



Rapid Naked-Eye Detection of Fluoride Ions using Near-Infrared (NIR) Organic Dyes in Aqueous and Non-Aqueous Medium

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The fluoride ion (F⁻) has received tremendous attention due to its significant utility in medicinal processes and biological systems.¹ Fluoride ion is useful to prevent dental cavities and osteoporosis.² Hence, it is useful additive in toothpaste and pharmaceuticals across the world.³ However, excessive intake of fluoride ion causes severe health problems like calcifying bones/teeth, skeletal/dental fluorosis, urolithiasis, and gastric kidney disorders.^{4,5} Therefore, fluoride ion detection is crucial for water sample, environmental samples and biological systems using suitable probe.

So far, plenty of methods have been designed to detect for fluoride ion.⁷⁻⁹ Out of the available fluoride detection methods, naked-eye detection approach (colorimetric probes) is useful and convenient due to their high effectiveness towards selectivity and sensitivity. Designing effective colorimetric sensors are mostly based on the intramolecular charge transfer (ICT) process, potential spectral shift properties during the anion binding via either directional hydrogen bonding or donating one or more hydrogen N-H fragments of the signalling unit.¹⁰⁻¹¹ Development of colorimetric probes for fluoride ion sensing, and it's the applicability is primarily limited to non-aqueous medium.^{15,16} Further, progress of colorimetric probes has been done to reduce the usage of organic solvents by replacing them with water (or biphasic system).¹²⁻¹⁴ However, most of cases, TBAF (organic fluoride source) is used as fluoride source for the colorimetric detection of fluoride in aqueous-organic medium. Only few reports are available where the recognition of fluoride from inorganic sources (NaF), are discussed in biphasic medium.¹⁵⁻¹⁶

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Recently our group has reported the TCP-based NIR colorimetric sensing dyes ((TCP-Tph and TCP-HyDe)) as highly effective, selective, and sensitive probes for fluoride ion detection in non-aqueous solvent and solid state using organic (TBAF) and inorganic fluoride source (NaF, and KF).¹⁷ The easy “naked eye” visualization of color variations and absorption studies demonstrate the potential sensing capability of the TCP probes with detection limit $\sim 10^{-7}$ (M) in nonaqueous solvents. Easily accessible and cost-effective paper-based fluoride sensing kit is also developed for effective detection of fluoride ion.¹⁷

In our latest development related to fluoride ion detection, we are reporting the modified TCP based D- π -A colorimetric NIR molecule (TCP-34Hy) as a sensitive, selective and ratiometric probe for naked-eye detection of fluoride ion (F⁻) in the aqueous medium.¹⁸ The probe (TCP-34Hy) shows distinguishable color change and large spectral shift of absorption maxima while interacting with fluoride ion (both from inorganic and organic fluoride source) with detection limit 2.3×10^{-6} M. These TCP-based NIR probes can efficiently detect fluoride ions in natural water samples, toothpaste, and soil samples.

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