International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
Available Online at www.journalijcar.org
Volume 9; Issue 02 (C); February 2020; Page No.21260-21263
DOI: http://dx.doi.org/10.24327/ijcar.2020.21263.4173

Research Article

A BRIEF REVIEW ON INDOLE (TRYPTOPHAN) BASED-FLUORIDE ANION RECEPTORS

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A R T I C L E I N F O

Article History:
Received 6th November, 2019
Received in revised form 15th December, 2019
Accepted 12th January, 2020
Published online 28th February, 2020

Key words:
Anion recognition, F^- anion, indole, tryptophan.

A B S T R A C T

This review article gives a brief description about critical factors pursuing to the importance of indole based receptors in recognizing halide anions specifically F^- anions from a biological, chemical and environmental perspective. Using representative examples, we analyse the design strategy of a few indole based anion receptors which involve mainly H-bonding, specifically indole NH…halide/F^- interaction. Further, we present illustrative examples to demonstrate the novel features of these interactions, how such interactions can contribute to anion-binding, recognition and catalytic events.

INTRODUCTION

Anion-receptor chemistry has got special attention in the field of supramolecular chemistry, given the implications in chemistry, biology and environment (Busschaert *et al*., 2015; Baker *et al*., 2012; Yerien *et al*., 2016; Perrin, 2016). Several binding interactions had already been developed such as H-bonding, Lewis acid-base interactions, electrostatic interactions, halogen-bonding, CH-anion interactions and anion-π interactions. Out of these interactions, in most of the cases, the main force of interaction was found to involve H-bonding.In natural system also the H-bonding plays a major role in anion binding and transport through the cell membrane. For example, the sulfate-binding proteins in Biomacromolecules, phosphate binding proteins,and a CIC chloride channel(Pflugrath and Quiocho, 1985; Luecke and Quiocho, 1990; Dutzler *et al*., 2002).Similarly, a wide variety of synthetic receptors containing amide, urea and pyrrolehas been explored as anion-receptors where the main force of interaction was found to be H-bonding (Gale *et al*., 2008; Prados and Quesada, 2008;Lim and Beer, 2018). Analogous receptors containing indole and related heterocycles, such as carbazole, imidazole, biindole and indolocarbazole have also been explored (Katayev *et al*., 2006; Sessler *et al*., 2003; Bąk *et al*., 2018; Mahapatra *et al*., 2015).

Indole based anion receptors

Indole NH is a strong hydrogen-bond donor group which is slightly more acidic than pyrrole (Bordwell *et al*., 1981). Previous studies have demonstrated that the indole motif can be utilized for the construction of anion-receptors which apparently involve strong NH···anion interactions (Shinde and Talukdar, 2018; Sessler *et al*., 2006).

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Gale *et al*. had studied the anion-complexation properties of 1,3-Diindolylureas and thioureas(**1**) (Figure 2.1) and found the remarkably high affinity of diindole urease towards dihydrogen phosphate anion (Caltagirone *et al*., 2008). Receptor **1d**, were expected to bind anions more effectively than **1c** due to the employment of the more acidic thioamide NHs, which are better hydrogen bond donors than amide NHs.

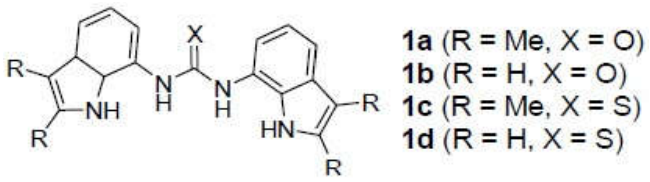

Figure 1 Diindolylureas and thioureas (**1**) receptors as $H_2PO_4^-$ anion receptors involving indole NH group as potential binding-site (Caltagirone *et al*., 2008).

The changes in the UV-visible, fluorescence spectra and ^{1}HNMR spectra have revealed that the receptor-anion interaction involved in all these receptors were H-bonding with the indole and amide NH group.

Gareth *et al*. reported the anion binding properties of indole functionalised isophthalamide and 2,6-dicarboxamidopyridine anion receptors (Bates *et al*., 2007). X-ray crystal structure analysis of the complexes revealed the higher selectivity of these receptors towards F^- anion compared to other anions. However, these receptors could also recognize Cl^- anion but to a less extent than F^- anion.

