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A hydrazone-based fluorescent chemosensor for Al³⁺: turn-on response induced by ESIPT suppression

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The Schiff-base *tert*-butyl(Z)-2-((2-hydroxynaphthalen-1-yl)methylene)hydrazine-1-carboxylate (**KH**) was synthesized *via* a condensation reaction between *tert*-butyl carbazate and 2-hydroxy-1-naphthaldehyde in methanol. The compound **KH** functions as an efficient fluorescent chemosensor for Al³⁺ ions, exhibiting a strong and selective fluorescence enhancement in methanol upon Al³⁺ addition. The limit of detection (LOD) for Al³⁺ was calculated to be 3.6×10^{-7} M, which is comparable to the values reported for structurally related probes. Al³⁺ addition also induced a distinct bathochromic shift and increased absorption intensity in the UV-vis spectrum. Spectroscopic titration studies revealed that **KH** binds Al³⁺ as a polydentate ligand with an association constant of $K_a = 1.75 \times 10^6$ M⁻¹, and Job's plots confirmed a 1:1 binding stoichiometry. Free **KH** shows negligible fluorescence due to an efficient excited-state intramolecular proton transfer (ESIPT) pathway mediated by the naphthol proton, which produces non-emissive tautomeric species. Coordination with Al³⁺ deprotonates the phenolic group, suppressing ESIPT and eliminating this major non-radiative decay route. Concurrently, metal–ligand coordination rigidifies the molecular structure and induces a chelation-enhanced fluorescence (CHEF) effect, collectively promoting radiative decay. DFT and TD-DFT calculations on **KH** and the Al³⁺–**K** complex were performed to rationalize the photophysical behavior and to probe the ESIPT and sensing mechanisms. The computed data closely match the experimental photophysical results. Analysis of optimized geometries of the enol and keto tautomers in both the ground (S₀) and excited (S₁) states indicates that ESIPT is significantly more favorable in S₁, consistent with the calculated potential energy profiles. X-ray crystallographic analysis showed hydrogen bonding between the phenolic OH and the –C=N– nitrogen, supporting that the molecular framework is structurally predisposed for ESIPT. Hirshfeld surface analysis and 2D fingerprint plots further quantified the intermolecular interactions within the crystal lattice. Additionally, NBO analysis of the Al³⁺–**K** complex is presented.

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Introduction

Aluminium is the third most abundant element in the Earth's crust and is commonly present in natural water sources and agricultural products. In everyday life, people are also exposed to it through food and medicinal storage materials.¹ The soluble forms of aluminium under physiological or environmental conditions can pose health risks, including links to neurodegenerative disorders, bone and kidney dysfunctions, and interference with other biologically relevant metal ions.^{2–6} Consequently, the development of rapid, sensitive and selective

sensors for Al³⁺ has attracted sustained attention in analytical chemistry.^{7–17} Fluorescent chemosensors based on organic ligands have emerged as powerful tools for metal-ion detection owing to their high sensitivity, potential for real-time monitoring, and relatively simple instrumentation.^{18–21} Among these, Schiff bases and their derivatives have been widely employed as fluorescent sensors due to their facile synthesis, tunable structures, and strong coordination ability through nitrogen and oxygen donor atoms.^{22–26} In particular, hydrazone Schiff bases formed by condensation of hydrazides with aldehydes/ketones offer additional binding sites and enhanced rigidity/conjugation, which are favorable for modulating photophysical responses.^{27–31}

In the context of Al³⁺ sensing, a number of factors pose challenges: (i) Al³⁺ is a hard Lewis acid with high charge density and a strong hydration shell, making selective coordination difficult in mixtures; (ii) interference from other metal ions

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