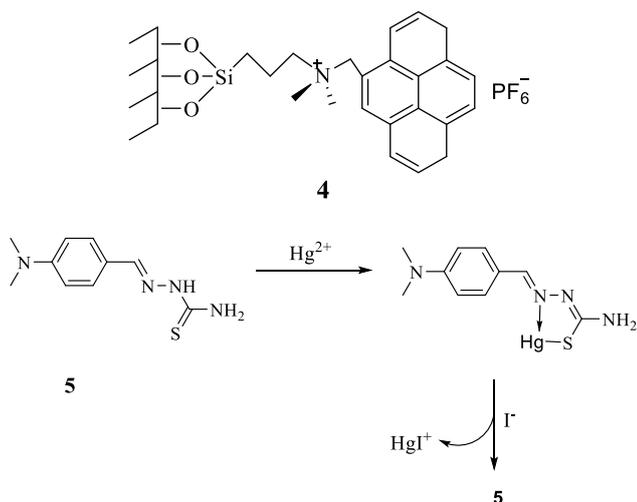

Figure 3: Structures of receptors 4 and 5 and sensing mechanism of 5.

Lin *et al*. prepared thiosemicarbazide-based receptor **5** which gave highly selective fluorescence quenching response toward Hg^{2+} in aqueous solution due to formation of 1:1 metal-ligand complex. This complex was found to show selectively and sensitively fluorescent enhancement response toward iodide over the other anions [18]. Otto *et al*. showed that two covalently linked cyclopeptide subunits effectively bound sulfate and iodide anions with micromolar affinity in aqueous solution [19]. Leclerc *et al*. reported two

cationic polythiophene derivatives **6a** and **6b** that offer an interesting methodology for simple optical (colorimetric or fluorometric) detection of iodide in aqueous medium. The binding induced conformational modification of the

conjugated backbone of cationic poly (3-alkoxy-4-methylthiophene) was supposed to be the key factor in sensing iodide [20].
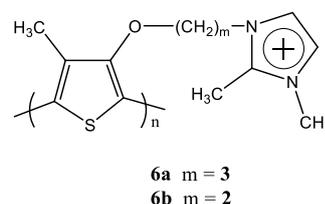

Figure 4: Structure of receptor 6.

Valiyaveettil *et al.* reported a new series of copolymers (**7 - 11**). The optical properties of these copolymers depend on the composition of the polymer backbone. The UV-vis and fluorescence spectra of the polymers were significantly affected by the addition of tetrabutylammonium iodide and other metal iodides. Moreover, a colourless polymer solution turns into deep yellow upon addition of only iodide salts. The colour of the solutions remains unaltered for other anions such as F^-, Cl^- and Br^- salts [21].
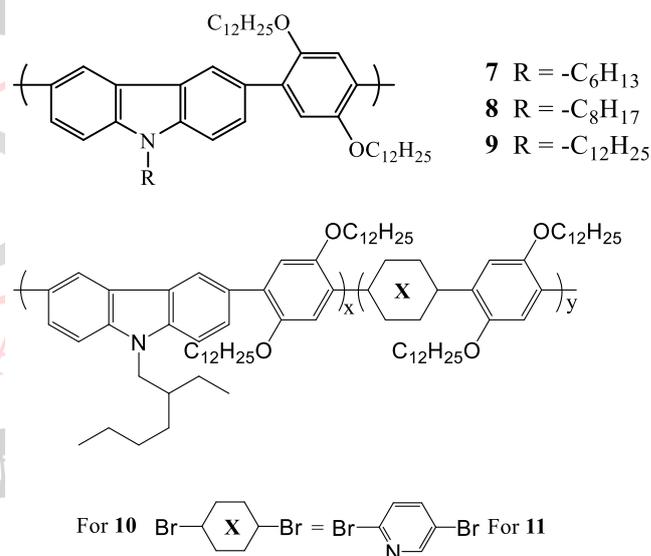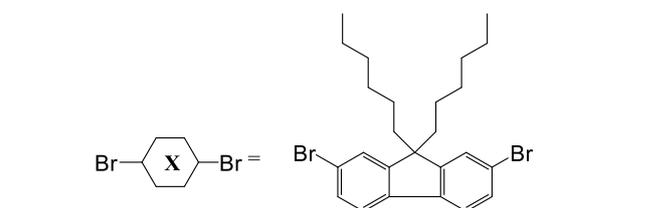

Figure 5: Structures of receptors 7-11.

