It is an All-rounder! On the Development of Metal Halide Perovskite-Based Fluorescent Sensors and Radiation Detectors

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Metal halide perovskites (MHPs) dominate the class of wet processed semiconductors due to high photoluminescence (PLQY), tunable emission over a wide wavelength range, high carrier mobilities, and high absorption coefficient. Owing to these remarkable properties, MHPs cover next generation applications such as solar cells, light emitting diodes, lasers, photocatalysts, etc. Likewise, high energy radiation detection was also displayed by the MHPs, like in scintillators. Here, we review the latest advances in MHPs fluorescent sensors and high energy X-ray, gamma-ray and beta detectors. We discuss the basics including match-mismatch of MHPs for fluorescent sensing and radiation detection applications. Moreover, the mechanistic understanding of fluorescent sensing
and radiation detection by MHPs is also elaborated. We conclude with outlooks on future opportunities for MHPs fluorescent sensors and high energy radiation detectors.

1. Introduction

Metal halide perovskites (MHPs, organic-inorganic hybrid or all inorganic metal halide perovskites) have awed the world by showing outstanding performance in optoelectronics since 2012 owing to their appearance in photovoltaic devices with high performance and moderate stability.[1] Afterwards, attention peaked for perovskite solar cells, but breakthroughs were also reported in a wide range of other solid state devices including light emitting diodes,[2] lasers[3] etc. Besides, these fascinating thin film devices, other MHPs based applications such as fluorescent sensing and high energy radiation detection were also getting boom. The motive for MHP materials for applications beyond optoelectronics is broad. The facile solution processed synthesis at low temperature both of nanocrystals and highly pure single crystals of large size is president in MHPs. Moreover, tunable band gap, high absorption coefficient (10^3 - 10^4 cm^-1),[4] and high photoluminescence quantum yield (PLQY) nearly reaching 100% are few of many attracting properties.[5]

The outstanding electrical and photophysical properties of MHPs make them suitable for fluorescent sensing and high energy radiation detection. The fluorescent sensing elements are generally molecules or nanoparticles giving information about the nature of chemical binding with targeted molecule by some photophysical phenomenon, making it achievable in any condition and at all kinds of interface between them. There is a demand for efficient fluorescent sensors for various chemical species and environmental changes. In this context, starting in 2014, MHPs were widely explored for nitroaromatic compounds, volatile organic solvents, metal ions, anions, and humidity, pH and temperature fluorescent sensing applications.
High energy radiation detectors are being used in many applications including medical diagnostic and therapeutic apparatuses, safety inspections, and various scientific equipment. Owing to their diversity in structural dimensionality with varying confinement effects and tunable emission wavelengths, MHPs have been explored for high energy radiation (X-, gamma-ray and beta) detectors.

2. Scope of the Review

This review is organized in three main sections: the first contains details of the electronic structure and photophysical properties of MHPs. The second represents an emergence of mechanisms involved in the fluorescent sensing of various analytes and the match-mismatch between MHPs and fluorescent sensing requirements. The performance of MHPs materials and figure of merits of fluorescent sensing by MHPs are given. The third part reviews applications in high energy radiation detection with emphasis on the scintillating ability of MHPs. The scintillation mechanism is also discussed, followed by figure of merits of the scintillation process. In overall, the current review focuses on the fundamental understanding of MHP compatibility in the fields of fluorescent sensing and radiation detection and advancements in these fields. Furthermore, this review could direct research directions towards further development in these fields.

Physical and photophysical properties of MHPs

2.1. Electronic structure and exciton binding energy: The optical properties of semiconductors are controlled by their electronic structures. The electronic structure of metal halide perovskite is shown in figure 1. Degenerate unoccupied $p$-orbitals of Pb, antibonding $s$-orbitals of Pb and antibonding $X np$-orbitals of halides contribute to the lower part of the conduction band (CB), making perovskite unique dual natured semiconductors (covalent and ionic). Moreover, Pb $p$-orbitals are less dispersed than the
s-orbitals. The valance band is formed by the Pb 6s-orbitals and X np-orbitals. The Pb s-orbitals are occupied with a lone pair of electrons which impart interesting optical properties to the lead halide perovskites. The density of state near band edge consists of Pb s-orbital, p-orbitals and X np-orbitals. Whereas the CH₃NH₃⁺ or Cs⁺ ions do not contribute to the band edges and have negligible contribution on the VB and CB. However, interaction of these cations with the inorganic framework induces lattice distortions that lead to changes in the electronic band structure and perform charge transfer. The hybrid lead halide perovskites show more interesting optical properties due to the CH₃NH₃⁺ ions orientation in the inorganic framework. For example, the photo-ferroic effect produced by the CH₃NH₃⁺ dipole can increase carrier collection. Metal halide perovskites have shown strong optical transitions due to the following two main features:

- **Interatomic and intraatomic transitions**: lower part of the CB in lead halide perovskite is made up of unoccupied p-orbitals and upper part of VB is made up of halogen p-orbitals mixed with small portion of Pb s-orbitals.

- **Direct band gap**: The excitons are also known as electron-hole pairs bound through coulomb interaction. Photon absorption generates excitons in MHPs and the energy required for exciton generation is lower than the band gap energy. There are two kinds of excitons:

  - **Frenckel excitons**: The excitons in which electrons and hole are very tightly bound that make them localized to the single unit cell.

  - **Wannier-Mott excitons**: the electron -hole pairs are weakly bound and are delocalized from the unit cell.
MHPs semiconductors support Wannier-Mott excitons owing to their high dielectric constant. Excitons are quantified by their binding energy which is a function of the dielectric constant and reduced mass of the electron.\cite{9} After the light absorption, the exciton generation takes place followed by the generation of electrons and holes in the CB and VB, respectively. Afterwards, the competition between radiative and nonradiative pathways occurs and pathway selectivity depends on the MHPs structure and dimensionality.\cite{10} It was found that the exciton binding energy for 3D lead iodide-based perovskite is in the range of 50 to 2 meV.\cite{11} The exciton binding energy is influenced by the nature of MHPs and their dimensionality. For example, 3D-lead bromide perovskites have much higher exciton binding energy in the range of 67-150 meV indicating high excitonic character.\cite{12} Likewise, the decrease in dimensionality in the MHPs increases the exciton binding energy monotonically. For example, the iodine based 2D perovskite has an exciton binding energy of 320 meV.\cite{13} The exciton binding energy in quasi-2D perovskites is lower than in 2D but larger than in 3D MHPs.\cite{14}

**2.2. Dephasing time, thermalization time and carrier cooling time:** After photoexcitation, the ground and excited states coexist in a superposition over the dephasing time. The 3D \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) perovskite has a dephasing time of around 220 fs. The dephasing time decreases with decreased confinement.\cite{15} The excited state population after dephasing undergoes thermalization followed by carrier cooling. The thermalization time for \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) perovskite was found in the 10-85 fs range and occurs through carrier-carrier scattering.\cite{16} The carrier cooling time was found to be 100 fs.\cite{17} This time increased under high photoexcitation densities.\cite{18}
Following these processes, the competition between radiative and nonradiative recombination (decay) starts. In MHPs, at low fluences nonradiative recombination happens via charge trapping.\cite{19} Charge trapping results in the decease of PLQY of MHPs (3D). Whereas, at high fluences due to large number of carriers, radiative recombination is dominant, resulting in high PLQY.\cite{20} The exciton binding energy is an important factor that plays a key role in preventing the dissociation of exciton before radiative recombination. The increase in exciton binding energy, increases the PLQY of MHP materials. The increase in exciton binding energy can be achieved by increasing the quantum confinement effect in the perovskite materials. For example, bulk CH$_3$NH$_3$PbBr$_3$ has exciton binding energy around 80 meV, whereas bulk CsPbBr$_3$ has exciton binding energy around 30 meV. These lead bromide perovskites have increased exciton binding energy up to 300 meV and 120 meV, respectively, upon size reduction.\cite{21}

Quantum confinement alters the optical properties of metal halide perovskite materials. It not only enhances PL intensity, but it also blue shifts the PL and absorption spectra. The quantum confinement based energy band in MHP nanomaterials can be calculated following equation 1.\cite{22}

\[
E_g = E_{bulk} + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R} \tag{1}
\]

Where $E_{bulk}$ is the band gap of bulk MHP materials, $\hbar$ is the Planck’s constant, $m_e$ and $m_h$ are the effective mass of electron and hole, respectively. $R$ is Bohr radius; $e$ is the electron charge and $\varepsilon$ is the dielectric constant. The expression $\frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)$ represents the confinement energy, which increases with decease of MHP nanomaterials size as $R^2$. The coulomb e-h interaction increases with decreasing of size as $R^{-1}$ and it determines the
exciton binding energy. The confinement energy is larger than the exciton binding energy when the size of the particle is small enough.[23]

2D MHPs have stable exciton at low temperature. 100% PLQY was observed in 2D perovskite at low temperature however, low PLQY was observed at room temperature. the decrease in PLQY is due to the thermal quenching of excitons. Moreover, moving from 3D to 2D, trap state density is increased.

Figure 1. Electronic structure and crystalline structure of MHPs.

**Key Terms:**

**Fluorescent Sensor:** The turn-on (enhancement) or turn-off (quenching) of fluorescence (photoluminescence) emission upon exposure to certain chemical species (organic compounds, metal ions, anions) or environmental factors (temperature, pH change, moisture) are known as fluorescent sensing events.

**Chemodosimeter:** The irreversible fluorescence turn-off or turn-on due to change in chemical composition of materials are known as chemodosimetry.
Fermi Golden Rule: The optical absorption of semiconductors is directly related with the transition matrix element from valance band (VB) to conduction band (CB) and their joint density of states (VB and CB). Transition matrix element measures the photoelectric transition probability, while joint density of states is the total number of possible photoelectric transitions.

Why metal halide perovskites are superior? Compared to indirect band gap materials (e.g: Si), metal halide perovskite materials have direct band gap and have transition probability two folds higher. Therefore, requires thin layer for efficient optical absorption.

Direct band gap: The Valence band maxima and conduction band minima are at same point of momentum. The two bands occur at the R point in the Brillouin zone. Thus, no extra momentum change is required that results in high absorption coefficient.

Indirect band gap: The valence band maxima and conduction band minima have mismatched momentum in the Brillouin zone. Therefore, the semiconductors require an extra momentum for photon absorption that decreases the absorption coefficient.

Exciton: The absorption of photon with an energy higher or equal to the band gap of semiconductors leads to the formation of quasi-particles know as exciton.

Exciton binding energy: The energy required to form the excitons is known as exciton binding energy.

Dephasing time: The time required in the dephasing of ground and excited states after the initial excitation.

Thermalization: It is the process, in which energy exchanges between the charge carriers.
**Carrier Cooling time:** The time required for the return of photoexcited charge carriers from $T_c$ (Boltzmann distribution with temperature) to the lattice temperature.

**Photoluminescence Quantum Yield (%):** It is the ratio between the number of photons emitted and number of photons absorbed.

