ABSTRACT

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TITLE: Design and Synthesis of Fluorescein Based Molecular Probes for Hg (II) Recognition

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Now-a-days fluorescence technique is a very essential tool for the detection very low concentration of metal ions in within a very short span of time. Several chemists, biologists and environmental scientists frequently use this tool for chemical sensing of analytes. Among the most hazardous and ubiquitous pollutants, mercury is the most toxic element, spreaded over the globe and a major theat to living bodies and environment because both elemental mercury and its ionic forms can be converted into methyl mercury by bacteria, which is subsequently bio-accumulated through the food chain.

$\mathbf{L^{28}}$ selectively recognizes Hg^{2+} with a low detection limit (1.24 μM), high formation constant K_f =(0.43 ± 0.04) × 10^4 M^{-1} and potent for cell imaging applications. The specific response of $\mathbf{L^{28}}$ towards Hg^{2+} was supposed to be based on the opening of the spirolactam as evidenced from ^{13}C NMR. It may be due to the reaction of Hg^{2+} with the chelating probe leading to the formation of a rigid complex $\mathbf{L^{28}}$-Hg^{2+} attributing to a chelation enhanced fluorescence (CHEF) effect. A 1:1 binding mole ratio was established by Job's method and ESI-MS^+ (m/z) studies. The tentative coordination environment in the $\mathbf{L^{28}}$-Hg^{2+}complex was established by DFT studies. The sensor demonstrates a reversible change in fluorescence intensity upon the alternate addition of Hg^{2+} (fluorescence ON) and S^{2-} (Fluorescence OFF) in $\mathbf{L^{28}}$ solution with negligible interference providing a fluorescence "OFF–ON–OFF" mode of interactions with $\mathbf{L^{28}}$ and finds applications in devising logic gate functions.

The selective sensing of Hg^{2+} by $\mathbf{L^{29}}$ probe was determined by various techniques like UV-Vis, fluorescence, Job's and HRMS (m/z) studies. The LOD of Hg^{2+} calculated by 3σ method gives a value of 92.7 nM. For the Hg^{2+} interaction towards $\mathbf{L^{29}}$ the binding constant was calculated to be (3.21 ± 0.05) x 10^4 M^{-1}. On addition of S^{2-} to a solution of $\mathbf{L^{29}}$–Hg^{2+}complex, the fluorescence intensity was totally quenched due to removal of Hg^{2+} from the complex by S^{2-} ion arising out of stronger affinity of Hg^{2+} towards S^{2-} resulting concomitant formation of ring closed form, $\mathbf{L^{29}}$. The tentative coordination environment in the $\mathbf{L^{29}}$–Hg^{2+}complex was established by DFT studies. $\mathbf{L^{29}}$ exhibits low cytotoxicity and cell permeability, which makes it capable of bioimaging of Hg^{2+} in living HepG2 cells.

$\mathbf{HL^{30}}$ deals with selective recognition Hg^{2+} which exhibits a lower detection limit (0.46 μM) and comparatively lower dissociation constant (k_d = 1.18 ± 0.01) x 10^{-4} M). The probe displayed excellent sensitivity and selectivity towards Hg^{2+} over other tested metal ions which could be ascribed to the Hg^{2+} mediated opening of the spirolactam ring of the flourescein moiety. The MTT assay revealed that $\mathbf{HL^{30}}$ exhibits low cytotoxicity toward living HepG2 cells.

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