

Fishing highly explosive and toxic TNP

Water pollution by anthropogenic sources such as industrial effluents, mining activities, use of fertilizers and pesticides, dumping grounds is increasing in alarming rate. Picric acid (2,4,6-trinitrophenol, TNP) is highly explosive molecule used in armour piercing shells, bombs, rocket warheads, grenades, and is major component of explosive formulations like Explosive D, Yellow D, Pentolite. Other than ordinance applications Picric acid is widely used in industrial processing on thousands of tonnes scale every year. During ordinance and industrial applications TNP is released in environment and is generally accumulated in water streams, due to high water solubility polluting ground and surface water. The TNP is highly toxic to both animals and plants and known to cause chronic diseases such as sycosis and cancer. Thus selective detection and monitoring of TNP in aqueous systems is utmost important for home land security, human health and environmental protection.

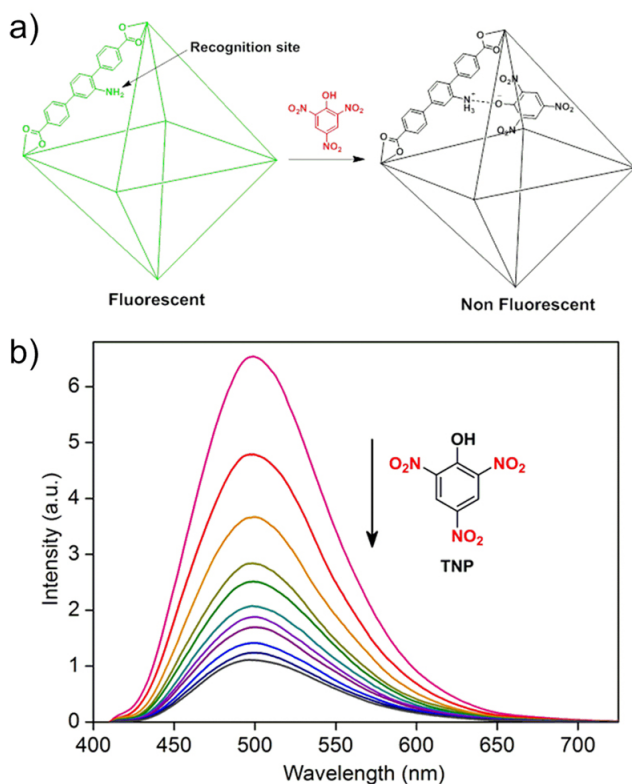


Fig. 1. (a) Scheme for MOF with amine (-NH₂) groups on surface acting as hooks for TNP to achieve selective detection in aqueous phase. (b) Fluorescence quenching observed for MOF in water when TNP solution added to it.

Metal-Organic Frameworks (MOFs), are composed of metal ions and organic ligands connected at

regular intervals contains forming porous structure similar to RCC structure of buildings made by columns and slabs but on nano-meter level. We thought to utilize the MOF for aqueous phase TNP sensing with luminescence based signal transduction. So the MOF will be luminescent initially, but when it comes in contact with TNP it reduces/loses its luminescence and by monitoring this luminescence change one can detect the presence of TNP. However, water contains variety of chemicals, salts, organic materials which can interfere in detection efficiency. Thus we plan to put additional recognition sites on MOF surface which will act as hooks only for TNP and thus interference from other species can be minimized.

We synthesized Zirconium (Zr) based porous MOF called UiO-68@NH₂ which is bio-compatible and has amine (-NH₂) group on surface which act as selective hooks for TNP providing selectivity for TNP (Fig. 1a.). More over the luminescence of MOF can be visualized by naked eyes on illumination by UV light which makes detection very easy. As expected, the powder of MOF dispersed in water showed bright fluorescence. To this when we added known amount of TNP solution the fluorescence of MOF decreased significantly with 84% quenching (Fig. 1b.). When other potentially competing analytes such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), aliphatic nitro compounds such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and explosive tag (molecule to be added to legally manufactured explosives) like 2,3-dimethyl-2,3-dinitrobutane (DMNB) showed lesser effect on MOF fluorescence with low quenching percent's (Fig. 2a.). In real applications these analyse will be present along with TNP in water. Thus to check if the MOF can detect TNP even in presence of competing analytes, we added TNP to the solution containing MOF powder and competing analytes. The effective fluorescence quenching was observed even in presence of competing molecules. This demonstrates unprecedented ability of the present MOF to selectively detect the TNP in aqueous phase. The detection limit of TNP was found to be 4 ppm which is very low compared to other materials currently used for TNP detection.

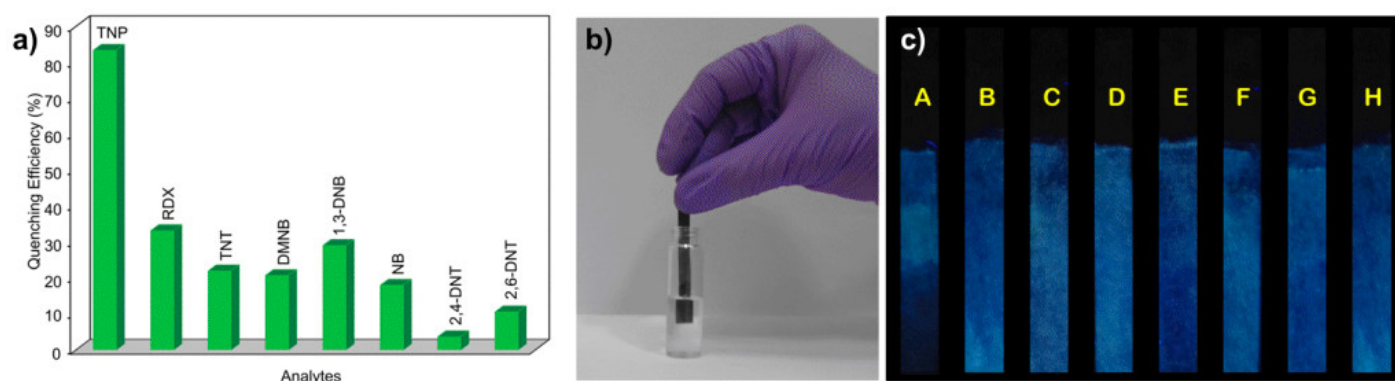


Fig. 2. (a) Fluorescence quenching performance of TNP and its comparison with different nitro analytes in water. (b) Paper strip based detection method for detection of TNP in the aqueous phase. (c) Comparison of luminescence behaviour MOF-coated paper strips when dipped in different nitro analytes viewed under UV light (A = TNP, B = TNT, C = RDX, D = 2,4-DNT, E = DNB, F = 2,6-DNT, G = NB, H = DMNB).

To further simplify the detection procedure for field application, we developed MOF coated strips which can be easily handled and on dipping in sample containing TNP will show reduced luminescence behaviour (Fig. 2b.). It can be clearly seen that the luminescence behaviour of strip dipped in TNP solution is reduced significantly compared to competing analytes demonstrating the applicability of MOF paper strips (Fig. 2c.).

In conclusion, we developed a MOF coated paper strips for the highly selective aqueous phase TNP sensing with low detection limit. The amine groups tethered on MOF are employed as selective hooks for naked eye detection of aqueous phase TNP for real time application.

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Publication

[Aqueous phase selective detection of 2,4,6-trinitrophenol using a fluorescent metal-organic framework with a pendant recognition site.](#)

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