

*Supporting Information for*

**Luminescent Hybrid Perovskite Nanoparticles as a New Platform  
for Selective Detection of 2,4,6-Trinitrophenol**

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# 1. Experimental Section

## 1.1. General

All chemicals were purchased from Aldrich, Alfa Aesar, Spectrochem and used as received. The Solvents were purified and dried by usual methods prior to use.

## 1.2. Measurements

<sup>1</sup>H NMR spectra were recorded on a 500 MHz Bruker Avance DPX Spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV-2600 UV-Vis spectrophotometer and the emission spectra were recorded on a SPEX-Fluouorolog F112X spectrofluorimeter. Optical properties in solution were measured by using a quartz cuvette with 1 cm path length and quartz plates were used for studies in film state. For emission studies, right angle geometry was used for solutions, whereas, front face geometry used for film state. X-ray diffraction studies were carried out on powdered samples with Xeuss Simultaneous 2D WAXs/SAXs using Cu-K  $\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ). TEM measurements were carried out using FEI-TECNAI T30, with EDAX at an accelerating voltage of 300 kV. Samples for TEM analysis were prepared by drop casting toluene solution of perovskite nanoparticles onto a carbon coated copper grid at the required concentrations at ambient conditions. The solvent was removed under vacuum. TEM images were obtained without staining.

## 2. Synthesis and Characterization

### 2.1. Synthesis of Methyl- and Octylammonium Bromides

The precursors, methylammonium bromide ( $\text{CH}_3\text{NH}_3\text{Br}$ ) and octylammonium bromide ( $\text{C}_8\text{H}_{17}\text{NH}_3\text{Br}$ ), were synthesized by reaction of the corresponding amine in water/HBr, using a reported procedure.<sup>S1</sup> Briefly, for the synthesis of methyl ammonium bromide, 2.5ml 40% of methyl amine (32.2 mM, 1 equivalent) was taken in the round bottom flask, and 8.67 ml of 30% HBr (32.2 mM, 1 equivalent) in glacial acetic acid was added to this at 0 °C. Then it

was allowed for stirring for about 2 hours, followed by the addition of diethyl ether for the precipitation of methyl ammonium bromide. It was then filtered, washed several times with diethyl ether, and dried under vacuum for overnight.

Yield: 98%.  $^1\text{H}$  NMR (500 MHz, DMSO, TMS)  $\delta$  (ppm): 2.34-2.38 (q,  $J$  6.0 Hz, 3H), 7.65 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 24.69.

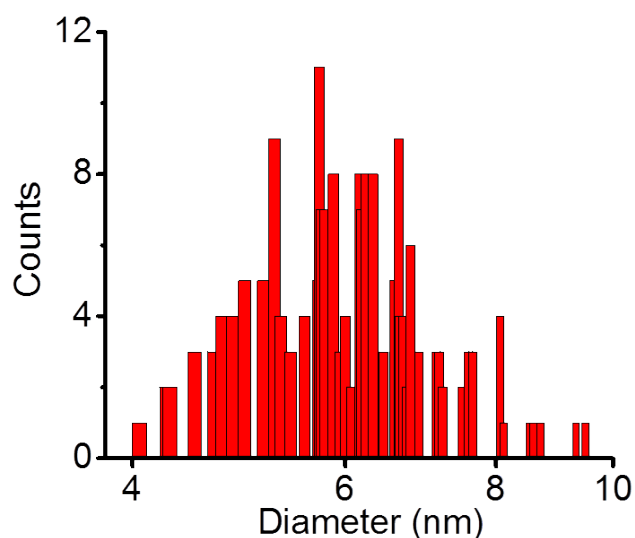
The same procedure was followed for the synthesis of octylammonium bromide. 1g of octylamine (7.7 mM, 1 equivalent) and 2.1 ml of 30% HBr (7.7 mM, 1 equivalent) in glacial acetic acid were used for the reaction.

Yield: 98%.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 0.87-0.89 (t,  $J$  6.5 Hz, 3H), 1.26-1.32 (m, 8H), 1.37-1.43 (p,  $J$  7.0 Hz, 2H), 1.78-1.84(p,  $J$  7.5 Hz, 2H), 3.00-3.07 (m, 2H), 7.96(s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ )  $\delta$  (ppm): 13.34, 21.94, 25.50, 26.64, 28.09, 28.14, 30.97, 39.51.

## 2.2. Synthesis of Perovskite Nanoparticles<sup>S2</sup>

A solution of oleic acid (85 mg, 0.3 mmol) in 2 ml of octadecene was stirred and heated at 80 °C. Octylammonium bromide (12.6 mg, 0.06 mmol) was added to this solution. Subsequently methylammonium bromide (4.4 mg, 0.04 mmol dissolved in 100  $\mu\text{L}$  of DMF) and lead(II)bromide (36.7 mg, 0.1 mmol dissolved in 100  $\mu\text{l}$  of DMF) were added. A yellow dispersion was formed and the nanoparticles were immediately precipitated by addition of acetone. Then the nanoparticles were centrifuged at 7000 rpm for 10 minutes, supernatant solution decanted and the residual nanoparticles were dispersed in toluene.

