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Chemodosimetric Mechanistic Insight through Trapping Intermediate for Selective Detection of Picric Acid in Aqueous Medium by a Dinuclear Cd^{II} Complex

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A fluorescent dinuclear cadmium(II) based discrete metal complex of composition $[Cd^{II}_2L(\mu\text{-}Cl)Cl_2]$ (1) is used {HL = 2,6-bis[2-(methylamino)ethyliminomethyl]-4-Ethylphenol} for the specific recognition of 2,4,6-trinitrophenol (picric acid; PA) via fluorescence quenching phenomenon among various nitroaromatic compounds through a chemodosimetric approach. It has been established that 1 is a chemodosimeter in pure water. We have successfully been able to isolate three compounds: chemodosimeter 1; an intermediate complex 2 of composition $[Cd^{II}(LH_2)Cl_2]$ (Picrate) and final association complex 3 of composition $[NH_3(CH_2CH_2)NH_2CH_3]$ (Picrate)$_2$. Compounds have been characterised by CHN elemental analyses, single crystal X-ray crystallography, PXRD, NMR and FTIR. Selective interaction of 1 with PA was evaluated by fluorescence, UV-Vis and life time measurements. Fluorescence quenching of 1 occurs definitely due to the formation of compound 3 via intermediate 2 involving partial decomplexation, hydrolysis and proton transfer phenomena in solution during the course of sensing. The quenching constant (K_{sv}), association constant (K_a) and detection limit (LOD) of the complex 1 for picric acid are $\sim 1.55 \times 10^5$ M^{-1}, $\sim 1.8 \times 10^{10}$ M^{-2} and ~ 0.47 µM (0.108 ppm), respectively. Mechanism of sensing is proposed and the very rare case of isolation and characterization of intermediate in picric acid sensing is discussed.

Introduction

Different hazardous chemicals or explosive molecules/ions are thrown out to the environment in industrial processes and obviously, their detection is an important aspect for national security and environmental issues. As a result, immense attention has been given in recent years for the design and studies of selective, sensitive and cost-effective fluorescent sensors.[1-4] Picric acid (PA; 2,4,6-trinitrophenol) is more powerful as an explosive than other common nitro-explosives and it is a highly water soluble hazardous chemical, which causes severe health anxieties. Therefore, detection of PA has received significant research attention in the field of chemosensors. In addition to fluorescence sensing methods, various analytical techniques (e.g. ion mobility spectrometry (IMS); gas chromatography-mass spectrometry (GC-MS); electrochemical methods; surface-enhanced Raman spectroscopy (SERS); nuclear quadrupole resonance (NQR) etc.) have been applied so far for its detection.[5-9] However, fluorescence sensing method by using a fluorescent probe has drawn much interest because of its simplicity, sensitivity, short response time and low cost. For application purposes, it is highly desirable that a fluorescent probe can be synthesized easily, sufficiently soluble in water and effective as sensor in aqueous medium with high selectively. So far, a considerable number of fluorescent materials have been utilized for selective detection of PA. Those sensors include small organic molecules,[10-21] organic polymers including conjugated polymers,[22-26] discrete metallo-organic coordination compounds[27-41] including macrocycles/cages[30-32] or AIEgens[40,41] coordination polymers including MOFs,[42-73] nanoaggregates[74-76] and carbon or quantum dots.[77,78] However, apart from their complicated multistep preparation procedures, these sensor materials are found to be efficient in organic medium, which is not feasible for their practical application. Clearly, as the number of sensors in aqueous medium is much less than those in organic medium, it deserves significant importance to develop the aqueous medium sensors.

In order to get a clear and deeper insight into the sensing behaviour, various signalling mechanisms (e.g. photoinduced electron transfer (PET), intramolecular charge transfer (ICT), förster resonance energy transfer (FRET), inner filter effect (IFE) and chemodosimetry) along with various supramolecular interactions (e.g. hydrogen bonding, metal-ligand coordination, electrostatic interactions) are rationally considered. It is evident from previous studies that detection of PA by considering all above mentioned signalling mechanisms[10,12-37,42-78] except chemodosimetry[11,38] have been well explored. Clearly, fluorescent chemodosimetric approach to detect PA needs special attention.

In general, for mechanistic interpretation of the sensing of any analyte, isolation/characterization of either intermediate or final association complex or both of these is required.

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