

Understanding selective Cu²⁺ detection by Ln³⁺ complexes through crystallography

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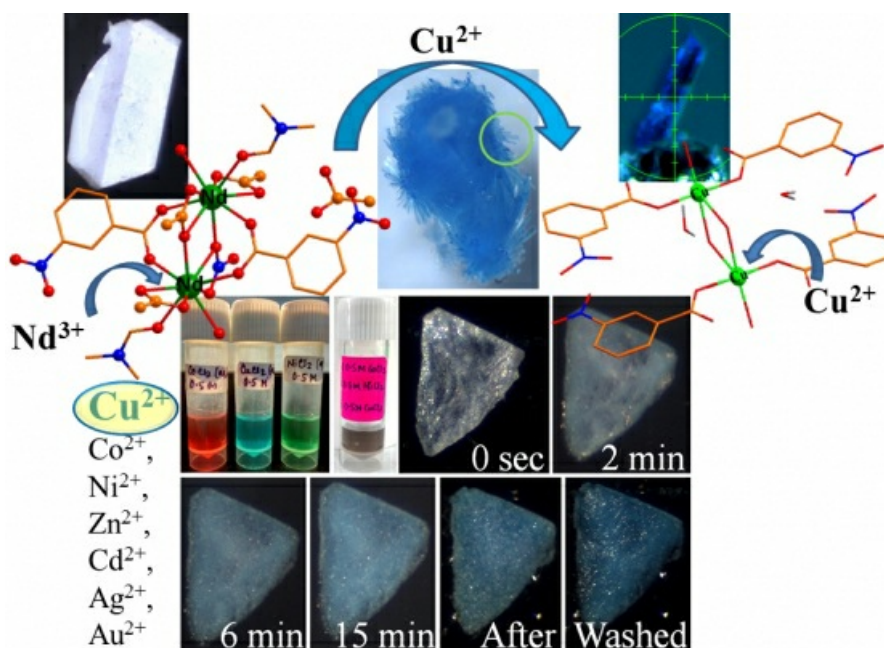
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Selective sensing of transitional metals like copper are of utmost importance due to its huge application in biology and material science. In this work, we have synthesized two rare earth (Dy³⁺ and Nd³⁺) based complexes using the ligands like bipyridine, p-amino benzoic acid and nitro benzoic acid. The complexes were characterized by single crystal and powder XRD, IR spectroscopy and thermogravimetric analysis. Both complexes showed characteristics luminescent properties of the lanthanides and weak metamagnetic transitions at low temperature. Both the Dy and Nd compounds were found to detect Cu²⁺ selectively in very low concentration of the transition metal salt in the mixture of other transition metals like Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Ag⁺ and Au³⁺. This selective copper uptake is associated with a fast distinct colour change of the crystals of the Ln³⁺ complexes, as a result of which, the detection of copper can be realized visually. The Nd compound showed higher selectivity and detected Cu²⁺ selectively till 10⁻⁵ M concentration of the Cu salt. The Cu²⁺ encapsulation in the Nd complex was characterized through a rare single crystal growth mediated transformation involving an irreversible exchange of the metal ion of the complex. Due to the unconventional crystal growth mechanism, the subsequent crystal was twinned in nature. The structure of this crystal on solving provided valuable insights into the mechanism of Cu²⁺ detection in these complexes, which was guided by HSAB phenomenon. This single crystal transformation facilitates the easy understanding of the copper encapsulation mechanism and provides information on the detector complex, which is rarely studied.

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