Pandey and coworkers designed and synthesized main-chain bile-acid based polymers **12a-c** using click chemistry involving Cu(I)- catalyzed azide-alkyne 1,3-dipolar cycloaddition. These polymers displayed remarkable ability to stabilize silver nanoparticles that showed selective colorimetric sensing for the iodide ion [22].
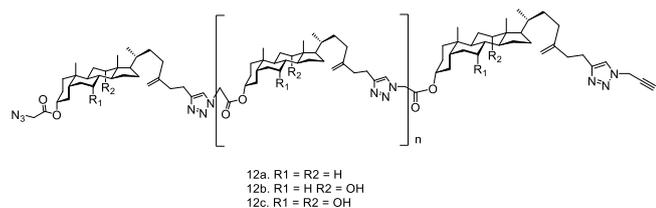
Figure 6: Structures of receptors 12a-12c.

Lin *et al.* reported a novel strategy for the rational design of a fluorescence *turn-on* probe **13** for I⁻, which is a notorious fluorescence quencher due to the heavy atom effect. The strategy was based on the redox reaction between Cu^{2+} and iodide (see scheme 4A.1). The probe exhibited a 20-fold fluorescence enhancement in the presence of 4 equivalents of iodide. Furthermore, the fluorescence detection of I⁻ was not affected by other anions such as of F⁻, Cl⁻, Br⁻, SO_3^{2-}, SO_4^{2-}, CO_3^{2-}, HCO_3^-, HPO_4^{2-}, BF_4^-, ClO_3^-, and NO_3^- etc [23].
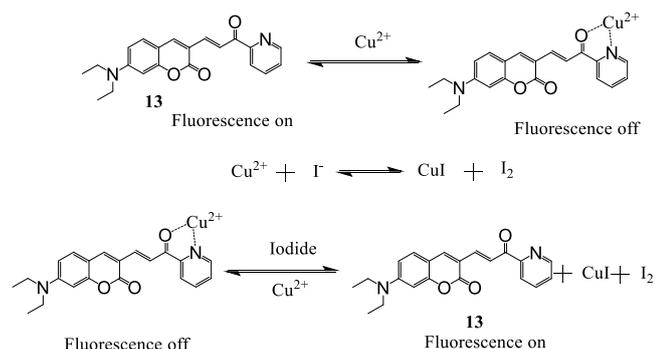
Figure 7: The design concept of a fluorescence *turn-on* probe 13 for Iodide

Rao *et al.* reported that molecular fluorescent sensor (**14**) exhibits fluorescence quenching towards Cu^{2+} among the eleven divalent ions, *viz.*, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ca^{2+}, Mg^{2+} and Pb^{2+} studied. The 1:1 stoichiometry of the Cu^{2+} complex thus formed recognizes I⁻ by changing its colour from colourless to pale-yellow in CH_3CN [24].

Resnati *et al.* showed that heteroditopic ligand **15a** simultaneously bind with both the counterions of alkali metal halides. **15b** was also effective in I⁻ binding. However, **15a** binds NaI more efficiently than the monotopic ligand **15b**, and it also effectively discriminates different halides in XB (Halogen bonding) driven exo recognition processes wherein I⁻ is coordinated preferentially over other halides. The preferential binding of **15a** to iodide anion was explained by the scale of XBs established in solution, where the strength of different XBs was decreasing in the order I⁻ > Br⁻ > Cl⁻ > F⁻ which is

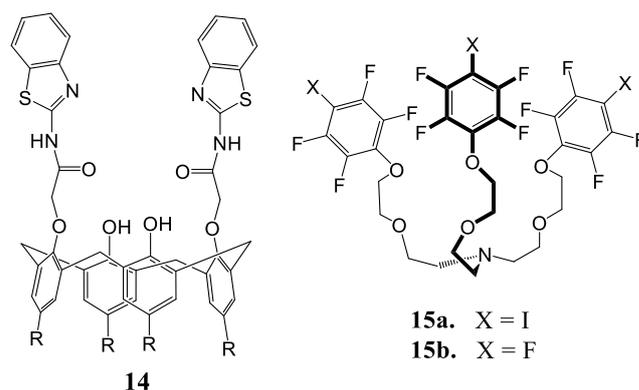opposite to that shown by most anion receptors that function through hydrogen bonding [25].

Figure 8: Structures of receptors 14-15a-b.