### 3. MHPs fluorescent sensors

**Towards Fluorescence Sensing**

The upsurge in chemical usage into to date industrial processes has enhanced the leaching of hazards in the environment that disturbs the ecosystem on large scale. Majority of these materials are colorless after leaching both in air and water, which consequence is to limit their detection in the real time by color. To date much effort has been made to research fluorescent probes for selective and sensitive detection of chemicals. Fluorescent probes using inorganic or hybrid materials considered to be efficient and reliable strategies for the detection of various chemicals and responses like temperature, pH etc. Photoluminescent sensing was pioneered by F. Goppelsroder in 1867. He developed a method for the detection of aluminum ion (Al$^{3+}$) by a strongly fluorescent morin chelate.$^{[24]}$ Since then various chemosensors were developed for the detection of metal cations, anions, neutral molecules. Fluorescent sensing is normally achieved by various photophysical mechanisms such as intramolecular charge transfer (ICT)$^{[24b]}$, photoinduced electron transfer (PET),$^{[25]}$ and fluorescence resonance energy transfer (FRET)$^{[26]}$

For an inorganic material to be employed as fluorescent probe, it should have some critical requirements such as suitable band gap with corresponding photoluminescence in the visible range, high photoluminescence emission, thermal stability, chemical stability in various solvents, and
photo stability. In theoretical prospective, the materials which show change in fluorescent intensity, fluorescence wavelength, anisotropy and fluorescence lifetime caused by exposure of certain concentration of any foreign species for some time can be used as a fluorescent sensing material.

3.1. Match and mismatch of MHP for fluorescent sensing probes

The basic requirements and optimizations for sensitive and wide range fluorescent sensing probes are as follows:

![Figure 2](image.png)

**Figure 2.** Illustration of the expected effect of MHPs concentration on the fluorescence signal in the presence of analytes.

- **Concentration of sensor material:** Generally, the amount of sensing receptor should be high enough to interact with the highest possible concentration of analyte. Ideally stoichiometric amount of sensing receptor must be loaded (**Figure 2**). But this is not possible in real situations. For example, in FQM (fluorescence quenching mechanism), the
change in fluorescence intensity is measured after the exposure of analyte to the receptor. Therefore, sensing receptor should have high fluorescent intensity but fluorescence intensity is independent on the amount of sensing receptors. After the optimum receptor concentration in the solution, the fluorescence intensity will start to decrease due to the self-quenching process. The effective collision frequency will increase in concentrated receptor solution that results in a nonradiative energy transfer process. For MHP fluorescent sensing probes, the amount of MHP materials required is very small due to highly intensity fluorescence. However, the photoluminescence quantum yield of the MHPs developed for sensing applications is still low and needs further attention.

- **pH Effect:** the performance and sensitivity of the fluorescent sensors is affected by the pH of the solution in which experiment was performed. In case of inorganic nanomaterial based sensors, the presence of protons may detach the ligands from the surface of sensing materials which may lead to effect the performance of the sensor.\(^{[27]}\) In the case of MHPs, the acidic and basic pH effects are very crucial. In basic media, MHPs will undergo acid-base reaction that results in the detachment of ligands from the surfaces, and it may also degrade MHPs structures. In both these conditions the fluorescent emission ability of the perovskite is largely affected. But on the other hand, this can also be exploited for the sensing of pH in the solution media. The effect of pH can be very interesting, when the emissions are originated form the surface defects.

- **Temperature:** The operational temperature is one of the key factors that can affect the performance of the materials. Generally for inorganic materials, temperature does not mainly effect the fluorescent lifetime, but, fluorescence intensity can be altered due to various thermal process.\(^{[27-28]}\) Like all other inorganic materials, MHPs show fluorescence
quenching with increase in temperature. However, this effect is reversible in most of the cases. For real time fluorescent sensing experiment, the effect of temperature should be added as a variable in data modelling. Moreover, MHPs response to temperature can also be transferred directly into temperature sensor application.

- **Repeatability**: This is the capability of sensor material to show consistent results and similar sensitivity when repeatedly tested. The sensors should be repeatable and regenerable. To measure the repeatability, the standard deviation of reading is recorded. Likewise, the reusability needs to be estimated. MHPs have shown good reproducibility and repeatability.

- **Stability**: materials used as a sensing probe should have high stability. In case of MHPs, stability is the major challenge that needs a serious attention. MHPs are unstable in polar solvents specially water limits the wide range usability for fluorescent applications. Although various attempts have been made to make MHPs water stable, but it need further exploration. The stability issues under various conditions like moisture, humidity, temperature, and solvent environment affect MHPs crystallinity, structure and morphology, thus perovskite-based sensor designing requires specific precautions.

- **Toxicity**: Toxicity issues of MHPs are one of the major challenges that needs immediate attention to be resolved for the development of MHPs based fluorescent sensing probes. Majority of the efficient fluorescent sensors are lead halide-based perovskites which limits their use for bio-samples or healthcare products.

- **Suitable Morphology**: The development of suitable nanomaterials for fluorescent sensing application, remains a challenge. Although, quantum dots, nanoparticles, nanocrystals,
nanorods, nanowires, nanosheets of MHPs were synthesized, it is difficult to identify the most suitable morphology for the fluorescent sensing applications.

**Fluorescent sensing mechanisms of MHPs probes**

MHPs sensing performance can be determined by three processes:

(i). Fluorescence peak quenching

(ii). Fluorescence peak enhancement

(iii). Fluorescence peak shifting

MHPs based sensors have shown these processes in the presence of analytes. The mechanisms that govern the above-mentioned process in MHPS are as follows.

(i). **Mechanism for Fluorescence Quenching of MHPs based sensors**

Fluorescence quenching of MHPs based sensors was observed in the presence of various analytes. Generally, the fluorescence peak quenching processes mainly occur in various ways:

a) Förster resonant energy transfer (FRET)

b) Electronic energy transfer (EET)

c) Structural deformation

d) Aggregation

The MHPs based sensors have shown fluorescence quenching against nitroaromatic compounds. The mechanism involved in the fluorescence quenching of MHPs was proposed and investigated by various groups. The fluorescence quenching of \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) NPs by TNP has been attributed to the interaction of the hydroxyl group of phenol. This interaction was confirmed by pXRD. The higher concentration of TNP results in the phase distortion of perovskite by forming hydrogen
bonding. Furthermore, it was observed that the presence of nitro groups in TNP also plays a key role in the fluorescence quenching mechanism.\[29\] Besides, hydrogen bonding interaction between perovskite structure and nitrophenol compounds, \(\pi-\pi\) stacking of the benzene ring was also proposed to be involved in the quenching mechanism by allowing the fast electron transfer from perovskite lattice to the Nitrophenols by photoinduced electron transfer process. For photoinduced electron transfer, the LUMO level of nitrophenol is at lower energy than the perovskite making it suitable for electron transfer from perovskite to nitrophenol. Based on these reports, it is difficult to understand the exact mechanism of fluorescence quenching against Nitrophenols.

To understand the quenching mechanism against nitrophenol exposure, femtosecond transient absorption spectroscopy (TAS) was performed for the CH\(_3\)NH\(_3\)PbBr\(_3\) thin films with and without TNT exposure.\[30\] The ground state bleaching (GSB) and excited state absorption (ESA) of the CH\(_3\)NH\(_3\)PbBr\(_3\) have shown fast decay at 540 nm within first picosecond and all other signals have shown decay between 1 ps and 6 ns.\[31\] Among these decay processes, the fast decay was attributed to the cooling of hot carriers, whereas, the delayed processes was the decay of exciton or carriers.\[18a, 32\] In the presence of TNT, no new peaks appeared in the spectra of perovskite and the decay kinetics was almost unchanged. The exposure of TNT has shown fast transient absorption decay from 100 ps to 6 ns indicating that trap states play an important role on the exciton carrier decay. These results show that the tarp states are generated in the perovskite and shorten the exciton life time.\[33\] These results are opposite to the charge transfer hypothesis developed in previous reports.\[34\] Recently, another thorough investigation explored the possibility of quenching mechanism among Förster resonant energy transfer (FRET), Inner filter effect (IFE), electronic energy transfer (EET) and formation of ground-state complex.\[31, 35\] The UV-Vis absorption of the CsPbBr\(_3\) solution was enhanced with the increasing concentration of TNP. Particularly the
enhancement was observed in the peaks located at 332 nm and 400 nm which indicate the formation of electrostatics interaction between oleylamine (capping agent) and TNP. This interaction was further confirmed by the XPS analysis of perovskite with TNP. Moreover, FTIR spectra have also supported the above discussed interaction. These results confirmed the electrostatic interaction of nitrophenols with perovskite.\textsuperscript{[31, 36]}

In the next step, the fluorescence quenching mechanism is examined. For FRET mechanism, the basic requirement is the spectral overlapping between absorption spectra of analyte and emission spectra of sensor, but no overlapping was observed in the case of CsPbBr\textsubscript{3} QDs and TNP, thus FRET can easily be ruled out.\textsuperscript{[37]} The possibility of IFE role in the fluorescence quenching effect was also determined. For IFE systems, the excitation or emission of fluorophore should be absorbed by the fluorophore or absorber.\textsuperscript{[38]} Therefore, fluorescence quenching titration experiment was performed for CsPbI\textsubscript{3} QDs. The strong quenching of the fluorescence intensity by the addition of 250 nM of trinitrophenol suggests that IFE is not the dominant reason for fluorescence quenching. Likewise, molecular polarity does not play a major role in the quenching efficiency. Some additional factors like functional groups, or acidity of the Nitrophenols can also play their role in the quenching process. The hydroxyl group alone was not found to be involved in the quenching efficiency. Moreover, the protonation of Nitrophenols has no effect on quenching.\textsuperscript{[31, 36]}

The EET occurrence in the quenching process was investigated by measuring the PL lifetime of CsPbBr\textsubscript{3} QDs. The PL lifetime of CsPbBr\textsubscript{3} QDs was decreased from 8.29 ns to 6.06 ns in the presence of 20 nM of trinitrophenol.\textsuperscript{[36]} The decrease in PL lifetime suggests that dynamic quenching process is involved in the fluorescence quenching.\textsuperscript{[39]} This observation was according to EET process, that involves the variation of fluorescence lifetime and speed of exciton decay.\textsuperscript{[40]}

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Moreover, the energy gap between donor and acceptor determined the EET in the materials. The above observations were further supported by the LUMO energy level of TNP (-3.897 eV), which is lower than the LUMO of the perovskite (-3.6 eV) and thus the excited electrons can be easily transferred from perovskite QDs to trinitrophenols. Besides, EET, the ground state complex is not possible in the perovskite QDs due to the fact that the ground state complex does not change the fluorescence lifetime.[36, 41]

MHPs have shown PL/fluorescence quenching in the presence of metals ions. For example, the Cu$^{2+}$ ions exposure to MHPs produces fluorescence quenching.[42] Two possible processes could take place by adding metal ions into a solution of MHPs, one Cu$^{2+}$ ions can replace the B-site metal in the MHPs composition or Cu$^{2+}$ can be adsorbed onto the surface of MHP surfaces.[43] It was found that PL lifetime of CsPbBr$_3$ QDs is decreased by the addition of Cu$^{2+}$ ions. Through DFT calculation, it was proposed that the Cu$^{2+}$-oleate is formed at the surface of CsPbBr$_3$ QDs by replacing Cs$^+$ ions. These observation suggests that the ground state complex formation could be the possible pathway for quenching,[43] but it is not supported by the PL spectra of Cu$^{2+}$ added CsPbBr$_3$ QDs. moreover, FRET was also excluded as the absorption spectra of Cu-oleate and PL spectra of CsPbBr$_3$ QDs were not found to overlap. Likewise, the PL wavelength remained unshifted indicating the absence of ground state complex-based quenching. The cation exchange induced quenching can also be excluded as PL lifetime change was observed in the CsPbBr$_3$ QDs. The mechanism for quenching process was proposed to be steric/charge shielding.[42]

