Poster Presentation

MS101.P03

Direct evidence for selective sensing of nitroaromatic compounds By MOF

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Drastic use of explosive type of materials in terrorism activities all around the world made it highly desirable to detect the traces of explosives materials with the easy and cost effective manner for security, military issues and environmental protection. Trinitrophenol (TNP) has the higher explosive power amongst the nitro aromatic explosives even more than trinitrotoluene (TNT) and causes strong irritation and allergic reactions.[1] Plenty of works are reported using MOFs to selectively sense TNP featuring Lewis basic pyridyl or free amine sites inside the pores that are expected to induce electrostatic and hydrogen-bonding interactions. However, no direct evidence has been affirmed till date about the interaction of TNP molecule with MOF which leaves the sensing mechanism of TNP and the use of other functionality in ambiguity. We synthesized hydroxyl functionalized new MIL-53 analogous MOF using Indium nitrate and 2,5-dihydroxyterepthalic acid which shows high water stability and strong fluorescence at 450 nm when excited at 352 nm. We hypothesized that availability of free hydroxyl group would provide extensive hydrogen bonding and pi-pi interaction with TNP molecule and align it in the close proximity to the host functionality for the plausible electron transfer and resonance transfer mechanism enhancing florescence quenching. The MOF was used for sensing of nitroaromatic compounds (NAC) and shows very high selective quenching for TNP. The Stern Volmer constant (Ksv) value for TNP was calculated to be $8.8*10^4$ /M.[2] We further investigated the dynamic of quenching, performing fluorescence lifetime experiment which resulted in no change for fluorescence lifetime of MOF and suggests that static quenching is the major reason behind quenching of TNP. Spectral overlap of absorbance of analytes and the emission of MOF indicate highest possibility of energy transfer mechanism for TNP in as compared to others. To understand better about the selective sensing of MOF for TNP we synthesized crystals of MOF with TNP in chloroform. Crystal structure evidently reveals good pi-pi interaction of TNP with ligand moiety of framework and hydrogen bonding with MOF framework. This study provides new insight into the study of luminescence quenching mechanism for selective sensing of TNP suggesting that functionality capable of having hydrogen bonding interaction with TNP can be a successful candidate for selective sensing for TNP. This MOF contains non-toxic metal and ligand showing rapid, selective and high sensitivity towards TNP in aqueous medium and as per our knowledge synthesized MOF has quenching constant (Ksv =$8.8*10^4$ /M) value comparable to highest values known for MOFs based sensor for TNP.

(1) Nagarkar, S. S. et al. (2016) Cryst. Eng. Comm. 18, 2994-3007.
(2) Qin. J. et al. (2015) J. Mater. Chem. A, 3, 12690–12697.

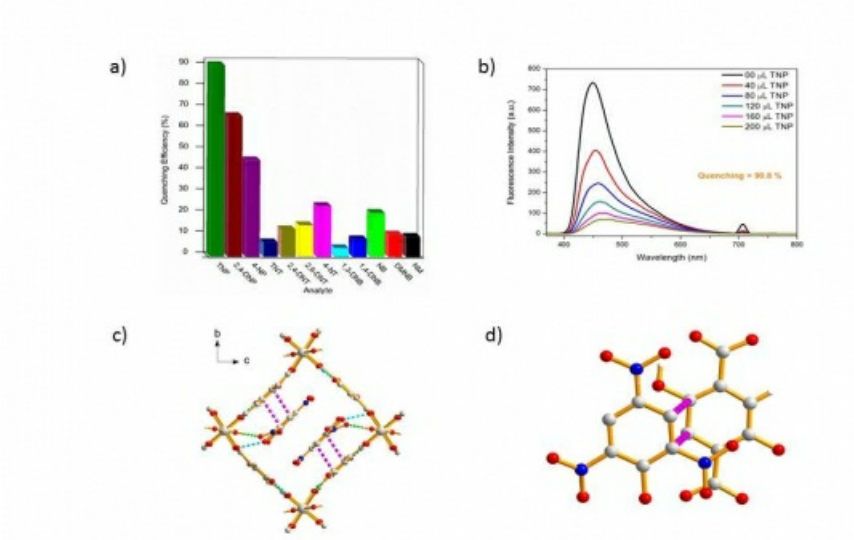

Fig: a) Quenching efficiency of different analytes. b) Emission spectra of MOF on addition of 1mM aqueous sol of TNP. c) & d) Interaction of MOF with TNP molecule as depicted by crystal structure.

Keywords: Explosives, quenching, resonance energy transfer