Thereafter, Beer *et al.* reported the use of solution-phase halogen bonding to control and facilitate the assembly of an interlocked structure through the bromide anion-templated formation of a rotaxane based upon an iodotriazolium axle. The incorporation of a halogen atom into the rotaxane host cavity dramatically improves the anion-recognition capabilities of the interlocked receptor. The receptor **16.7PF₆⁻** showed strong binding towards Br⁻ and I⁻ in competitive aqueous medium ($CDCl_3$: CD_3OD: D_2O, 45: 45: 10, v/v) with a selectivity preference for I⁻. This preference for I⁻ was explained on the ground of the accessibility of the binding site to larger anions and weaker competition for the more lipophilic halide by the aqueous solvent medium [26].
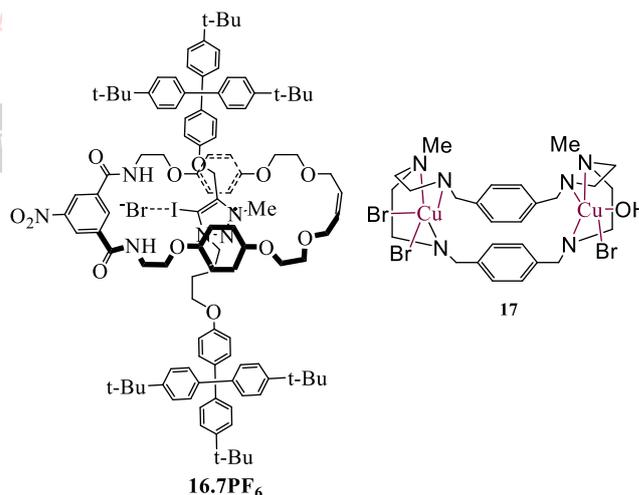

Figure 9: Structures of receptors 16-17.

Hossain *et al.* reported a macrocyclic dinuclear copper complex [**17**] that provides a bowl-shaped cavity for anion recognition. UV-vis spectroscopic studies in water-acetonitrile (1:3, v/v) and water revealed that the receptor exhibits a strong affinity and selectivity for iodide [K_a = 23900 and 125 M^{-1} in water-acetonitrile and water,

respectively] over other halides having the selectivity trend I⁻> Cl⁻> F⁻ >Br⁻. Furthermore, the receptor changes its colour from blue to green only in presence of I⁻ in water-acetonitrile (1:3, v/v) [27].

Ghosh *et al.* investigated the halide binding behaviour of octaaminocryptand **19** in its hexaprotonated and tetraprotonated states. Monotopic iodide recognition inside the cavity of [H₆**19**]⁶⁺ receptor in complex **B** is preferred over the ditopic recognition of a molecule of water and a fluoride ion in case of complex **A**. In **B**, the encapsulated iodide resides in distorted square pyramidal fashion with four intramolecular (N-H)⁺ --- I⁻ interactions and one intermolecular O-H --- I⁻ interaction from lattice water molecule (where hydrogen atom could not be located), although it is important to note that in case of halides four and six-coordination numbers are common. Iodide being the largest member in the halide family, its encapsulation inside the [H₆**19**]⁶⁺ did not allow further entry of solvent guest. The tetraprotonation of **19** by hydrochloric acid showed the formation and encapsulation of a bichloride inside the cavity, which is examined from the single-crystal X-ray study (**C**). [28]. On the other hand ligand **18** can encapsulate I⁻ ion in its octaprotonated states. This study shows that degree of protonation and its distribution in the receptor architecture play an important role in guest encapsulation [29].
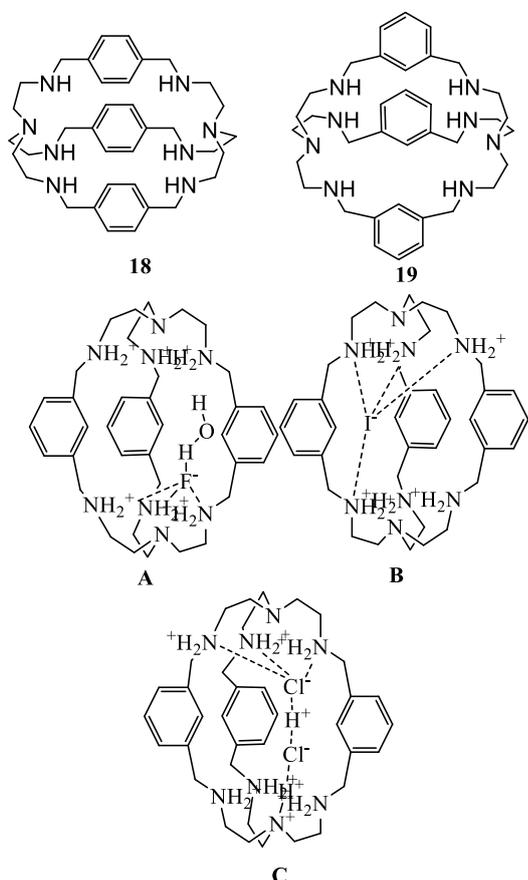