Fluorescence quenching was also observed in the Hg$^{2+}$ ion sensing by using (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$ and spirolactam rhodamine B ethylenediamine system. Hg$^{2+}$ can form a complex with spirolactam rhodamine B ethylenediamine which has shown fluorescence quenching mechanism by FRET process. The fluorescence emission of (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$ was found
overlapping with the absorption spectrum of rhodamine B, which matches the pre-requisites of the FRET.\[^{[44]}\] The fluorescence emission of CH\(_3\)NH\(_3\)PbBr\(_3\) QDs was also quenched by the Hg\(^{2+}\) ions. The PL/fluorescence quenching was due the ion exchange phenomenon, in which the Pb\(^{2+}\) ions were replaced by the Hg\(^{2+}\) ions on the surface of the QDs.\[^{[45]}\] The CsPbBr\(_3\) QDs encapsulated with monolith polystyrene membrane has also shown fluorescence quenching by FRET mechanism in the presence of Rhodamine 6G.\[^{[26]}\]

Likewise, the Fe\(^{3+}\) ions have also produced quenching of fluorescence emission by electron withdrawing effect. The electron paramagnetic resonance (EPR) spectrum shows that the Fe\(^{3+}\) ion concentration was deceased in the mixture of perovskite and Fe\(^{3+}\) ions indicating the reduction of Fe\(^{3+}\) ions, which is the possible reason for the fluorescence quenching.\[^{[46]}\] \[^{[47]}\]

Structural deformation driven fluorescence quenching is another kind of process that takes place in perovskite. The aliphatic amines vapors have quenched the fluorescence emission of CH\(_3\)NH\(_3\)PbBr\(_3\) thin films. XRD analysis revealed that the aliphatic amines vapors have destroyed the crystalline structure of perovskite materials. These structural changes are reversible and thus fluorescence emission is recoverable.\[^{[48]}\]

The aggregation of nanoparticles to larger size also quenches the fluorescence emission of the perovskite QDs. F\(^-\) ion exposure induced the aggregation of CH\(_3\)NH\(_3\)PbBr\(_3\) QDs resulting in the increase of size from 3.5 ± 0.4 nm to 8.5 ± 0.6 nm. Thermal fluorescence quenching was also observed in the perovskite materials. MHPs have shown thermal induced fluorescence quenching by increasing of the exciton recombination. The exploration of quenching by increase in temperature in perovskites is limited.\[^{[49]}\]

**Fluorescence resonance energy transfer (FRET)**
FRET is the non-radiative process in which the donor in an excited state transfers energy to the acceptor at ground state. Energy transfer happens via dipole-dipole interaction within less than 10 nm. Prerequisites for donor and acceptor selection follow:[50]

1. Absorbance energy of the acceptor must be equal to the emission energy of the donor, but it is not necessary for an acceptor to emit fluorescence.[50a]

2. The rate of energy transfer \( k_t (r) \) is controlled by the distance between donor and acceptor and is expressed as \( R_o \) (Forster distance).

\[ R_o = 9.78 \times 10^3 [k^2 n^{-4} Q_D(\lambda)]^{1/6} \]  
(2)

Where, \( k^2 \) is the relative orientation of dipoles (donor and acceptor) and its value can range from 0 to 4.[50b] \( n \) is the refractive index of the medium, \( Q_D \) is the quantum yield of emission from the donor molecule and \( J(\lambda) \) is the overlap integral of the donor and acceptor emission and absorption spectra, respectively.[50b, 50c]

3. The energy transfer efficiency in FRET mechanism can be calculated from steady state photoluminescence or time resolved photoluminescence by using equations 3 and 4 respectively.

\[ E = 1 - \frac{\Phi_{DA}}{\Phi_D} \]  
(3) For steady state photoluminescence

\[ E = 1 - \frac{\tau_{DA}}{\tau_D} \]  
(4) For time resolved photoluminescence
Where, the relative donor fluorescence signal intensity is presented by $F$ in the presence $F_{DA}$ and absence $F_D$ of acceptor molecules. Likewise, life time fluorescence of donor molecule is $\tau$ in the presence $\tau_{DA}$ and absence $\tau_D$ of the acceptor.$^{[50c]}$

4. Donors with long fluorescence lifetime (> 100 ns to ms) are more favorable to FRET.$^{[50c]}$

**Mechanism for Fluorescence enhancement of MHPs based sensors**

MHPs show fluorescent enhancement in the presence of various analytes. The mechanism of fluorescence enhancement operates through various pathways. Fluorescent enhancement of CsCuBr$_3$ perovskite was observed by the addition of water in DMF. It was proposed that water is a better electron donor and thus enhances fluorescence emission.$^{[51]}$

Moreover, the fluorescence emission was observed in the chemodosimetric sensing of Pb$^{2+}$ ions by using CsCuCl$_3$ perovskites.$^{[52]}$ Pb$^{2+}$ undergoes ionic exchange reaction to enhance the perovskite fluorescence emission. Pb$^{2+}$ ions also replace the Sn$^{2+}$ ions in CsSnBr$_3$ QDs and enhance the fluorescence emission. $^{[53]}$

**Mechanism for Fluorescence emission shifting of MHPs based sensors**

MHPs show emission wavelength shifting as a fluorescence response for the detection of various analytes. The dominant mechanism in peak shifting is based on the anion exchange reaction. For example, the exchange of bromide ion in CsPbBr$_3$ with chloride or iodide ion results in blue shifting or red shifting, respectively. Halide ion exchange can change the energy band gap and thus the fluorescence emission.$^{[54]}$

**4.4. Performance of MHPs based fluorescent sensors**

**4.4.1 Nitrophenol Sensing**
Explosive materials are the chemical or nuclear materials having an enormous amount of energy that can undergo fast self-propagating decomposition after initiation resulting in explosion.\[^{55}\]

Nitrophenols are the most potent explosives, which are very stable and used in the military. These are involved in lethal weapons especially, like land mines that contain 2, 4, 6-trinitrophenol (TNP). Moreover, TNP is also used in rocket fuels, fireworks, analytical reagents, photographic emulsions etc. Besides use as explosive, It is also present in several industrial wastes and pollutes our environment being present in soil, groundwater and plant foods.\[^{56}\]

Nitrophenols have a benzene ring functionalized with nitro and hydroxyl groups making them electron deficient, therefore they act as electron acceptor.\[^{57}\]

The efficient fluorescent detection of nitrophenol is a challenge due to poor selectivity and sensitivity. Poor selectivity is due to the powerful fluorescence quenching of any electron donating materials by nitrophenols,\[^{29}\]

whereas, the poor sensitivity, is due to low volatility. Furthermore, they have a sticky nature.\[^{58}\]

Metal halide perovskite due to their excellent optical properties were explored for the selective and sensitive detection of nitrophenols. In a pioneering work, Muthu et al.\[^{29}\]

used highly fluorescent hybrid perovskite CH\(_3\)NH\(_3\)PbBr\(_3\) as fluorescent probe for the detection of nitrophenols down to femtomolar scale (10\(^{-15}\) M). The sensor consists of CH\(_3\)NH\(_3\)PbBr\(_3\) spherical nanoparticles of 6.1 nm average diameter. A toluene suspension of CH\(_3\)NH\(_3\)PbBr\(_3\) nanoparticles was used in this work, which shows narrow emission at 531nm with about 21 nm FWHM. The fluorescence quenching for trinitrotoluene (TNT), dinitrotoluene (DNT) and trinitrophenol (TNP) were tested. Among these nitoarenes, TNP shows 97% fluorescence quenching while TNT and DNT show 9% and 5% fluorescence quenching, respectively. This high fluorescence quenching in the presence of TNP makes hybrid perovskite CH\(_3\)NH\(_3\)PbBr\(_3\), a selective TNP sensor. This material shows femtomolar (10\(^{-15}\) M) LOD level with 6% fluorescent quenching and 10\(^{-15}\) to 10\(^{-3}\) M detection
range. Furthermore, the vapor phase detection of TNP was also studied. Although, the vapor pressure of TNP was $7.48 \times 10^{-7}$ Torr at 25 °C, which is very low compared to DNT and TNT,[59], 12 % fluorescence quenching of CH$_3$NH$_3$PbBr$_3$ perovskite nanoparticles was observed after two minutes exposure. It reached 65% quenching after one hour exposure.[34a] This excellent fluorescence quenching is due to the interaction of the nitrophenol hydroxyl group with the CH$_3$NH$_3$PbBr$_3$ perovskite nanoparticles and lead to the phase distortion, which is responsible for fluorescence quenching along with the electron withdrawing effect of the nitro groups. The hydroxyl group can form hydrogen bonding with the perovskite nanoparticle surface, which may favor efficient electron transfer between the perovskite and TNP. This study illustrates that the optical properties of the perovskite can be exploited for their sensing application.[34a] Further to this report, interest in the fluorescence sensing application of metal halide perovskite got boosted.

Efforts in exploring an efficient perovskite material sensitive for nitrophenol detection led to study all-inorganic metal halide perovskite materials due to the advantage of high stability compared to hybrid perovskites. Aamir et al.[34b] developed all-inorganic CsPbBr$_2$I perovskite based fluorescent sensor for TNP detection in DMF solution. In this work, CsPbBr$_2$I perovskite pure microcrystals were employed to detect nitrophenols up to 0.1 mM level. The study focused on nitrophenol detection and their substitution effect on the fluorescence quenching. TNP shows strong fluorescence quenching compared to 2-nitrphenol (2-NP) and 3-nitrophenol (3-NP) due to greater number of nitro groups on the benzene ring. Another observation suggests that the nitro group position on the benzene ring also plays a role in fluorescence quenching, like 2-NP shows 14% quenching, while 3-NP produces 18% quenching. Quenching was due to the hydrogen bonding of the hydroxyl group of nitrophenol ring, which allows the efficient transfer of electron between the perovskite and TNP ring.
Shan et al.\cite{30} reported the trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and trinitroglycerin (TNG) explosives detection by using porous CH$_3$NH$_3$PbBr$_3$-PVDF nanocomposite that is stable in water/isopropanol medium and showed no degradation on exposure to the water contents. The nanocomposite showed 4% PL quenching upon addition of 2 ng of TNT solution. Likewise, this nanocomposite was also found sensitive to RDX and TNG. Interestingly, PL quenching was recoverable under vacuum (10$^{-5}$ Torr) at 40 °C for 24 h, which suggests that TNT interaction with the nanocomposite is weak. Moreover, this weak interaction does not deform the provskite lattice. It was proposed that TNT introduces trap states into the MHP lattice and decreases its exciton life time resulting in PL quenching of MHPs.