Pratihar *et al*. developed a diindole based F^- anion sensitive optical chemoreceptor (Mallick *et al*., 2012).^{1}H NMR and DFT (density functional theory) studies explained that the receptor-F^- interaction mainly involed H-bonding between the indole NH and F^- anion followed by deprotonation.

Manivannan *et al*. reported a series of indole based receptors containing different acceptors units of varying electron acceptor strengths (Manivannan *et al*., 2015).UV-Visible, fluorescence, DFT and ^{1}H NMR titration demonstrated that the receptors could specifically detect F^- over other anion. The receptor-F^- interactions led to 1:2 binding stoichiometry through H-bonding between the indole NH group and F^- anion. Moreover, it was observed that the receptor containing the naphthoquinone group as an acceptor unit, could act as the better H-bond donor due to its greater electron deficiency.

Beer *et al*. reported a family of simple indolo(**2-5**) carbazoles (Figure 2.1) and demonstrated their ability to recognize anions using UV-visible spectroscopy, fluorescence spectroscopy and ^{1}H NMR analysis (Curiel *et al*., 2005).These receptors were found to interact with different anions following the order as $C_6H_5COO^->H_2PO_4^-> F^->Cl^->HSO_4^-$. It was observed that these receptors involved the indole NH-protons of the respective indolocarbazole derivative to interact with the respective anions.

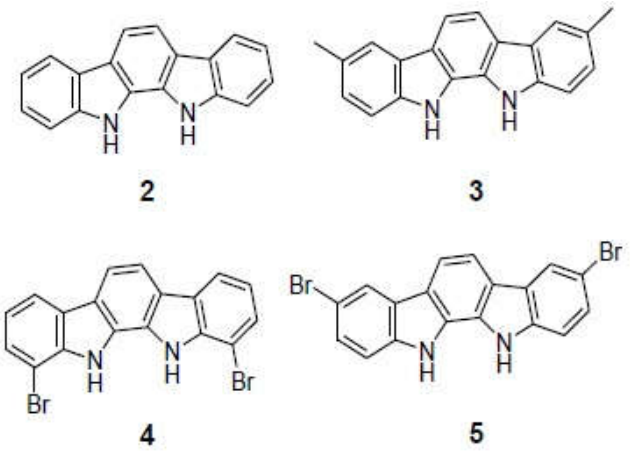

Figure 2 Indolocarbazole based receptors (**2-5**) involving indole NH group as potential binding-site (Curiel *et al*., 2005).

Jeong *et al* had reported the anion-binding properties of alkyne-linked biindole and indolocarbazole containing macrocycles **6-7** (Figure 2.3) which were found to have very high affinities for F^- followed by other halides as $F^->Cl^->>Br^->I^-$ in CH_3CN (Chang *et al*., 2005). UV-visible and ^{1}H NMR studies revealed the formation of a 1: 1 receptor: anion binding stoichiometry with F^- and Cl^- and a 2:1 receptor: anion binding stoichiometry with Br^- and I^- involving H-bonding between indole NH and halide ion.

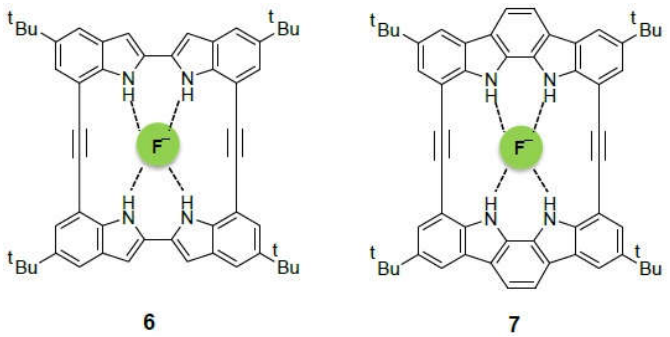

Figure 3 Alkyne-linked biindole and indolocarbazole containing macrocycles (**6-7**) involving indole NH group as potential anion-bindingsite (Chang *et al*., 2005).

