Exploring Azacrown-Functionalized Fluorophores as Promising Metal Cation Detectors

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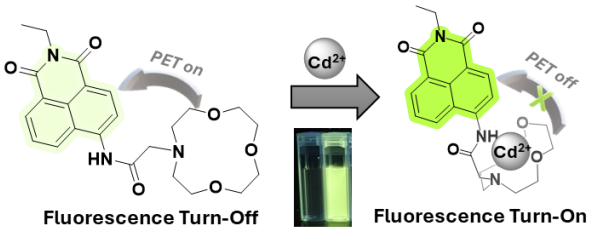
Detecting and quantifying metal ions is crucial across various industries. However, traditional methods like Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-AES) are expensive and require complex sample preparation. [1, 2] Fluorescent chemosensors offer a simpler and more cost-effective alternative, providing a clear optical response to specific metal ions, even at low concentrations.[3] Those molecules emerge as a solution because, in the presence of an analyte, they are capable of producing a different signal from the original one, remaining selective even at low concentrations. These compounds have two distinct moieties: the fluorophore, which serves as the signalling unit, and the receptor, which allows direct metal ion interaction.

Azacrown receptor derivatives have attracted significant attention due to their ability to selectively interact with a wide range of metal ions. In this work, we emphasize 1-aza-12-crown-4 and 1-aza-15-crown-5. Interestingly, the same azacrown moiety can exhibit different metal ion selectivity when paired with different fluorescent dyes. This variation arises from the distinct environments and the final structure of the fluorophores, which can modulate the binding affinity and selectivity toward specific metal ions.

To evaluate the photophysical properties of these compounds, UV-Vis and fluorescence titrations were performed with a broad spectrum of metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}). The experimental results demonstrated the selective properties of some of the azacrown-functionalized fluorophores toward calcium, copper, lead, magnesium, and cadmium. [4]



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References

1. J. Zhao *et al*. *Coordination Chemistry Reviews* 378, **2019**, 415–444.
2. M. N. Sweilam et al., ACS Sens. **2018**, 3, 1802.
3. T. Sakamoto, A. *et al*. *Chemical Communications.* **2009**, 141–152.
4. Gomes, L. *et al*. *Molecules*. **2024**, 29(2):527