Chen et al.\cite{60} reported all inorganic MHP QDs for the detection of picric acid in cyclohexane. The fluorescence intensity of CsPbBr$_3$ QDs was quenched within 1 min exposure to picric acid solution. The LOD was 0.8 nM. Moreover, the electron transfer mechanism was explored in detail for CsPbBr$_3$ QD sensing probes. The mechanism responsible for fluorescence quenching of CsPbBr$_3$ QDs in picric acid solution was explored for possible electronic energy transfer (EET), Förster resonant energy transfer (FRET), formation of ground-state complex and inner filter effect (IFE). It was found that the PL quenching of CsPbBr$_3$ QDs in the presence of picric acid was due to electrostatic assisted electron transfer. Moreover, the selectivity of CsPbBr$_3$ QDs to picric acid depends upon the hydroxyl group and nitro group.\cite{60}

Harwell et al.\cite{61} studied the effect of dimensionality on the fluorescent sensing of dinitrotoluene (DNT). Bulk CsPbBr$_3$ (3D), layered phenethylammonium based (PEA)$_2$Cs$_2$Pb$_3$Br$_{10}$ (2D) and CsPbBr$_3$ NCs (0D) were used for DNT sensing. Only 30-40% PL quenching was observed for the bulk 3D CsPbBr$_3$ thin films with no PL recovery in 3 minutes of DNT gas exposure. Whereas, under same condition, 2D layered (PEA)$_2$Cs$_2$Pb$_3$Br$_{10}$ materials show only 25% PL quenching from
the initial value. However, 0D CsPbBr$_3$ NCs show 70% PL quenching in 3 min of DNT exposure and fastest PL recovery of 50% in just one min. Moreover, DNT shows higher PL quenching response compared to TNT, RDX, and PETN. This enhanced effect is due to the higher vapor pressure of DNT compared to other landmine explosives.$^{[61]}$

Recently, Deng e al.$^{[62]}$ employed the super hydrophobic porous organic polymer framework (SHFW) protected CsPbBr$_3$ QDs (CsPbBr$_3$@SHFW) to detect o-nitrophenol in dichloromethane. Fluorescence intensity of the CsPbBr$_3$@SHFW was quenched with the small amount of o-nitrophenol in one minute. The LOD was found as $7.69 \times 10^{-3}$ µM. The selectivity of the CsPbBr$_3$@SHFW sensor was also tested among K$^+$, Ni$^{2+}$, Ba$^{2+}$, Na$^+$, Fe$^{3+}$, Ca$^{2+}$, Al$^{3+}$, Zn$^{2+}$, Mg$^{2+}$, NH$_4^+$, Cd$^{2+}$, Pb$^{2+}$, Ag$^+$, Br$^-$, S$_2$O$_3^{2-}$, H$_2$PO$_4^-$, SO$_4^{2-}$, Cl$^-$, NO$_3^-$, S$^{2-}$, I$^-$, o-nitrophenol, p-nitrotoluene, p-chlorophenol, phenol, resorcin. This fluorescence quenching was due to the dynamic quenching between CsPbBr$_3$@SHFW and o-nitrophenol.$^{[62]}$
Table 1. Fluorescent sensing performance of various MHPs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Target</th>
<th>Medium</th>
<th>Fluorescence Response</th>
<th>Performance</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>TNP</td>
<td>Toluene</td>
<td>Quenching</td>
<td>LOD: Femtomolar (10$^{-15}$ M), Detection Range: 10$^{-15}$ M to 10$^{-3}$ M, Selectivity among: 2-NP, 3-NP, TNP, TNT</td>
<td>[34a]</td>
</tr>
<tr>
<td>CsPbBr$_2$I</td>
<td>TNP</td>
<td>DMF</td>
<td>Quenching</td>
<td>LOD: 0.1 mM, Detection Range: 0.1 mM to 0.6 mM, selectivity among: 2-NP, 3-NP, TNP</td>
<td>[34b]</td>
</tr>
<tr>
<td>MAPbBr$_3$- PVDF</td>
<td>TNT</td>
<td>water–Isopropanol (1:1 volume ratio)</td>
<td>Quenching</td>
<td>Detection Range: 15 ng to 90 ng, LOD: 15 ng, Selectivity among: TNT, RDX, TNG</td>
<td>[30]</td>
</tr>
<tr>
<td>CsPbX$_3$ (Br/I)</td>
<td>TNP</td>
<td>cyclohexane</td>
<td>Quenching</td>
<td>Detection Range: 0-180 nM, LOD: 0.8 nM, selectivity among: TNT, TNP, DNT, NB, DNB, BA, and BD</td>
<td>[36]</td>
</tr>
<tr>
<td>Material</td>
<td>Stimulus</td>
<td>Environment</td>
<td>Effect</td>
<td>LOD/Selectivity</td>
<td></td>
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<tr>
<td>CsPbBr₃@SHFW</td>
<td>o-Nitrophenol</td>
<td>Dichloromethane</td>
<td>Quenching</td>
<td>LOD: $7.69 \times 10^{-3}$ μM, Detection range: 0-280 μM, Selectivity among: K⁺, Ni²⁺, Ba²⁺, Na⁺, Fe³⁺, Ca²⁺, Al³⁺, Zn²⁺, Mg²⁺, NH₄⁺, Cd²⁺, Pb²⁺, Ag⁺, Br⁻, S₂O₃²⁻, H₂PO₄⁻, SO₄²⁻, Cl⁻, NO₃⁻, S²⁻, I⁻, o-nitrophenol, p-nitrotoluene, p-chlorophenol, phenol, resorcin.</td>
<td></td>
</tr>
<tr>
<td>CsPbBr₃ NCs</td>
<td>DNT</td>
<td>Gas</td>
<td>Quenching</td>
<td>70% in 3 minutes</td>
<td></td>
</tr>
<tr>
<td>CsCuBr₃</td>
<td>Water</td>
<td>DMF</td>
<td>Enhancement</td>
<td>LOD: 50 μL, selectivity among: water, dichloromethane, chloroform, toluene, hexane, ethanol and acetone</td>
<td></td>
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<tr>
<td>CH₃NH₂PbBr₃</td>
<td>Humidity</td>
<td>Closed</td>
<td>Blue Shift</td>
<td>Detection range: 7-98%, LOD: 0.68%, Percentage Quenching: 8.50%</td>
<td></td>
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<tr>
<td>Cs₂InBr₅·H₂O</td>
<td>Water</td>
<td>Humidity, water in THF</td>
<td>Shift</td>
<td>LOD: 0.025 vol% water in THF, detection range: 0%-0.05%, Recycling: 20 cycles</td>
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<tr>
<td>(C₁₆H₃₃NH₃)₂PbI₄</td>
<td>pH</td>
<td>Water</td>
<td>Turn-on</td>
<td>Detection range: (pH) 3-11</td>
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<tr>
<td>Compound</td>
<td>Target Ion</td>
<td>Solvent/Enhancer</td>
<td>Method</td>
<td>Detection Range</td>
<td>Selectivity Among</td>
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<tr>
<td>CsCuCl₃</td>
<td>Pb²⁺</td>
<td>DMF</td>
<td>Enhancement</td>
<td>1 x 10⁻⁷ mole/L to 1.5 x 10⁻⁶ mole/L, LOD: 10 x 10⁻⁷ mole/L, Selectivity among: Cr³⁺, Ag⁺, Cd²⁺, Co²⁺, Fe²⁺, Hg²⁺, Mn²⁺, Pb²⁺, Zn²⁺</td>
<td>[66]</td>
</tr>
<tr>
<td>CsSnX₃ QDs</td>
<td>Pb²⁺</td>
<td>ODE, OA, OAm</td>
<td>Enhancement</td>
<td>LOD: 3.5 x 10⁻⁹ M, detection range: 1 x 10⁻⁸ M to 1 x 10⁻² M, selectivity among: K⁺, Al³⁺, Cs⁺, Na⁺, Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Mn²⁺, Fe³⁺, Zn²⁺, Pb²⁺, Yb³⁺, Er³⁺, Sn²⁺, Au³⁺, Cu²⁺, or Ag⁺</td>
<td>[53]</td>
</tr>
<tr>
<td>CH₃NH₂Br</td>
<td>Pb²⁺</td>
<td>DMF</td>
<td>Enhancement</td>
<td>LOD: 1.6 x 10⁻³ M, detection range: 0.2 x 10⁻¹ M, selectivity among: Pb²⁺, Ga²⁺, Co²⁺, Cu²⁺, Fe³⁺, Mg²⁺, Ni²⁺, Sn²⁺, Sr²⁺, and Zn²⁺, Cs¹⁺</td>
<td>[67]</td>
</tr>
<tr>
<td>CsPbBr₅ QDs</td>
<td>Cu²⁺</td>
<td>Cyclohexane</td>
<td>Quenching</td>
<td>LOD: 2 x 10⁻⁹ M, detection range: 2 x 10⁻⁹ to 2 x 10⁻⁵ M, Selectivity among: K⁺, Na⁺, Cs⁺, Mg²⁺, Ca²⁺, Co²⁺, Al³⁺, Ni²⁺, Mn²⁺, Fe³⁺, Zn²⁺, Yb³⁺, Er³⁺, Sn²⁺, Pb²⁺, Au³⁺, or Ag⁺</td>
<td>[43]</td>
</tr>
<tr>
<td>QDs Type</td>
<td>Cations</td>
<td>Solvent</td>
<td>Detection Method</td>
<td>LOD</td>
<td>Detection Range</td>
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<tr>
<td>CsPbBr₃ QDs</td>
<td>Cu²⁺</td>
<td>Hexane</td>
<td>Quenching</td>
<td>LOD: 0.1 nM, detection range: 0-100 nM</td>
<td>Selectivity among: In³⁺, Ag⁺, Cd²⁺, Fe³⁺, Hg²⁺, Mg²⁺, Mn²⁺, Na⁺, Pb²⁺, Zn²⁺, Ni²⁺, and Cu²⁺</td>
</tr>
<tr>
<td>Eu³⁺-Cs₃Bi₂Br₉ QDs</td>
<td>Cu²⁺</td>
<td>Water</td>
<td>Quenching</td>
<td>LOD: 10 nM, Detection range: 5 nM - 3 μM,</td>
<td>selectivity among: Pb²⁺, Cd²⁺, Cr³⁺, Er³⁺, Au³⁺, Al³⁺, Fe²⁺, Zn²⁺, Co²⁺, Fe³⁺, Ag⁺, K⁺, Hg²⁺, Ni²⁺, and Cu²⁺</td>
</tr>
<tr>
<td>(NH₃(CH₂)₁₀NH₃)PbBr₄</td>
<td>Hg²⁺</td>
<td>DMSO:H₂O (1:9)</td>
<td>Quenching New peak</td>
<td>LOD: 2.36 μM, detection range: 20 to 90 μM,</td>
<td>selectivity among: Na⁺, K⁺, Ba²⁺, Ce³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Pd²⁺, Cu²⁺, Ag¹⁺, Zn²⁺, Cd²⁺, Al³⁺, Pb²⁺</td>
</tr>
<tr>
<td>CH₃NH₃PbBr₃ QDs</td>
<td>Hg²⁺</td>
<td>Toluene</td>
<td>Quenching</td>
<td>LOD: 0.124 nM, Detection Range: 0 nM - 100 nM,</td>
<td>Selectivity Among: Na⁺, K⁺, Zn²⁺, Ba²⁺, Cd²⁺, Pb²⁺, Mn²⁺, Cu²⁺, Mg²⁺, Ca²⁺ and Ag⁺</td>
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<tr>
<td>(C₆H₅NH₃)₂Pb₃I₈·2H₂O</td>
<td>Fe³⁺</td>
<td>DMF</td>
<td>Quenching</td>
<td>LOD: 7.51 × 10⁻⁸ mol/L, Detection range: 0.1–100 μM/L,</td>
<td>Selectivity: 97.41% selectivity among: Fe²⁺, Hg²⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Pd²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Al³⁺, Pb²⁺</td>
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<tr>
<td>Sample</td>
<td>Quencher</td>
<td>Medium</td>
<td>Quenching Mode</td>
<td>LOD</td>
<td>Detection Range</td>
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<tr>
<td>CsPbBr$_3$ QDs</td>
<td>UO$_2^{2+}$</td>
<td>Toluene</td>
<td>Quenching</td>
<td>LOD: 19.83 ppb, detection range: 0-3300 nM, Selectivity among: Ni$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Ca$^{2+}$, and Cu$^{2+}$ along with UO$_2^{2+}$</td>
<td>[70]</td>
</tr>
<tr>
<td>CsPbBr$_3$ QDs</td>
<td>Rhodamine 6G</td>
<td>Water</td>
<td>Quenching</td>
<td>LOD: 0.01 ppm, Detection range: 1-10 ppm</td>
<td>[26]</td>
</tr>
<tr>
<td>(C$_5$N$_2$H$_9$)CdCl$_3$</td>
<td>Acetonitrile</td>
<td>Acetonitrile</td>
<td>Quenching</td>
<td>acetonitrile, dimethyl formamide, deionized water, absolute methanol, anhydrous ethanol and dimethyl sulfoxide</td>
<td>[71]</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>Aliphatic Amines</td>
<td>Vapor</td>
<td>Quenching</td>
<td>Selective: EtNH$_2$, Et$_2$NH, and Et$_3$N, response time: &lt;1 s for Et$_3$N, and ~15 s Et$_2$NH</td>
<td>[48a]</td>
</tr>
<tr>
<td>(C$<em>9$NH$</em>{20}$)$_2$MnBr$_4$</td>
<td>Acetone</td>
<td>Vapor</td>
<td>Quenching</td>
<td>Response time = 10 s, Selectivity among: acetone, n-hexane, ethanol, methanol, toluene</td>
<td>[72]</td>
</tr>
<tr>
<td>CsPbBr$_3$ NCs@BaSO$_4$-Au NPs</td>
<td>Melamine</td>
<td>Tris-H$_2$SO$_4$ buffer (pH 6.0)</td>
<td>Enhancement</td>
<td>LOD: 0.42 nmol/L, Detection range: 5.0–500.0 nmol/L, Selectivity Among: vitamin C, vitamin B$_1$, glucose, tryptophan. Histidine, threonine, lysine, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, NH$_4^+$, K$^+$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$</td>
<td>[73]</td>
</tr>
<tr>
<td>Material</td>
<td>Gas Exposure</td>
<td>Detection Method</td>
<td>LOD, Detection Range</td>
<td>Selectivity</td>
<td></td>
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<tr>
<td>HPbBr3/PbBr2@SiO2 nanospheres</td>
<td>Methylamine Gas</td>
<td>Red Shift</td>
<td>70 ppb, 1.0–95 ppm</td>
<td>dimethylamine (DMA), trimethylamine (TMA), NH3, ethylamine (EA), propylamine (PA), butyl amine (BA) 200ppm, methanol (MeOH), acetone, acetonitrile (ACN), tetrahydrofuran (THF), diethyl ether (DEE)</td>
<td></td>
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<tr>
<td>CsPbBr3 QDs</td>
<td>Ammonia Gas</td>
<td>Enhancement</td>
<td>8.85 ppm, 25–350 ppm</td>
<td>acetone, water, isopropanol, HCl, ethanol, CO2, ammonia</td>
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<tr>
<td>CsPbBr3 NFs</td>
<td>Ammonia Vapors</td>
<td>Quenching</td>
<td>&lt;10.0 mg/L, 10.0–100.0 mg/L</td>
<td>H2O, NH3, Li+, Na+, k+, Ca2+, Mg2+, Fe3+, Ni2+, Al3+, Cl−, I−, NO3−, SO42−, PO43−</td>
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<tr>
<td>MAPbBr3</td>
<td>Ammonia Vapors</td>
<td>Quenching</td>
<td>0.3 Wt%</td>
<td>water, methanol, ethanol, acetone</td>
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</table>