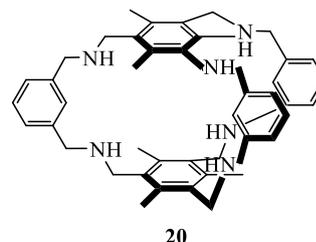**Figure 10: Structures of receptors 18-19 and their halide complexes.**

Figure 11: Structure of receptor 20.

Later on, the same group reported a C_3-symmetric drum-shaped homoditopic haxaamino bicyclic cyclophane **20**. Single-crystal X-ray analysis illustrated that bicyclic cyclophane has a cavity and side pockets for acetone molecules. The hexaprotonated state of this bicycle showed encapsulation of an iodide inside its cavity, and in hexachloride complex, chloride is recognized as Cl⁻---H₂O in each of the three side pockets which are in extensive hydrogen bonding interactions with the water and chlorides [30].

Jang *et al.* designed and synthesized the compound **21** and investigated both cation and anion binding behaviour of it. Receptor **21** exhibited selective recognition of I⁻ with UV–vis spectroscopy and selective analysis of Fe³⁺ with fluorescence spectroscopy. Thus, this sensor exhibited a new method to assay both I⁻ and Fe³⁺ using two different detection modes [31]. Recently, the same group reported that 1, 3, 5-substituted triethylbenzene derivative **22** with a 2-aminobenzimidazole moiety as a binding and signalling subunit can recognize I⁻ in a buffered CH₃CN/H₂O (99:1, v/v) solution. This receptor was shown to be operational over a large iodide concentration range. Moreover, the system was absolutely free from interference due to the presence of other anions. [32].

21. Fe³⁺ complex   **21**. I⁻ complex

22

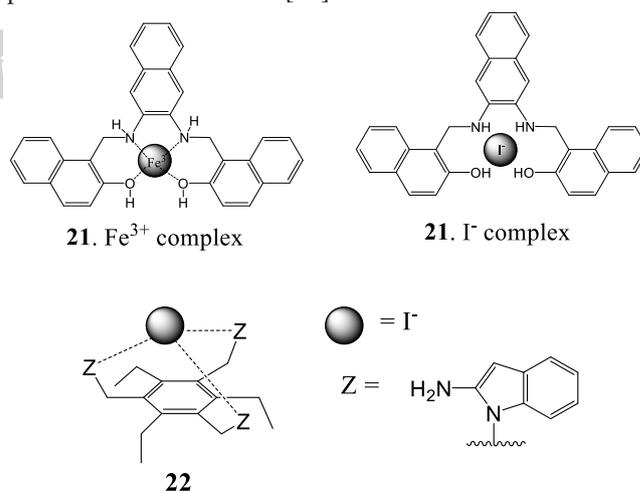**Figure 12: Structures of 21.Fe⁺, 21.I⁻ complexes and structure of 22.**

In recent past, adenine-based urea derivatives **23** and **24** for the study of adenine in anion recognition were reported from our laboratory. Both the receptors selectively detect iodide in CHCl₃ by showing quenching of the fluorescence

of the naphthalene and anthracene units in **23** and **24**, respectively. Other anions such as carboxylates, F⁻, Cl⁻ and Br⁻ were discriminated from iodide by an opposite effect in the fluorescence [33].
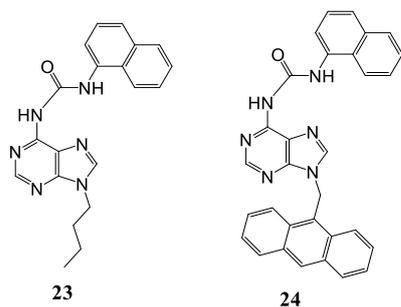