Xian-He Bu *et al*. had developed two biindole and indolocarbazole derived polydentate conjugated molecules (**8**, **9**) (Figure 2.4) as fluorescent active F^- anion receptors (Liu *et al*., 2012).

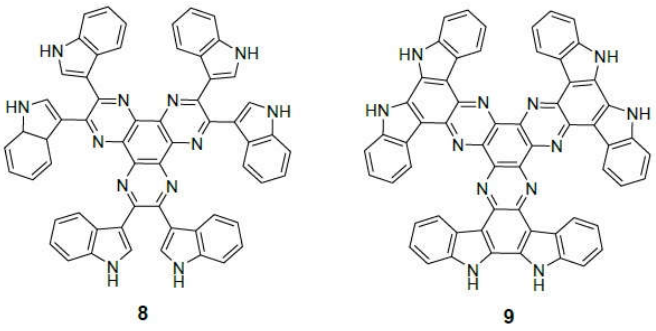

Figure 4 Biindole and indolocarbazole derivatives (**8, 9**) as fluorescent active F^- anion receptors containingindole NH group as potential anion-bindingsite (Liu *et al*., 2012).

The prominent changes of **8**and **9** were observable by naked eye with a change in colour from yellow to goldenrod. ^{1}HNMR and UV-visible spectra of these ligands with the addition of F^- revealed the formation of H-bonding followed by deprotonation of indole NH by fluoride. This resulted in enhancement in the extent of intramolecular charge transfer (ICT) from the indole anion to the phenyl rings.

However, the elucidation of the halide binding site in *haloalkane dehalogenase* provided further impetus on exploration of the nature of interactions between indole (i.e. tryptophan) and the halide anions has illuminated the hitherto unknown chemistry of tryptophan in binding and recognition of halide anions (Pavlova, *et al*., 2009; Tang *et al*., 2003; Verschueren *et al*., 1993; Bose and Ghosh, 2010). Indole had been employed (as tryptophan, Trp) in the complex of haloalkanedehalogenase as a H-bond donor in Cl^- binding, which had been demonstrated by X-ray crystallography (Figure 2.5) (Verschueren *et al*., 1993).

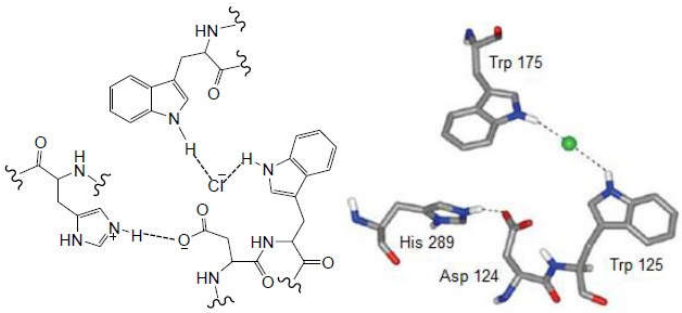

Figure 5 X-ray crystallographic structure of haloalkanedehalogenase depicting Cl^- binding site (Verschueren *et al*., 1993).

Recently, a few tryptophan-based ligands were developed by Sarma *et al* which could show strong affinity towards halide anions in presence of other basic anions (Deka *et al*., 2014; Devi *et al*., 2014).