[74][75][76][77]
<table>
<thead>
<tr>
<th>System</th>
<th>Response</th>
<th>LOD Detection Range</th>
<th>Selectivity Among</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>CsPbBr₃ NCs</td>
<td>Iodine number (peroxide number)</td>
<td>Edible oil</td>
<td>Red Shift</td>
<td>LOD: 0.139 mg/100 g, edible oil used: Extra virgin olive, Sesame oil, Pressed first-grade, Corn oil, Peanut oil, Linseed oil</td>
</tr>
<tr>
<td>CsPbBr₃ QDs</td>
<td>Total polar materials</td>
<td>Edible oil</td>
<td>Quenching</td>
<td>LOD: For olive oil 17%, soybean oil 25%, and sunflower oil 21.5%, detection range: For olive oil 17%–31.5%, soybean oil 25%–31.5%, and sunflower oil 21.5%–33%.</td>
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<tr>
<td>CH₃NH₃PbBr₃ QDs</td>
<td>Fluoride</td>
<td>Toluene</td>
<td>Quenching</td>
<td>LOD: 3.2 µM, Detection range: 10–50 µM, Selectivity Among: Cr₂O₇²⁻, SCN⁻, WO₄²⁻, HPO₄²⁻, SeO₂⁻, CO₃²⁻, H₂PO₄⁻, SeO₃²⁻, HCO₃⁻, S²⁻, SO₃²⁻, S₂O₃²⁻, I⁻, Br⁻ and Cl⁻</td>
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<td>CsPbBr₃ NPs</td>
<td>HCl</td>
<td>Vapours/ thin film</td>
<td>Blue shift</td>
<td>LOD: 5 ppm, Detection range: 5-500 ppm, selectivity among: acetic acid, ammonia, formic acid, hydrobromic acid, water, nitric acid, hydrochloric acid</td>
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<tr>
<td>System</td>
<td>Surface Modification</td>
<td>Stabilizer</td>
<td>Water Solvent</td>
<td>Spectroscopy</td>
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<tr>
<td>CsPbBr$_3$ QDs-Cellulose</td>
<td>Chloride and Iodide ions</td>
<td>Water/thin films</td>
<td>Blue/Red Shift</td>
<td>For I$^-$ ions: LOD = 2.56 mM, detection range: 0.0001 to 1 M For Cl$^-$: LOD = 4.11 mM, detection range: 0.0001 to 1 M, selectivity among: Na$^+$, Co$^{2+}$, Fe$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$, SO$_4^{2-}$, HCO$_3^-$, and NO$_3^-$</td>
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<tr>
<td>CsPbBr$_3$ NCs</td>
<td>Chloride ion</td>
<td>n-hexane/water</td>
<td>Blue shift</td>
<td>LOD: 4.0 μM, detection range: 10 to 200 μM, Selectivity among: Br$^-$, F$^-$, ClO$^-$, K$^+$, Na$^+$, Mg$^{2+}$ and Fe$^{3+}$.</td>
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<tr>
<td>CsPbBr$_3$/TPPS Nanocomposite</td>
<td>Sulfide ions</td>
<td>Water</td>
<td>Quenching</td>
<td>LOD: 0.05 nmolL$^{-1}$, Detection range: 0.2–15.0 nmolL$^{-1}$, Selectivity among: K$^+$, Al$^{3+}$, Zn$^{2+}$, Ba$^{2+}$, Cu$^{2+}$, Ca$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Mg$^{2+}$, Na$^+$, Cl$^-$, SO$_4^{2-}$, SiO$_3^{2-}$, NO$_3^-$, HCO$_3^-$, CO$_2^-$, PO$_4^{3-}$, SO$_2^-$, NO$_3^-$</td>
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<tr>
<td>Cs$_4$PbBr$_6$ MDs</td>
<td>Temperature</td>
<td>Powder</td>
<td>Quenching</td>
<td>Detection range: 30–200°C</td>
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<tr>
<td>Mn-CsPb(Cl/Br)$_3$</td>
<td>Temperature</td>
<td>Glass matrix</td>
<td>Quenching-enhancement</td>
<td>Detection range: 80K-293K, Relative Sensitivity: 10.04% K$^{-1}$ at 143 K for CsPbCl$_3$ QDs@glass</td>
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<tr>
<td>System</td>
<td>Material</td>
<td>Method</td>
<td>Detection Range</td>
<td>Sensitivity</td>
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<tr>
<td>CsPbBr$_3$ QDs-Eu$^{3+}$</td>
<td>MOF</td>
<td>Temperature</td>
<td>20-100 °C</td>
<td>3.9% °C$^{-1}$</td>
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<td></td>
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<td>-</td>
<td></td>
<td>at 20 °C,</td>
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4.4.2 Water and humidity sensing

Water is one of the major impurities in organic solvents that can control the yield and selectivity of a final product. Water detection in organic solvents and in the atmosphere i.e humidity is very important to avoid chemical effects from water that ultimately affect laboratory and industrial chemical processes.[87] Water has a large dielectric constant and amphoteric nature, which make it interact with other molecules. Owing to these characteristic interactions, water can be detected by fluorescent sensing probes. So far various fluorescent probe materials were reported in the literature,[88] however, the fluorescent turn off, slow response time and less selectivity are their major limitations.

Recently, Aamir et al.[51] pioneered the use of lead free all inorganic CsCuBr$_3$ perovskite material as a fluorescent sensing material to detect water contamination in organic solvent. Perovskite are very sensitive to water and exposure to water contents leads to sudden change in the optical properties of the materials. They tested 50 μL water contamination in different organic solvents including acetone, toluene, hexane, chloroform, DMF, dichloromethane and ethanol, however, water contents in DMF gave the fluorescent turn on signal (figure 3b). In all other solvents, water contamination does not produce any change in the fluorescence of the lead-free perovskite material. The selectivity for aqueous contamination in DMF was due to the electron donor effect of both solvents. Water is better electron donor than DMF, therefore, efficient transfer of electron increases the fluorescent intensity of the perovskite material.[51]
On the other hand, hybrid perovskite CH$_3$NH$_3$PbBr$_3$ shows quenching of the fluorescence peaking at 530 nm when humidity is increased from 7% to 98%, as reported by Xu et al.\cite{89} Fluorescence was also blue shifted due to the insertion of water molecules in the crystal structure of the hybrid perovskite (figure 3b). However, fluorescence lifetime remained unchanged upon changing humidity, which suggests that humidity-induced fluorescence quenching is static quenching. This material show humidity detection limit of about 0.68% which is higher than previously reported nanomaterial based fluorescent sensors.\cite{90}

Interestingly, the humidity induced quenching behavior of hybrid perovskite is reversible and upon drying. Fluorescence was recovered, however, long-term storage under humid condition effects the hybrid perovskite sensing characteristics. The storage of this materials over 24 h time in humidity >50 % leads to instability in hybrid perovskite. Upon exposure to water molecules, the hybrid perovskite undergoes the formation of CH$_3$NH$_3$PbX$_3$.H$_2$O.\cite{91} The water molecule forms a

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**Figure 3.** (a) Photoluminescence enhancement factor for water content in various organic solvents. Reproduced from ref.[51] with copyright permission Elsevier©2016 and (b) humidity dependent fluorescence spectra of CH$_3$NH$_3$PbBr$_3$ perovskite sensing film. Reproduced from ref.[89] with copyright permission Royal Chemical Society©2016.
hydrogen bonding with the halides of perovskite materials and are responsible for the blue shift in fluorescence under humid conditions. Furthermore, Loi et al.\cite{92} revealed that the surface recombination rate of CH$_3$NH$_3$PbBr$_3$ perovskite is controlled by physisorption of oxygen and moisture molecules. Furthermore, the PL quenching induced by moisture was recovered after drying the sample. 93.4% recovery was recorded for ten cycles.\cite{89}

Lead free indium based Cs$_2$InBr$_5$·H$_2$O perovskite has shown good water sensitivity. The Cs$_2$InBr$_5$·H$_2$O contains a water molecule coordinated within the perovskite lattice. Upon heating at 150 °C, it undergoes dehydration, and the resultant dehydrated perovskite exhibits bright yellow PL. The dehydration is reversible resulting in the hydration of perovskite material upon exposure to air with recovered red PL. This reversible hydration provides the basis to use the material for humidity sensing in air. For sensing application, the dehydrated Cs$_2$InBr$_5$·H$_2$O perovskite was exposed to the 30% humidity, PL evolves from yellow to red in 120 s. The water dependent repeatable PL recovery was achieved even up to 20 cycles. The dehydrated Cs$_2$InBr$_5$·H$_2$O perovskite material was also employed to detect water content in organic solvents like THF containing 0.025 vol% of water.\cite{64}

### 4.4.3 pH Sensing

Fluorescence pH sensing is an attractive technique due to small volume detection and high sensitivity.\cite{93} Metal halide perovskites can be an ideal pH sensor due to their ionic nature and acidic the presence of organic cations in their compositions. Furthermore, the solubility in water, aggregation and quantum well structure in the case of 2D perovskite can be disturbed by pH change, that can provide a platform to exploit metal halide perovskite for pH sensing application.\cite{65} Niu et al.\cite{65} have reported the synthesis of 2D layered (C$_{16}$H$_{33}$NH$_3$)$_2$PbI$_4$ perovskite material for pH sensing application. They have explored the fluorescence of this metal halide
perovskite in the pH 3-11 range. \((C_{16}H_{33}NH_3)_2PbI_4\) perovskite in water of different pH shows emission at low pH values. However, it become non-missive at higher pH values. In 8.4 to 3.0 pH range the PL intensity was increased swiftly. There was no emission to pH values ranged from 11.0 to 9.2. At higher pH values the dissociation of bonds between \(C_{16}H_{33}NH_3^+\) and \(PbI_4^{2-}\) by \(OH^-\) takes place and breaks the perovskite crystallinity (figure 4). Additionally, the material is converted to the amorphous form. This form is reversible when pH is changed to acidic. Niu et al.\(^{[65]}\) tested the recyclability for up to 6 cycles and found that the PL emission is recovered with the change in pH from basic to acidic media.\(^{[65]}\)
Figure 4. (a) Photographs of (C$_{16}$H$_{33}$NH$_3$)$_2$PbI$_4$ solution/suspensions with different pH values under UV-365 nm irradiation and ambient light, (b) PL spectra at various pH values. (c) PL response during pH cycles. Reproduced from ref.[63] with copyright permission from John Wiley and Sons@2014.