Figure 13: Structures of receptors 23-24

Jin *at al.* described that the fluorescence of water-soluble luminescent CdSe quantum dots surface-modified with triethanolamine (TEA–CdSe-QDs) was greatly quenched only when Hg^{2+} and I⁻ coexisted in the solution, whereas addition of either Hg^{2+} or I⁻ individually has no noticeable effect on the fluorescence emission (Scheme 13) [34]. It has been shown that I⁻ anions could bridge between TEA–CdSe-QDs and Hg^{2+} to form a stable complex (QDs–I⁻–Hg^{2+}) and the following effective electron transfer from the QDs to the Hg^{2+} could be responsible for the fluorescence quenching of QDs. The detection limits of Hg^{2+} or I⁻ ion were 1.9×10^{-7} molL⁻¹ or 2.8×10^{-7} molL⁻¹, respectively. Such a unique quenching effect demonstrates the reciprocal recognition of mercury (II) ions and/or iodide anions in aqueous solution with rather high selectivity and sensitivity. Li and co-workers also described that cadmium selenide quantum dots modified with thiourea type ligands was useful as fluorescent probes for iodide ions [35].
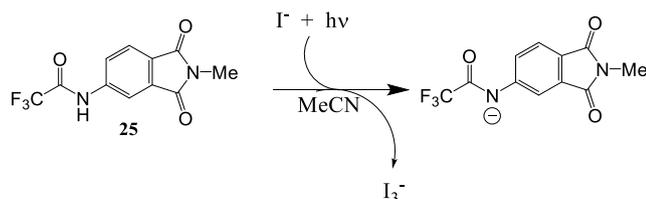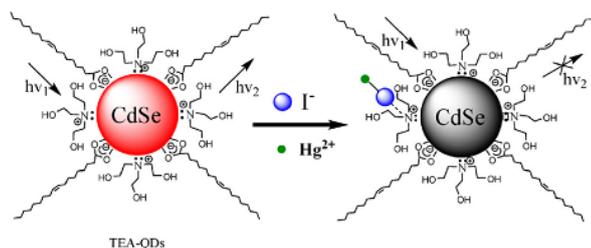

Figure 14: Schematic illustrations of the interaction between TEA-caped CdSe QDs and ion pair of Hg^{2+}.I⁻ and structure of receptor 25.

Okamoto *et al.* showed that the trifluoroacetylaminophthalimide derivative **25**, can serve as a potential I⁻ recognition probe in MeCN. The compound **25** produced a violet fluorescence in MeCN, and it displayed a green emission after irradiation at 254 nm in the presence of iodide ions. The corresponding amidate ion of the trifluoroacetamide was identified as the green fluorescence emitter. The deprotonation reaction was supposed to be caused by proton-abstracting solvated electrons generated by a photochemical charge-transfer-to-solvent process from I⁻ to MeCN [36].

Beer *et al.* designed and synthesized two heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl receptors **26a** and **26b** and investigated their both cation and anion coordination properties through ¹H NMR titration experiments in CD₃CN solution [37]. These molecules exhibited simultaneous alkali metal cations and iodide anion binding behaviour with positive cooperativity. Moreover, **26b** exhibits the largest positive cooperative iodide anion binding effect with the sodium cation, which is known to form highly selective complexes with lower rim tetrasubstituted ethyl ester calix[4]arenes [38].
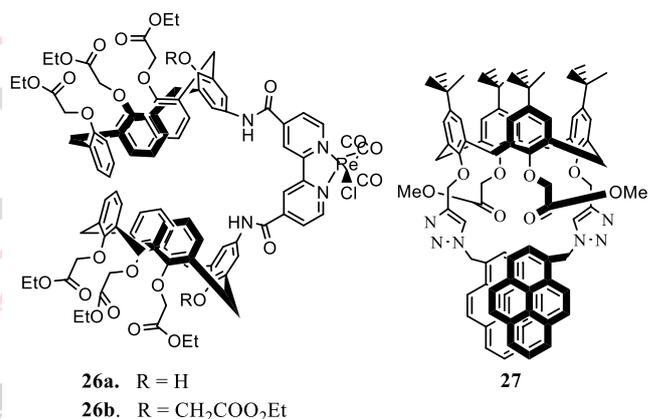

26a. R = H
26b. R = CH₂COO₂Et

27

Figure 15: Structures of receptors 26a-b and 27

Kim *et al.* reported a ratiometric fluorescent probe **27** where the two methyl ester and two pyrene triazole groups are in opposite side of the calix[4]arene. It was shown to be selective for the binding of I⁻. The encapsulation induced conformational changes of the frame removes one pyrene residue from the other that results in an increase in monomer and decrease in excimer emission [39].