### 2.3. Size Distribution of Perovskite Nanoparticles

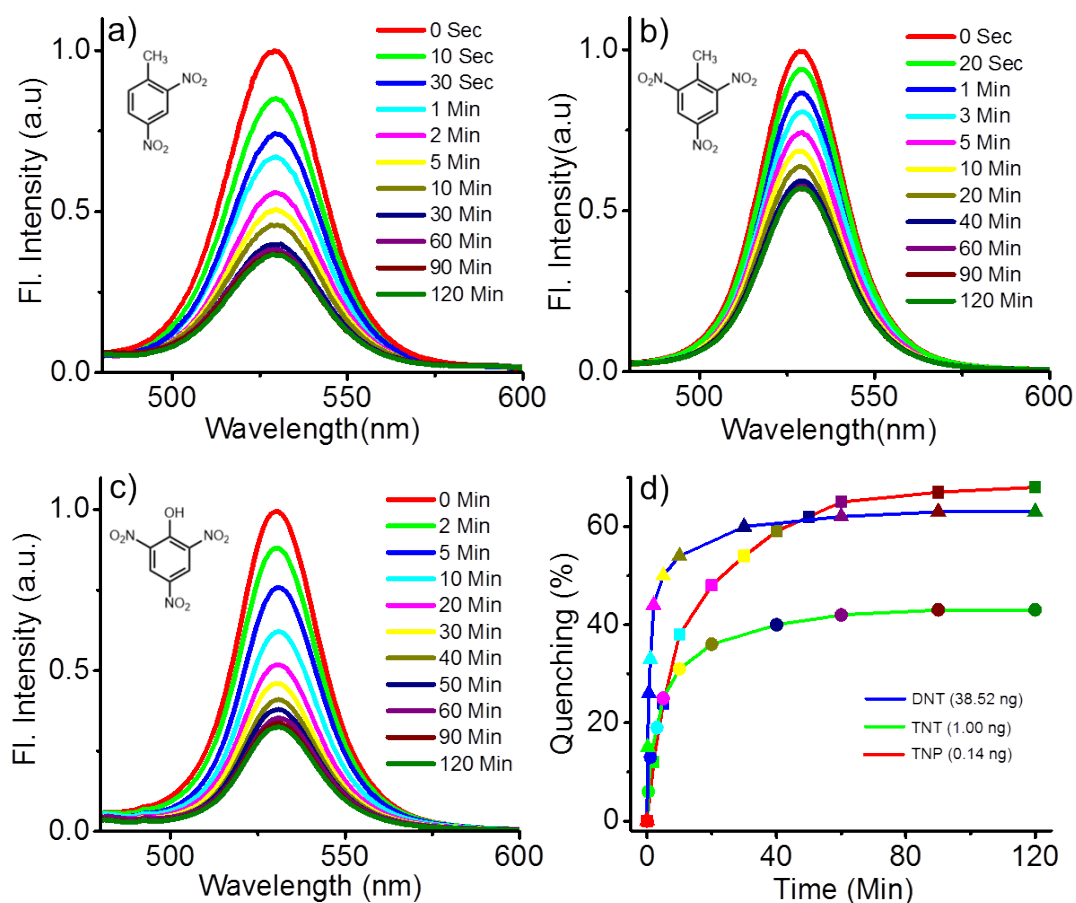


**Fig. S1** Size distribution profile of the perovskite nanoparticles obtained from TEM image given in Figure 1b using GATAN Digital Micrograph software (Ver. 2.31.734.0). The average diameter found to be 6.1 nm.

### 3. Photophysical Measurements

All the quenching studies in solution state were done in toluene. The perovskite nanoparticles dispersions were prepared in toluene by sonication. Optically matching solutions were prepared for each experiment. The analytes, TNP, DNT, TNT, 4-Nitrophenol and phenol were also prepared in toluene in varying concentrations. 50  $\mu\text{L}$  of analyte was added to the 3ml of perovskite nanoparticle solution for each measurement. For the vapor state detection, the perovskite nanoparticles dispersed in toluene was drop casted on a non-fluorescent Whatmann filter paper and allowed it for drying in a vacuum desiccator. Then the Filter paper was fixed on a quartz plate and the quartz plate was kept in a well closed vial containing 1g of TNP covered with cotton. The emission of the nanoparticle film was monitored at different time intervals.

### 3.1. Fluorescence Quenching Studies in Vapour State

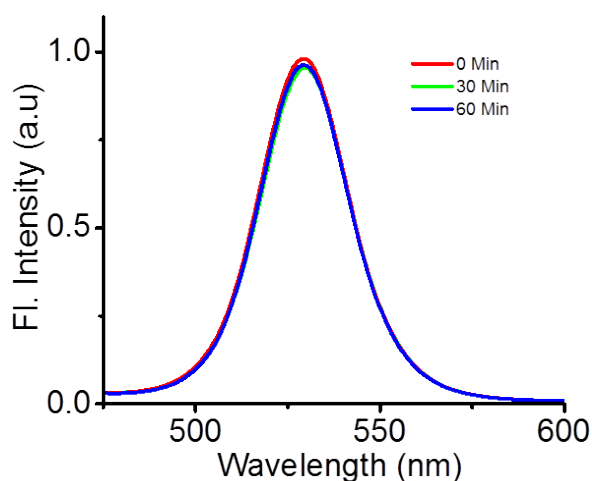


**Fig. S2** Fluorescence spectral changes of perovskite nanoparticle film in the presence of saturated vapours of (a) DNT, (b) TNT and (c) TNP with increasing time. (d) Comparison of the corresponding % quenching of fluorescence. Amount of each analytes present in a 15 mL vial at its saturated vapour pressure is shown in Figure S2d.