4.4.4 Metal ion sensing

Various metal ions such as copper (Cu$^{2+}$), zinc (Zn$^{2+}$) and iron (Fe$^{3+}$) etc. play vital role in biological systems. However, heavy metal ions are toxic and may threaten health and cause serious environmental harms. These include lead (Pb$^{2+}$), cadmium (Cd$^{2+}$) and mercury (Hg$^{2+}$) among
others. Fluorescent probes based on metal halide perovskite for the detection of metal ions were recently reported. Ion exchange is responsible for the enhancement or quenching of PL in metal halide perovskite.

4.4.4.1 Pb\(^{2+}\) ion sensing

Aamir et al.\[^{66}\] have developed a chemodosimetric, lead free CsCuCl\(_3\) perovskite fluorescence probe for the detection of Pb\(^{2+}\) ions. The unique feature of this work was that the CsCuCl\(_3\) perovskite was weak PL emitter and Pb\(^{2+}\) ions addition in CsCuCl\(_3\) perovskite solution leads to replacing the Cu\(^{2+}\) ions in the perovskite structure via ion exchange phenomenon. The formation of CsPb(Cl/Br)\(_3\) perovskite show enhanced PL emission up to the detectable limit. The resultant PL emission was unrecoverable even by the addition of Hg\(^{2+}\) and Ag\(^{+}\) ions which quenches the perovskite PL. The CsCuCl\(_3\) perovskite was found to be sensitive (LOD = 1 \times 10^{-7} \text{ mole/L}) and selective (by 25-fold over other metal ions) towards Pb\(^{2+}\) ions (figure 5).\[^{66}\]

Likewise, Pb\(^{2+}\) can also replace Sn\(^{2+}\) ions in the lead free CsSnBr\(_3\) QDs and can produce PL enhancement and red shift in the signals. After treating CsSnBr\(_3\) QDs with Pb\(^{2+}\) ions, the lattice constant was increased due to the substitution of Sn\(^{2+}\) by Pb\(^{2+}\) ions. moreover, the PL intensity was gradually increased with the addition of Pb\(^{2+}\) solution. These QDs were found selective to the detection of Pb\(^{2+}\) ions with response time of 6 minutes for maximum PL intensity and retain PL for > 10 days. Moreover, lead free CsSnBr\(_3\) QDs were also sensitive for the detection of Pb\(^{2+}\) ions in oily products. The LOD was 3.5 \times 10^{-9} \text{ M} with linear range from 1 \times 10^{-8} \text{ M} to 1 \times 10^{-2} \text{ M}. The sensing mechanism was based on the chemodosimeter based mechanism. \[^{53}\] Yan et al.\[^{67}\] have adopted an interesting approach to detect Pb\(^{2+}\) ions in a solution. The CH\(_3\)NH\(_3^+\) ions solution in DMF was treated with various metal ions and it was observed that Pb\(^{2+}\) ions change the solution color under UV lamp as observed with naked eyes.
4.4.4.2 Cu$^{2+}$ ion sensing

The Cu$^{2+}$ ions detection was also performed by using CsPbBr$_3$ quantum dots (QDs) \[43\]. The fluorescent detection of Cu$^{2+}$ ions by perovskite QDs was based on defect induced fluorescence quenching phenomenon. The detection test was performed by adding Cu-oleate in colloidal solution of CsPbBr$_3$ QDs in cyclohexane. The PL quenching was due to the induced surface defect caused by Cu$^{2+}$ ions which act as non-radiative recombination centers, unlike cadmium chalcogenide based Cu$^{2+}$ ions sensor, in which PL quenching is due to the reduction of Cu$^{2+}$ to Cu$^+$ state.\[94\] Partial PL recovery can be achieved by adding oleylamine into the solution of CsPbBr$_3$ QDs quenched by Cu$^{2+}$ ions due to the strong binding of oleylamine with Cu$^{2+}$ ions due to complexation. Therefore, it can be deduced that perovskite nanomaterials, which have amines/oleylamine in their solution could not be suitable materials for copper ion sensing. The sensitivity of CsPbBr$_3$ QDs to detect metal ions was checked by testing 17 metal-oleates. Among
these metal ions, only Cu$^{2+}$ ions show detectable PL change. The sensitivity of CsPbBr$_3$ QDs in terms of detection limit for Cu$^{2+}$ ions was 2 x10$^{-9}$ mole/L. Further, Sheng et al.$^{[43]}$ have also successfully detected the Cu$^{2+}$ ions in edible oils, fresh and after frying food, as well as in lubricating oils, unused and used. To detect Cu$^{2+}$ ions in aqueous solution, the CH$_3$NH$_3$PbBr$_3$@MOF-5 composite was used.$^{[95]}$ The composites have advantage of being water resistant for days, making them suitable for the sensing application in aqueous media. Moreover, this complex has shown good thermal stability as well. The strong acidic and strong basic pH quenched the PL of CH$_3$NH$_3$PbBr$_3$@MOF-5 composites, which also suggest its wide application in aqueous media. $^{[95]}$

Ma et al.$^{[96]}$ have adopted interesting approach to detect Cu$^{2+}$ in aqueous media using perovskite. They synthesized 2D benzylammonium lead iodide (PEA$_2$PbI$_4$) in aqueous media, with various benzylammonium iodide concentrations. These water stable PEA$_2$PbI$_4$ perovskite were tested for Cu$^{2+}$ ion detection. These 2D perovskite showed detection limit down to 5 x 10$^{-10}$ M of Cu$^{2+}$ concentration, which was more sensitive than reported by Zhang et al.$^{[95]}$ (20 x 10$^{-5}$ M) using CH$_3$NH$_3$PbBr$_3$@MOF-5 composites. Furthermore, PEA$_2$PbI$_4$ perovskite also showed selectivity for Cu$^{2+}$ ions under fluorescent detection in aqueous media. The PL quenching induced by Cu$^{2+}$ ions is due to the formation of new trap-states produced by the strong interaction of Cu$^{2+}$ ions with I atom in PEA$_2$PbI$_4$. These new trap-states limit the recombination of holes and electrons, consequentially leading to strong PL quenching.$^{[94,96-97]}$

To further enhance sensitivity for the detection of Cu$^{2+}$ ions, Wang et al.$^{[98]}$ fabricated CsPbBr$_3$ Perovskite quantum dots based fiber membrane encapsulated with polymethylmethacrylate (PMMA) by electrospinning. These fiber membranes were then functionalized by cyclam, which is selective to Cu$^{2+}$ ions detection in aqueous media. The detection limit of CsPbBr$_3$
QDs@PMMA@cyclam was $10^{-15}$ M, which was most sensitive among previous reports. This high sensitivity was due to the high surface area of the fiber membrane. Quenching in this study followed the fluorescence resonance energy transfer (FRET) mechanism.

Besides, Liu et al. used CsPbBr$_3$ QDs to detect Cu$^{2+}$ ions in hexane. Their major focus was to elucidate the mechanism of quenching caused by Cu$^{2+}$ ions (figure 6). The PL quenching mechanism was explained as FRET before this report. In their study, they tested all the possibilities to elucidate the PL quenching mechanism. Generally, PL quenching caused by metal ions was explained by various processes including FRET, cation exchange and electron transfer.

The absence of peak shifting in the emission and absorption spectra of CsPbBr$_3$ QDs, indicates that Cu$^{2+}$ addition does not produce the conformational changes in the CsPbBr$_3$ QDs, or aggregation of QDs or etching of QDs, which always results in wavelength shift. On the other hand, in FRET phenomenon, the basic requirement is an overlap between absorption spectra of acceptor and emission spectra of donor. In the case of Cu-oleate and CsPbBr$_3$ QDs, such overlap is missing, which ruled out the FRET based PL quenching. The third possibility that can be involved in PL turn off mechanism is electron transfer. To validate the electron transfer mechanism induced by Cu$^{2+}$ addition, the first step is to explore the composition of CsPbBr$_3$ before and after exposure to Cu$^{2+}$ ions. Energy dispersive X-ray spectroscopy revealed the presence of Cu$^{2+}$ ions in the composition of CsPbBr$_3$ QDs suggesting that quenching is due to Cu$^{2+}$ ions. Furthermore, the PL lifetime dropped in the presence of Cu$^{2+}$ ions, supporting the electron transfer process between CsPbBr$_3$ QDS and Cu$^{2+}$ ions. Moreover, in electron transfer, a straight line is generally obtained. However, in the case off CsPbBr$_3$, two linear functions appeared, which indicates that the quenching behaviors happen by some steric/charge shielding process under high Cu$^{2+}$ concentration. The Cu$^{2+}$ has d$^9$ electronic configuration, which makes Cu$^{2+}$ ions suitable
to receive an electron from CsPbBr$_3$ QDs to form the more stable d$^{10}$ configuration. This is responsible for the selectivity of CsPbBr$_3$ QDs for Cu$^{2+}$ ions.\textsuperscript{[101]}

Recently, lead free Eu$^{3+}$ doped Cs$_3$Bi$_2$Br$_9$ QDs were used for the detection of Cu$^{2+}$ ions in aqueous media. The use of Eu$^{3+}$ ion-doped lead-free perovskite QDs is due to the fact that the Cs$_3$Bi$_2$Br$_9$ QDs have low PLQY and green emission. High PLQY is required for Cu$^{2+}$ ion detection. The Eu$^{3+}$ ion-doped Cs$_3$Bi$_2$Br$_9$ QDs have shown high PLQY, water stability and multicolor emission. The addition of Cu$^{2+}$ ions solution into the Eu$^{3+}$ doped Cs$_3$Bi$_2$Br$_9$ QDs solution results in PL quenching. The PL quenching of Eu$^{3+}$ doped Cs$_3$Bi$_2$Br$_9$ QDs is due to the adsorption of Cu$^{2+}$ ions onto the surface of QDs and by the formation of Br-Cu-OOCH species that results in the introduction of trap states to facilitate nonradiative recombination pathways. The addition of EDTA recovers the PL due to the removal of Cu$^{2+}$ ions form the perovskite QDs surface, that supports the proposed PL quenching mechanism.\textsuperscript{[68]}