The use of polar C-H bonds in complexing anions is also well established [40, 41]. Combination of these binding sites and their synergistic interplay are very crucial in the design of an effective receptor. In this chapter, we report a new receptor **28**, which is built on benzimidazolium motif. The hydrogen bonds as contributed by polar C-H bond of benzimidazolium motif in combination with amide hydrogens in **28** differentiate the anions with selectivity.

The receptor **28** fluorometrically recognizes iodide by showing significant quenching of emission of anthracene. Structural modification of **28** by placing a hydroxyl group (-OH) in the aliphatic amide chain led to the new structure **29** which displayed higher affinity for iodide ion.
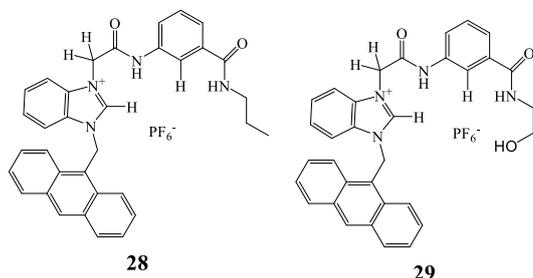

Figure 16: Structures of receptors 28-29.

Recently, Ghosh et al. reported pyridinium based iodide selective receptor **30-31** [42]. Using fluorescence, UV-vis and ^{1}H NMR, they have shown that these receptors are capable of sensing iodide ion in THF as well as in aqueous THF. The iodide induced quenching of emission of **30** and **31** was ascribed to hydrogen bond mediated formation of charge-transfer complex that facilitates spin-orbit coupling between iodide ion and flourophore (heavy atom effect).
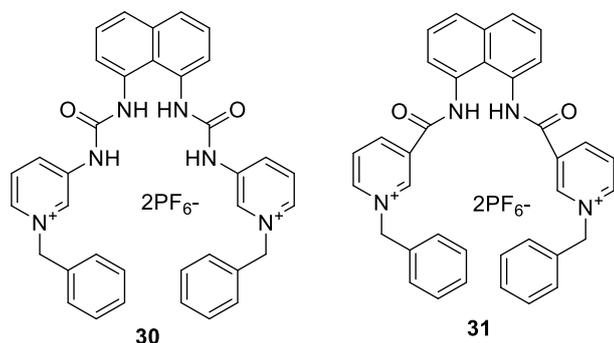

Figure 17: Structures of receptors 30 and 21

III. CONCLUSION

The different synthetic strategies to develop materials capable of interaction with large-sized iodide anion having high polarizability such as amide-based cavities, heteroatomic ring formations, and cavities of supermolecules have been well explained. Interestingly, it has been observed that the molecules engraved with amide bonds, pyridyl functionalities, sulfur, and nitrogen atoms are more susceptible to interact with iodide ions. This mini review describes several important molecular constructs that detect iodide ions using supramolecular interaction. The brief overview given here will be helpful for researcher to design and synthesis new iodide sensors capable of detecting and quantifing iodide ion in biological as well as environment samples. The selective sensing of iodide is an active area of research and much effort has been invested

due to global interest owing its crucial role in biological, chemical and environmental sciences.

REFERENCES

[1] (a) Wygladacz, K.; Bakker, E. *Analyst* **2007**, *132*, 268 and references in. (b) Butler, E. C. V. *Trends Anal. Chem.* **1996**, *15*, 45. (c) Jayaraman, S.; Teiltler, L.; Skalski, B.; Verkman, A. S. *Am. J. Physiol. Cell Physiol.* **1999**, *277*, 1008.

[2] Yang, S. X.; Fu, S. J.; Wang,M. L.; *Anal. Chem.* **1991**, *63*, 2970.

[3] Hassan, S. S. M.; Marzouk, S. A. M.; *Electroanalysis* **1993**, *5*, 855.

[4] Fujiwara, T.; Mohammadzai, I. U.; Inoue, H.; Kumamaru, T.; *Analyst* **2000**, *125*, 759.

[5] Anderson, K. A.; Casey, B.; Diaz, E.; Markowski, P.; Wright, B. *J. AOAC Int.* **1996**, *79*, 751.

[6] Arena, M. P.; Porter, M. D.; Fritz, J. S. *Anal. Chem.* **2002**, *74*, 185.

[7] Prost, R. C. *Anal. Chem.* **1977**, *49*, 1199.

[8] Larsen, E. H.; Ludwigsen, M. B. *J. Anal. Atom. Spectrom.* **1997**, *72*, 435.

[9] Hakedal, J. T.; Egeberg, P. K. *Analyst* **1997**, *122*, 1235.

