

# Dual (Fluoride and Cyanide) Anion Recognition via BODIPY Receptors

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## Abstract

Diverse means of interactions for dual anion recognition is pretty fascinating area of research. From last few decades, polarized free amine fragments, bond breakage, and related approaches have been tried to achieve the dual anion recognition and discrimination of fluoride ( $F^-$ ) and cyanide ( $CN^-$ ). In this regard, signaling unit in the form of BODIPY dye has been regularly brought in for the purpose. This is attributed to the fascinating fluorescent properties of the fluorophore. In this work, I will be focusing on the basic aspects of the reports besides mechanism of interaction.

**Keywords:** Polymerization; Emulsion; Micelles

## Introduction

Among the various anions,  $F^-$  and  $CN^-$  occupy an important place in the field of anion recognition, owing to their fundamental role in chemistry, catalysis, environment and biology [1-3]. Thus, considerable attention has been paid by the research community to develop a library of single-molecule based receptors for these analytes [4-6]. From the literature survey, it clear that both the anions exhibit similar binding behaviour with urea or amide based scaffolds [7-9]. The  $F^-$  and  $CN^-$  recognition has usually been achieved by hydrogen-bonding or deprotonating through excited state intra or intermolecular proton transfer mechanism [10,11]. Even though certain reaction-based approaches in the form of distillation for fluoride and nucleophile substitution for cyanide have been introduced [12-18], but single molecular systems providing naked-eye recognition of both fluoride and cyanide anion is very rare. Further, detection of  $F^-$  and  $CN^-$  is reported either by colorimetric or fluorimetric

signalling response. Therefore, it has always been a challenge to develop novel approaches for their dual-modal recognition. Further, there are only a handful of reports available wherein both recognition as well as discrimination of  $F^-$  and  $CN^-$  was accomplished.

## Literature Overview

Structural robustness and strong fluorescence quantum yield of BODIPY dye has been the reason for its extensive use in molecular recognition studies for various environmental and biological applications [19]. Many such attempts have been carried out for  $F^-$  and  $CN^-$  recognition. Among the existing reports, Akkaya *et al.* reported monostyryl-boradiazaindacene BODIPY for selective sensing of  $CN^-$ . Presence of a trifluoroacetyl group in the compound, impart exclusive selectivity towards the cyanide anion [20]. The authors further reported dual anion recognition of  $F^-$  and  $CN^-$  via tethering difluoro Boron Bridge in to the BODIPY [21]. The presence of  $F^-$

and CN<sup>-</sup> dislodges difluoro boron bridge during their interaction with the receptor and results in the modulation of the photo physical behaviour of the compound.

Ravikanth *et al.* achieved selective detection of cyanide by direct incorporation of formyl group into the BODIPY [22]. Formation of cyanohydrin via attack of CN<sup>-</sup> on the formyl group was reported with both visible fluorescence as well as chromogenic changes during recognition events. Similar type of results was also revealed with *meso*-salicylaldehyde substituted BODIPY [23]. Same group further reported selective fluoride recognition by benzimidazole substituted boron-dipyrromethene [24]. The existence of intramolecular hydrogen bonding between hydrogen atom (N-H) of benzimidazole and fluorine atoms of BF<sub>2</sub> in BODIPY polarizes the -N-H bond, sufficient enough to under anion recognition. The presence of F<sup>-</sup> in the receptor solution promotes blockade of electronic communication between imidazole and BODIPY via the disruption of intramolecular hydrogen bonding between them. The corresponding events were visually marked with colour and fluorescence output.

In addition to these reports, Thilagar *et al.* presented F<sup>-</sup> recognition from dimesitylboryl appended BODIPY. The recognition events were via a dual-emission response [24]. They further reported tricolour emission based response for selective F<sup>-</sup> recognition with borane-bithiophene-BODIPY triad [26]. The recognition was visually signalled through colorimetric changes in the receptor solution.

## Conclusion

Highly sensitive and selective fluoride and cyanide recognition, along with their discrimination has been achieved so far through BODIPY based molecular receptor framework. The fluorophore framework has been structurally tuned to bring in such dual anion sensing events. We believe besides structurally modulation, solvent tuning might offer another useful platform to achieve the similar. In addition, there is a need to explore and develop new molecular systems which might decipher dual-channel visual display (colorimetric and fluorogenic) for each recognition event. Most importantly, dual-anion sensing under aqueous conditions need attention.

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