4.4.4.3 Hg$^{2+}$ ion sensing

Huang et al.\textsuperscript{[44]} have developed a 2D (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$ perovskite and Rhodamine B (RhB) composite as a FRET system for the detection of Hg$^{2+}$ ions. The absorption spectra of RhB and emission spectra of (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$ overlap at 550 nm, making this system suitable for FRET. The PL emission of (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$ perovskite decreases at 550 nm (excited at 270 nm) with increasing RhB concentration. Hg$^{2+}$ exposure deceases the PL emission intensity located at 550 nm of (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$, the and appearance of new emission peak at 585 nm for RBEA-Hg(II) complex. Furthermore, the color change was observed for (NH$_3$(CH$_2$)$_{10}$NH$_3$)PbBr$_4$@ RhB with increasing Hg$^{2+}$-ion concentration.\textsuperscript{[44]}
The direct interaction of Hg\(^{2+}\) ions with CH\(_3\)NH\(_3\)PbBr\(_3\) QDs in toluene solution also results in the PL quenching of the perovskite materials. Moreover, the green fluorescence changes to colorless. PL quenching is due to the replacement of Pb\(^{2+}\) ions by Hg\(^{2+}\) ions onto the surface of the perovskite lattice. The CH\(_3\)NH\(_3\)PbBr\(_3\) QDs were found selective and sensitive to Hg\(^{2+}\) ions detection in toluene. The CH\(_3\)NH\(_3\)PbBr\(_3\) QDs have LOD of around 0.124 nM. Moreover, spot plate test was employed for the detection of Hg\(^{2+}\) ions, which shows visual color change.\(^{[45]}\)

**Figure 6** (a) Absorption spectra of CsPbBr\(_3\) QDs under different concentrations of Cu\(^{2+}\) ions; (b) PL spectrum of CsPbBr\(_3\) QDs and UV-vis spectrum of copper oleate; (c) an EDS spectrum of as-obtained CsPbBr\(_3\) aggregate and the corresponding elemental ratios (inset) after centrifugation at 10 000 rpm for 5 min, the inset shows the elemental ratios of Cs, Pb, Br and Cu; and (d) the time-resolved PL decay curves of CsPbBr\(_3\) QDs with different concentrations of Cu\(^{2+}\) ions (emission at 520 nm, with an excitation wavelength of 370 nm) and the corresponding average lifetimes (inset). Reproduced from ref.\(^{[42]}\) with copyright permission from Royal Chemical Society@2018.
4.4.4.4 Fe$^{3+}$ ion sensing

Fluorescence sensing of Fe$^{3+}$ ions have advantages over electrochemical detection methods. Fluorescent detection of Fe$^{3+}$ ions was achieved using several materials, but rapid detection with high selectivity and sensitivity is still a challenge that need to be addressed. In this context, MHPs are strong candidates due to their ionic nature, and high PLQY. Recently, it was reported that the PL emission of (C$_6$H$_5$NH$_3$)$_2$Pb$_3$I$_8$·2H$_2$O perovskite was quenched by the addition of Fe$^{3+}$ ions solution in DMF.\[^{102}\] The Fe$^{3+}$ ion concentration of around 1.0 x 10$^{-5}$ mol/L has almost completely quenched the PL of (C$_6$H$_5$NH$_3$)$_2$Pb$_3$I$_8$·2H$_2$O perovskite. Moreover, perovskite showed LOD of 7.51 x 10$^{-8}$ and selectivity of 97.4% for Fe$^{3+}$ ions. The mechanism of PL quenching by Fe$^{3+}$ ions was evaluated by electron paramagnetic resonance (EPR). It was observed that the Fe$^{3+}$ ions act as oxidants and gain electron from the perovskite, resulting in PL quenching as it inhibits radiative recombination of electrons and holes. Furthermore, the Fe$^{3+}$ ions have smaller radius with high polarization and high electron gaining potential that make these ions to penetrate into the inorganic framework.\[^{102}\]

4.4.4.5. Uranyl ions sensing

Uranium exists in the form of uranyl ions (UO$_2^{2+}$) under normal conditions. The uranyl ions are toxic and harmful for humans.\[^{103}\] Concentration of uranyl ions in the drinking water must be below 30 ppb according to WHO standards.\[^{104}\] Halali et al.\[^{70}\] could detect uranyl ion using CsPbBr$_3$ QDs in toluene. The fluorescent intensity of CsPbBr$_3$ QDs was quenched by uranyl ions in the range of 0-3.3 µM via Förster resonance energy transfer and electron transfer. The LOD was found as 19.83 ppb. Moreover, the selectivity of CsPbBr$_3$ QDs for the uranyl ion sensing was studied among Ni$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Ca$^{2+}$, Cu$^{2+}$ and UO$_2^{2+}$ ions.\[^{70}\]
Figures of Merit

**Limit of Detection (LOD):** The lowest quantity of an analyte that can be determined with the help of any sensor probe. LOD can be calculated with the help of standard deviation $\sigma$ of the signals and $s$ is the slope of the linear calibration plot, with the following relationship:

$$LOD = \frac{3\sigma}{s}$$

The standard deviation of blank signal can be determined by the relation:

$$\sigma = \sqrt{\frac{\sum (F_n - F)^2}{n}}$$

Where, $F_n$ is the fluorescence intensity for $n^{th}$ measurement and $F$ is the average of fluorescence intensities.[105]

**Selectivity (%):** Selectivity of fluorescent probes for the metal ion sensing is determined by the equation. $S = S(\%) = \left(\frac{F_o - F}{F_o}\right) \times 100$

Where $F_o$ is the fluorescence intensity of the probe without metal ions/analyte and $F$ is the fluorescence intensity in the presence of metal ions/analyte.

**Stern-Volmer equation:** The ratio between the fluorescence intensities of sensing probe in the absence and presence of analyte: $\frac{I_o}{I} = 1 + K_{sv}[\text{Quencher}]$

Where, $I_o$ and $I$ are the fluorescence intensities of sensing probe in the absence and presence of quencher and $K_{sv}$ is the Stern-Volmer constant. This equation is used to calculate the fluorescence quenching ability.
**Stern-Volmer Plot:** The plot describes the $I/I_0$ as a function of quencher concentration. The linearity of the graph is the indicator that a single class of fluorophores is present in the sensors. If two fluorophores are present, then linearity deviates towards x-axis. Moreover, linearity of the graph also indicates the utilization of materials for sensing.

**Percentage quenching:** The % quenching can be calculated by using the initial and final fluorescent intensities. It is the factor of sensitivity towards the change. The quenching percentage is determined by the relationship.

$$\text{% Quenching} = \frac{I - I_0}{I_0} \times 100$$  (9)

Where, $I$ and $I_0$ are the initial and final fluorescent intensities.

**Fluorescence Quenching:** the process which decreases the fluorescence intensity of the sample under the influence of any interacting moieties. The processes that are responsible for fluorescence quenching include excited-state reactions, structural rearrangements, energy transfer, complex formation, and collisional quenching.

**Fluorescence Enhancement:** the enhancement in the fluorescent intensity of materials with increasing concentration of enhancer. It is due to the reduction of collisional quenching. The fluorescent enhancement can be described by equation:

$$\frac{I}{I_0} = S|Q| + K$$  (10)

Where, $|Q|$ is the concentration of enhancer, $S$ is the value of the slope and $K$ is the intercept of the slope. The positive slope value and the value of intercept represent the sensitivity of the sensor.\(^{[53]}\)
**Rancidity of Oil**: The oxidation of fatty acids or fats results in the spoilage of the edible oils, which is known as rancidity of oil. The oxidation of edible oils leads to the formation of peroxides which convert into ketones, aldehydes and oxides.

**Iodine Number**: The gram equivalent of iodine in 100 g of an edible oil sample. The rancidity degree of edible oil can be measured by iodine number. The peroxide value is determined by calculating the amount of iodine formed by the reaction of iodide ion with peroxides of fats/fatty acids.

\[
2I^- + H_2O + H_2O_2 \rightarrow H_2O + 2OH^- + I_2
\]

**Optical Temperature Sensor**: These sensors are based on the fluorescence response of materials at various temperatures. These fluorescent temperature sensors have been based on amplified spontaneous emission or fluorescence lifetime to fluorescence intensity ratio (FIR).

**FIR**: Generally, the fluorescent intensities originate from thermally coupled levels. FIR is the fluorescence intensity ratio and can be calculated by equation:\[^{[106]}\]

\[
FIR = \frac{I_2}{I_1} \propto \exp \left( \frac{-\Delta E}{kT} \right) - - - - - - - - - (11)
\]

Where \( I \) is the fluorescence intensity, \( \Delta E \) is the energy gap between two levels, \( k \) is the Boltzmann constant and \( T \) is absolute temperature. This relationship shows that the temperature can be inferred from the fluorescence intensity ratios of two peaks.

**Absolute Sensitivity (S_a) and Relative Sensitivity (S_r)**: The ratiometric temperature sensing activity of materials can be calculated by absolute sensitivity and relative sensitivity using following equations:\[^{[106]}\]
\[ S_a = \left| \frac{\partial \Delta}{\partial T} \right| \hspace{1cm} (12) \]

\[ S_r = \left| \frac{S_a}{\Delta} \right| \hspace{1cm} (13) \]

*Where \( \Delta \) is the PL intensity ratio and \( T \) is the temperature.*

**Temperature Resolution (\( \delta T \))**: can be calculated by:

\[ \delta T = \frac{1}{S_r} \frac{\partial \Delta}{\Delta} \hspace{1cm} (14) \]

Where, \( \partial \Delta/\Delta \) is the relative error in thermometric measurements caused by the equipment.\(^{[107]}\)

### 4.4.5 Organic Compounds Sensing

MHPs were tested as the fluorescent probes for the detection of volatile organic molecules. To sense such molecules, the potential energy transfer mechanism that could be responsible for the change in MHP emission signals. MHPs as a donor has high quantum yield, narrow emission with broad excitation spectra. Moreover, the acceptor like volatile organic compounds (VOCs) that could produce weak interaction with donors (MHP lattice surfaces) and maintain few nanometer distance. These facts have directed the use of MHPs based systems for the sensing of VOCs by FRET based sensing platforms.

MHPs quantum dots are one of the ideal candidates in this context. The polystyrene encapsulated CsPbBr\textsubscript{3} QDs membranes were fabricated with electrospinning method and the detection of Rhodamine 6G was performed in water. The emission spectra of perovskite QDs and Rhodamine 6G overlap, which further meets the prerequisites of FRET process. The polystyrene encapsulated
CsPbBr$_3$ QDs membrane emission signal was quenched by exposing them into the solution of Rhodamine 6G dye with corresponding increase in emission intensity of Rhodamine 6G. These results have shown the energy transfer by FRET mechanism. The PS encapsulation makes perovskite QDs stable over long-term in water and under light irradiation.