[10] Bichsel, Y.; Von-Gunten, U. *Anal. Chem.* **1999**, *77*, 34.

[11] Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302.

[12] Books, special issues, and reviews on fluorescent chemosensors. (a) Czarnik, A. W. *Chem. Biol.* **1995**, *2*, 423. (b) *Chemosensors for Ion and Molecule Recognition. NATO ASI Series*; Desvergnes, J. P., Czarnik, A. W., Eds., Kluwer Academic: Dordrecht, 997. (c) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (d) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (e) Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181. (f) Fabrizzi, L. Ed., Luminescent Sensors; *Coord. Chem. Rev.* **2000**, *205*, 1. (g) Kuswandi, B. *Jurnal ILMU DASRA* **2000**, *1*, 18. (h) Bren, V. A. *Russ. Chem. Rev.* **2001**, *70*, 1017. (i) Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79. (j) Valeur, B. *Molecular Fluorescence*; Wiley-VCH: Weinheim, 2002. (k) Diamond, D.; Nolan, K. *Anal. Chem.* **2001**, *73*, 22A-29A. (l) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 486. (m) Ludwig, R.; Dzung, N. T. K. *Sensors* **2002**, *2*, 397. (n) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (o) Callan, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551. (p) Dallali, N.; Darabi, A.; Agrawal, Y. K. *Rev. Anal. Chem.* **2005**, *24*, 263. (q) Amendola, V.; Fabbrizzi, I.; Forti, F.; Pallavicini, P.; Poggi, A.; Sacchi, D.; Tagleitti, A. *Coord. Chem. Rev.* **2006**, *250*, 273. (r) Mancin, F.; Rampazzo, E.; Tecilla, P.; Tonellato, U. *Chem. Eur. J.* **2006**, *12*, 1844. (s) Kungwandi, B.; Nuriman.; Verboom, W.; Reinhoudt, D. N. *Sensors* **2006**, *6*, 978. (t) Mancin, F.; Rampazzo, E.; Tecilla, P.; Tonallato, U. *Chem. Eur. J.* **2006**, *12*, 1844. (u) Valeur, B.; Leray, I. *Inorg. Chem. Acta* **2007**, *360*, 765. (v) Löhr, H.-G., Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65. (w) Yang, X.-F.; Guo, X.-Q.; Zhao, Y.-B. *Talanta* **2002**, *57*, 883. (x) Zhu, L.; Anslyn, E. V. *Angew. Chem. Int. Ed.* **2006**, *45*, 1190. (y) Anslyn, E. V. *J. Org. Chem.* **2007**, *72*, 687. (z) Bell, T. W.; Hext, N. M. *Chem. Soc. Rev.* **2004**, *33*, 589. (α) Nohta, H.; Satozono, H.; Koiso, K.; Yoshida, H.; Ishida, J.; Yamaguchi, M. *Anal. Chem.* **2000**, *72*, 4199. (β) Okamoto, A.; Ichiba, T.; Saito, I. *J. Am. Chem. Soc.* **2004**, *126*, 8364. (χ) Kim, H. N.; Lee, M. H.; Kim, H. J.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2008**, *37*, 1465.

[13] Review articles on anions sensing. (a) Kim, S. K.; Lee, D. H.; Hong, J.-I.; Yoon, J. *Acc. Chem. Res.* **2009**, *42*, 23. (b) Gale, P. A. *Chem. Commun.* **2008**, 4525. (c) Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780. (d) Anslyn, E. V. *J. Org. Chem.* **2007**, *72*, 687. (e) Gunnlaugsson, T.; Ali, P. H. D. ; Glynn, M.; Kruger, P. E.; Hussey G.

M.; Pfeffer, F. M.; Martinez-Manez, R.; Sancemon, F. *J. Fluor.* **2005**, *15*, 267. (f) dos Santos, C. M. G.; Tierney, J. *J. Fluor.* **2005**, *15*, 287. (g) Schmidtchen, F. P. *Top. Curr. Chem.* **2005**, *255*, 1. (h) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486. (i) Geddes, C. D. *Meas. Sci. Technol.* **2001**, *12*, R53. (j) Fabbrizzi, L.; Lichelli, M.; Rabaioli, G.; Taglietti, A. *Coord. Chem. Rev.* **2000**, *205*, 85. (k) Robertson, A.; Shinkai, S. *Coord. Chem. Rev.* **2000**, *205*, 157.

[14] Kim, H.; Kang, J. *Tetrahedron Lett.* **2005**, *46*, 5443.