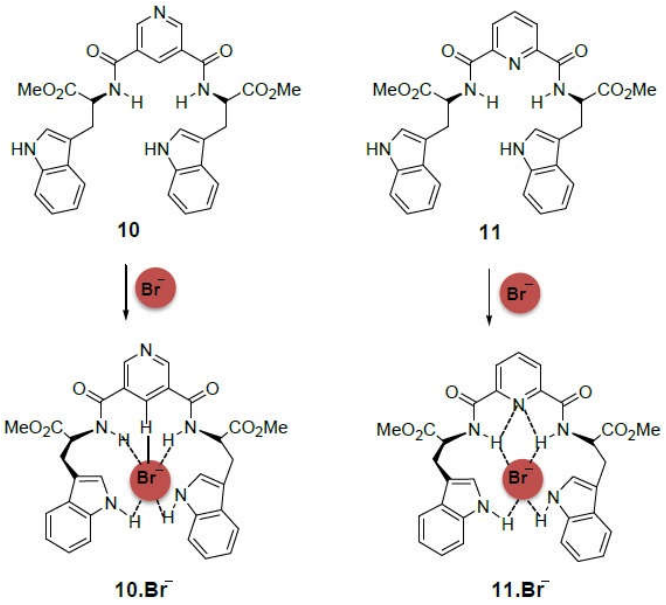

Figure 6 Tryptophan-based pyridine dicarboxamide ligands (**10, 11**) as Br^- anion receptor involving amide and indole NH and CH groups as potential binding-site (Deka *et al*., 2014).

Sarma *et al*. had developed two tryptophan-based pyridine dicarboxamide ligands (**10** and **11**) (Figure 2.6) as Br^-receptor (Deka *et al*., 2014). UV-visible and ^1H NMR studies indicated that these ligands are capable of coordinating to Br^- anions through amide and indole NH and CH groups. Based on ^{1}HNMR studies, which indicated complexation induced chemical shifts for the indole and amide NH resonances it was evident that organic bromides selectively bind to/with one of the ligands through H-bonding with the indole and amide NH proton.

A few more tryptophan-derived isomeric urea receptors (**12a-c**) (Figure 2.7) were also investigated by Sarma *et al*. using various spectroscopic techniques like UV-visible, fluorescence and ^1H NMR spectroscopy (Devi *et al*., 2014).

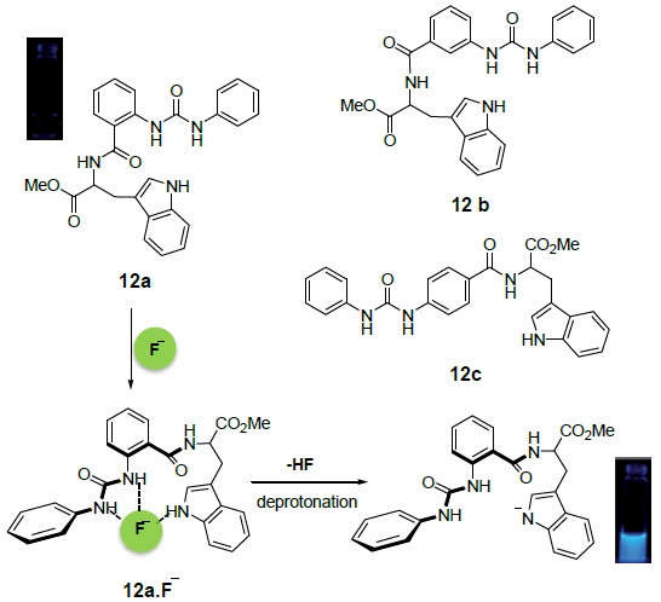

Figure 7 tryptophan-based urea ligands (**12a-c**) as F^- anion receptor involving urea and indole NH groups as potential binding-site (Devi *et al*., 2014).

These studies revealed the potential involvement of indole NH group along with the urea NH group in receptor-F interaction in case of ortho-isomer **12a**. The interaction could be visible from the enhanced fluorescence emanating from intramolecular charge transfer in case of receptor followed by F^- induced deprotonation of the indole NH proton.

Most of these F^- receptors were found to be colorimetric. Colorimetric receptors have got special attention due to their easy "naked eye" detection of target species and also have the viability to offer both qualitative and quantitative insights of the receptor-guest interactions by using inexpensive spectroscopic techniques. These colorimetric anion-receptors could be further developed as a sensor targeted for a specific anion like F^- or other anions which is an important application in the field of supramolecular chemistry (Mahapatra *et al*., 2015; Manivannan *et al*., 2015).Further investigations of such receptors are needed to understand the nature of interactions between anions and chemical (*cf*. biological) receptors, particularly in the context of F^- recognition and catalysis.

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How to cite this article:

Dr. Barnali Deka (2020) 'A Brief Review on Indole (Tryptophan) Based-Fluoride Anion Receptors', *International Journal of Current Advanced Research,* 09(02), pp. 21260-21263. DOI: http://dx.doi.org/10.24327/ijcar.2020. 21263.4173

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