The vapour pressure of TNT ( $5.50 \times 10^{-6}$  Torr) and DNT ( $2.63 \times 10^{-4}$  Torr) is 1-2 order higher than that of TNP ( $7.48 \times 10^{-7}$  Torr). This results higher concentration of DNT, and TNT than that of TNP at the saturated vapour pressure (in a 15 mL vial, the saturated vapour pressures of the analytes corresponds to 38.52 ng of DNT, 1.00 ng of TNT and 0.14 ng of TNP). Figure S2 shows the plots showing the fluorescence quenching of perovskite nanoparticles in presence of DNT, TNT and TNP vapours, and a comparison of their quenching efficiencies. This study revealed that the quenching efficiency follows the order TNP > DNT > TNT, but the selectivity between TNP and DNT is less. Both TNT and DNT

showed faster quenching in the initial time probably due to high vapour pressure, and reached a plateau region in 15-20 minutes. The plateau formation could be attributed to the equilibrium between the adsorption and desorption processes of the analytes on the film surface. On the other hand, the quenching was slow for TNP at the initial time scale due to low vapour pressure. Similarly, the plateau formation was appeared only after 60 minutes. This could be attributed to the presence of hydroxyl group in TNP, which facilitate the binding of TNP with perovskite nanoparticles through hydrogen bonding. This binding process enhances the adsorption but reduce desorption, and hence delay the equilibrium. Enhanced adsorption through hydrogen bonding also explains the higher quenching efficiency for TNP though it has much lower vapour pressure than that of TNT and DNT.

### 3.2. Effect of Humidity on Fluorescence Quenching

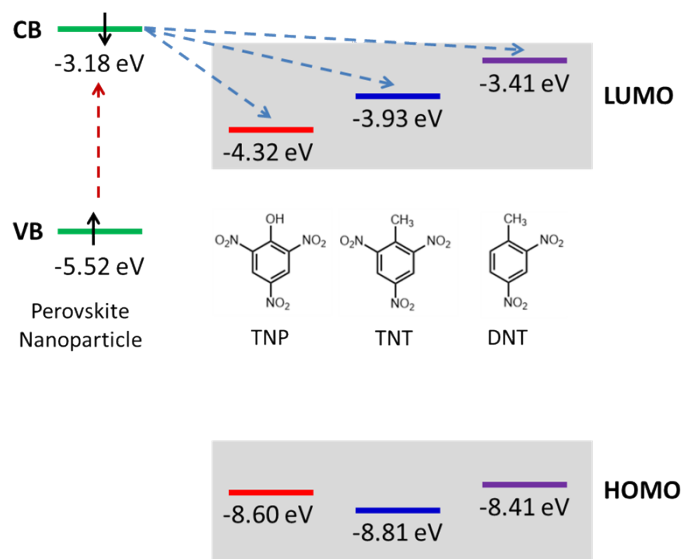


**Fig. S3** Fluorescence spectral changes of perovskite nanoparticle film on exposure to ambient humidity (about 70%) with increasing time.

Since the quenching mechanism of perovskite nanoparticles with TNP involves hydrogen bonding, we have carried out an experiment to study the role of humidity on the fluorescence properties of the former. In this experiment, the perovskite nanoparticle film was exposed to the ambient humidity (about 70%) and measured the fluorescence at different

time intervals. As shown in Figure S3, the changes in fluorescence with time was negligible, which indicates humidity has no influence on the quenching of perovskite fluorescence.

### 3.3. Energy Levels of Perovskite Nanoparticles and Explosive Analytes



**Fig. S4** Schematic representation of the energy levels of perovskite nanoparticles, TNP, TNT and DNT.

Energy levels of the perovskite nanoparticles were calculated from the oxidation potential (obtained using cyclic voltammetry) and optical band-gap (calculated from absorption and emission spectral crossover point). Using these values, the energy levels of perovskite nanoparticles were calculated. The oxidation potential corresponds to the valence band energy, and the addition of the band-gap to it gave the conduction band energy. The HOMO-LUMO values of TNP, TNT and DNT were obtained from literature.<sup>S3</sup> The energy level diagram proves that the electron transfer process from perovskite nanoparticles to the explosive analytes is energetically feasible.

#### 4. References

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- S3. Z. Hu, K. Tan, W. P. Lustig, H. Wang, Y. Zhao, C. Zheng, D. Banerjee, T. J. Emge, Y. J. Chabal and Jing Li, *Chem. Sci.*, **2014**, DOI: 10.1039/C4SC02157F.