[15] Singh, N.; Jang, D. O. *Org. Lett.* **2007**, *9*, 1991.

[16] Singh, N.; Jung, H. J.; Jang, D. O. *Tetrahedron. Lett.* **2009**, *50*, 71.

[17] Corma, A.; Galletero, M. S.; Garcia, H.; Palomares, E.; Rey, F. *Chem. Commun.* **2002**, 1100.

[18] Lin, L. R.; Fang, W.; Yu, Y.; Huang, R. B.; Zheng, L. S. *Spectrochim. Acta*, Part A. **2007**, *67*, 1403.

[19] Rodriguez-Docampo, Z.; Pascu, S. I.; Kubik, S.; Otto, S. *J. Am. Chem. Soc.* **2006**, *128*, 11206.

[20] Ho, H. A.; Leclerc, M. *J. Am. Chem. Soc.* **2003**, *125*, 4412.

[21] Vetrichelvan, M.; Nagarajan, R.; Valiyaveettil, S. *Macromolecules* **2006**, *39*, 8303.

[22] Kumar, A.; Chhatra, R. K.; Pandey, P. S. *Org. Lett.,* **2010,** *12*, 24.

[23] Lin, W.; Yuan, Lin.; Cao, X.; Chen, B.; Feng, Y. *Sensors and Actuators B.* **2009**, *138*, 637.

[24] Joseph, R.; Chinta, J. P.; Rao, C. P. *Inorganica Chimica Acta.* **2010**, *363*, 2833.

[25] Mele, A.; Metrangolo., P.; Neukirch, H.; Pilati, T.; Resnati, G. *J. Am. Chem. Soc.* **2005***, 127,* 14972.

[26] Kilah, N. L.; Wise, M. D.; Serpell, C. J.; Thompson, A. L.; White, N. G.; Christensen, K. E.; Beer, P. D. *J. Am. Chem. Soc.* **2010**, *132*, 11893.

[27] Mendy, J. S.; Saeed, M. A.; Fronczek, F. R.; Powell, D. R.; Hossain, M. A. *Inorg. Chem.* **2010**, *49*, 7223.

[28] Ravikumar, I.; Lakshminarayanan, P.; S.; Suresh, E.; Ghosh, P. *Inorg. Chem.* **2008**, *47*, 7992.

[29] Lakshminarayanan, P.; S.; Ravikumar, I.; Suresh, E.; Ghosh, P. *Crystal Growth & Design*, **2008**, *8*, 2842.

[30] Arunachalam, M.; Ravikumar, I.; Ghosh, P. *J. Org. Chem.* **2008**, *73*, 9144.

[31] Jung, H. J.; Singh, N.; Lee, D. Y.; Jang, D. O. *Tetrahedron Letters* **2010**, *51*, 3962.

[32] Lee, D. Y.; Singh, N.; Kim, M. J. Jang, D. O. *Org. Lett.* **2011**, *13*, 3024.

[33] Ghosh, K.; Sen, T. *Tetrahedron Letters* **2008**, *49*, 7204.

[34] Shanga,Z. B.; Wanga,Y.; Jin, W. J. *Talanta* **2009**. *78*, 364.

[35] Li, H.; Han, C.; Zhang, L. *J. Mater. Chem.* **2008**, *18*, 4543.

[36] Okamoto, H.; Konishi, H.; Kohno,M.; Satake, K. *Org. Lett.* **2008**, *10*, 3125.

[37] Cooper, J. B.; Beer, P. D. *Chem. Commun.* **1998.** 129.

[38] Arnaud-Neu, F.; Collins, E. M.; Deasy, M.; Ferguson, G.; Harris, S. J.; Kaitner, B.; Lough, A. J.; McKervey, M. A.; Marques, E.; Ruhl, B. L.; Schwing-Weill, M. J.; Seward, E. M. *J. Am. Chem. Soc.* **1989**, *111*, 8681.

[39] Kim, J. S.; Park, S. Y.; Kim, S. H.; Thuéry, P.; Souane, R.; Matthews, S. E.; Vicens, *J. Bull. Korean Chem. Soc.* **2010**, *31*, 624.

[40] Ghosh, K; Saha, I.; *Supramol. Chem.* **2010**, *22*, 311.

[41] Ghosh, K; Saha, I.; *J. Mol. Struc.* **2013**, 1042, 57.

[42] Panja, S.; Kumar, A.; Mira, N.; Ghosh, S.; Raza, R.; Ghosh, K, *ChemistrySelect* **2021**, 6, 6353.