The volatile organic solvents can also show similar behaviors. For example, the lead free 2D hybrid perovskite (C$_5$N$_2$H$_9$)CdCl$_3$ based on 1,2-dimethylimidazole was synthesized and used for the detection of acetonitrile. Acetonitrile quenches the emission of (C$_5$N$_2$H$_9$)CdCl$_3$ by FRET. The FRET platform was developed by the interaction of “CN” of acetonitrile and imidazole of (C$_5$N$_2$H$_9$)CdCl$_3$.[108] However, hygroscopic nature of the imidazole moiety in (C$_5$N$_2$H$_9$)CdCl$_3$ perovskite limits its practical application.[109]

Besides FRET based systems for detection of VOCs, Kim et al.[48a] have adopted another approach by fabricating the thin films of CH$_3$NH$_3$PbBr$_3$ nanoparticles by blade coating and using them for the detection of aliphatic amines including EtNH$_2$, Et$_2$NH and Et$_3$N. The sensing mechanism was different in this approach. The emission intensity of CH$_3$NH$_3$PbBr$_3$ nanoparticle thin films was quenched by changes in the perovskite lattice structure. The primary amine gas exposure produced quick response by quenching the strong green emission of CH$_3$NH$_3$PbBr$_3$ nanoparticles. Contrarily, the secondary and tertiary amines showed slow response. Furthermore, the recovery time of PL signal worked in other ways. The quenching produced by primary amine was irreversible compared to the other two amines. This on-off emission signal was based on the perovskite structure reversibility. The primary amine exhibits strong hydrogen bonding interaction due to small interaction distance resulting in irreversible structural changes in the perovskite lattices.[48a]
Moreover, acetone vapors were detected by using 0D lead free \((\text{C}_9\text{NH}_{20})_2\text{MnBr}_4\) perovskite and green emission was quenched to 50 folds in just 10 s, whereas methanol, ethanol, n-hexane and toluene did not affect fluorescent response.\[^{[72]}\]

Melamine is the precursor for the synthesis of melamine-formaldehyde resin. Melamine has also been added into the dairy products to increase the nitrogen contents of the products due to the rich nitrogen-based structure. It has also been reported as a possible endocrine disruptor and neurotoxicant. Therefore, the selective and sensitive detection of melamine in dairy products is highly demanded. Li et al.\[^{[73]}\] fabricated the intense green fluorescence emitting CsPbBr\(_3\) NCs decorated with positively charged BaSO\(_4\) to generate electrostatic interaction with Au NPs. The mixing of Au NPs strongly quenched the fluorescence of the CsPbBr\(_3\) NCs@BaSO\(_4\) due to the inner filter effect. The addition of melamine induces the agglomeration of Au NPs that results in the reduction of the inner filter effect which in turn recovered the fluorescence intensity of the CsPbBr\(_3\) NCs@BaSO\(_4\). In the absence of Au NPs, melamine does not interact with CsPbBr\(_3\)NCs@BaSO\(_4\). The LOD was 0.42 nM melamine. Moreover, CsPbBr\(_3\)@BaSO\(_4\) + Au NPs was selective for the detection of melamine compared to the presence of various other potential interfering species such as vitamin C, vitamin B\(_1\), glucose, tryptophan, histidine, threonine, lysine, Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4^+\), K\(^+\), Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\).

Recently, Huang et al.\[^{[74]}\] adopted an interesting strategy to develop a fluorescent sensing probe based on perovskite materials. They synthesized HPbBr\(_3\)/PbBr\(_2\)@SiO\(_2\) nanospheres and treated it with methylamine gas that results in the formation of MAPbBr\(_3\) which turns-on the fluorescent signal. The fluorescent intensity was enhanced in the concentration range of 1.0-95 ppm with LOD of 70 ppb. Moreover, the selectivity was tested against various volatile molecules including dimethylamine (DMA), trimethylamine (TMA), NH\(_3\), ethylamine (EA), propylamine (PA), and...
butyl amine (BA) is 200 ppm; the concentration for methanol (MeOH), acetone, acetonitrile (ACN), tetrahydrofuran (THF), and diethyl ether (DEE) is 2000 ppm.

4.4.6 Ammonia Sensing

Food products undergo biological, chemical, and physical changes upon ageing. The freshness of food stuff can be indexed by gauging these changes.[110] Food decomposition results in many products including hydrogen sulphide, amines, methane, and ammonia.[111] Ammonia is a colorless gas, highly corrosive and emits a strong odor. It is a toxin for human. It also effects the respiratory, circulatory, and digestive systems.[112] Therefore, detection of ammonia is a source of attention for several researchers.

Huang et al.[75] used CsPbBr$_3$ QDs for the fluorescent sensing of ammonia gas. The perovskite QDs selectively detect ammonia gas under turn-on PL mode. Under ammonia exposure, PL intensity is dramatically enhanced due to the effective surface defective passivation of QDs. This process of PL enhancement was found reversible making it an ideal material for ammonia sensing. The detection range from 25 to 350 ppm was found using CsPbBr$_3$ QDs and limit of detection was as low as 8.85 ppm. Moreover, the fast response time is around 10 s and recovery time is 30 s.[75] Recently, Park et al.[76] reported the fabrication of porous CsPbBr$_3$ nanofibers (NFs) by using electrospinning for the detection of gaseous and aqueous ammonia. The PL intensity of CsPbBr$_3$ NFs selectively dropped under gaseous and aqueous ammonia exposure. The LOD was around 10 mg/L which was larger than Huang et al.[75] Differences in LOD values and PL responses are due to the perovskite surfaces. In the case of NFs, the porous polystyrene (PS) matrix allows more ammonia to contact with the NFs that results in the breakdown of the structure and ultimately causes PL quenching. However, Huang et al.[75] claimed the surface passivation by ammonia to enhance the PL intensity. Likewise, Ruan et al.[77] reported that MAPbBr$_3$ exposure to gaseous...
NH₃ results in strong PL quenching. This PL quenching is due to the formation of weakly coordinated NH₄⁺PbBr₃-MA complex which can be thermally decomposed to produce MAPbBr₃ by releasing ammonia.

4.4.7 Rancidity of oil

Edible oil is spoiled by oxidation. The peroxide number is the degree of oxidation of fatty acid and fats. Peroxides are produced by the oxidation of functional groups in the edible oils, which can cause destruction of the cell membrane, gastric cancer, myocardial infarction, hair loss, arteriosclerosis and various other chronic diseases. The peroxide number can be measured by calculating the amount of iodine produced by the reaction of peroxides with iodide ion.\[78,113\]

The CsPbBr₃ NCs can undergo anion exchange reaction with halide ions resulting in fluorescence shifting. The halide ion exchange can be used to detect the peroxide number by measuring the iodide ions in the edible oils. The halide exchange reaction was performed with oleylammonium iodide. This exchange results in the gradual change in emission of CsPbBr₃ NCs from green to red. To detect the rancidity, the edible oil was mixed with the oleylammonium iodide solution followed by the addition of CsPbBr₃ NCs. The higher concentration of peroxides in edible oil samples consumes more oleylammonium iodide that results in the small iodide ion exchange with CsPbBr₃ NCs and apparent color change of perovskite NCs was changed from red to pink to orange and finally to green. The LOD of peroxide number was found as 0.139 mg/100 g. The reported LOD in this study was much lower than in many other methods.\[78\] Recently, Huangfu et al.\[79\] detected the quality of edible oil by estimating the total polar materials in the edible oil. Determination of the quality of edible oil by measuring the total polar materials is a very reliable method. The legal standards for total polar materials in edible oils is between 23% to 30%.\[114\] Fluorescent sensing of total polar materials in edible oil was achieved by using CsPbBr₃ QDs. It was found that the PL
of CsPbBr$_3$ QDs was quenched in the presence of olive oil, soybean oil, sunflower oil. The CsPbBr$_3$ QDs exhibits PL quenching effect in the presence of total polar materials range of 17 %–31.5 % for olive oil, 25 %–31.5 % for soybean oil, and 21.5 %–33 % for sunflower oil. Moreover, a paper based fluorescent sensing system was also developed for the real time detection of total polar materials.$^{[79]}$

### 4.4.8 Anion sensing

The compositional variation in MHPs materials, especially halide ions, results in tunable PL emission. Therefore, the anion-exchange reaction can result in the fluorometric response and can be used for sensing of halide ions. In this context, HCl sensing was performed by exposing the CsPbBr$_3$ nanocrystals with the vapors of HCl.$^{[115]}$ The red shift in PL emission represents the sensing of HCl molecules. The sensing mechanism was based on the change in halide composition with the formation of CsPbBr/Cl$_3$ nanocrystals.$^{[115]}$

However, Lu et al.$^{[80]}$ adopted a different approach for the detection of F$^-$ ion. Generally, CH$_3$NH$_3$PbBr$_3$ QDs were synthesized by using long chain alkyl ammonium or amine or acids, which make perovskite QDs to emit intense fluorescence by controlling crystallization kinetics and size of QDs.$^{[116]}$ However, these surfactants do not respond to fluoride ions due to their nonpolar long chains. Lu et al. fabricated the CH$_3$NH$_3$PbBr$_3$ QDs capped with 6-amino-1-hexanol. The amino group of capping agents is attached to the surface of perovskite QDs with hydroxyl group on the other end. The free hydroxyl group can hydrogen bind with F$^-$ ions.$^{[117]}$ The interaction of capping agent with fluoride ions detached them from the QDs surface that allows the aggregation of QDs resulting in quenching of the emission signals. The CH$_3$NH$_3$PbBr$_3$ QDs showed selective and sensitive detection of fluoride ion with LOD of 3.2 μM.
The MHP nanomaterials have an advantage of rapidly changing their halide ion composition via anionic exchange reaction. The detection of chlorine and iodine in the domestic sewage and drinking water can be performed by monitoring the PL emission of the CsPbBr\(_3\) QDs-cellulose composites. Iodine ion exposure causes the change in PL from green to red in 2.5 s and chloride ions result in the change in PL from green to blue in 150 s. The sensing of iodide and chloride ions in the real samples was also explored by adding the water stable CsPbBr\(_3\) QDs-cellulose composites into tap water solution containing 1.0 M of I\(^-\) ions.\[^{54b}\] Recently, Huang et al.\[^{82}\] have also reported the use of CsPbBr\(_3\) NCs for the fluorescent sensing of chloride ion at acidic pH (1.0). The halide exchange results in the wavelength shift and LOD was 4.0 \(\mu\)M with a linear detection range of 10-200 \(\mu\)M. This LOD was lower than the in previous works.

Apart from halide ion sensing, MHPs were used for the detection of sulfide ions. Sulfide ions are by-products during various industrial processes and can cause serious health issues.\[^{118}\] Recently, Wang et al.\[^{83}\] fabricated the tetraphenylporphyrin tetrasulfonic acid (TPPS) based CsPbBr\(_3\) nanocomposite for the selective and sensitive sensing of sulfide ion in water. During sensing, it was observed that the green fluorescence of CsPbBr\(_3\) was quenched whereas, the red fluorescence of TPPS remained unaffected. This effect is due to the destruction of the CsPbBr\(_3\) perovskite lattice. The detection range was 0–20.0 nmolL\(^{-1}\) for sulfide ion with LOD of 0.05 nmolL\(^{-1}\).

### 4.4.9 Temperature sensing

Luminescence properties of the MHPs can be greatly affected by temperature. Increase in temperature increases the non-radiative transitions that decrease the luminescence intensity. This is called thermal quenching. Cs\(_4\)PbBr\(_6\)-PDMS (polydimethylsiloxane) composites show PL quenching at high temperature. The uniform bright green emission of Cs\(_4\)PbBr\(_6\)-PDMS shows excellent recovery in the temperature range 30-200 °C. This rise in temperature does not produce
any structural deformation, which confirms that PL quenching is due to thermal quenching.\[84\] Cryogenic temperature sensing was also achieved by using Mn-doped CsPb(Cl/Br)\textsubscript{3} perovskites embedded in glass.\[49\] Mn\textsuperscript{2+} doping induces multiple emission properties of the perovskite, but Pb\textsuperscript{2+} and Mn\textsuperscript{2+} radius mismatch can result in the expulsion of Mn\textsuperscript{2+} from the perovskite lattice. Moreover, the perovskites are unstable and to overcome this issue, the Mn-doped CsPb(Cl/Br)\textsubscript{3} perovskites were embedded in a glass matrix. The water stable, Mn-doped CsPb(Cl/Br)\textsubscript{3}@glass was explored for temperature sensor between 80 K to 293 K. Starting from 80 K, the increase in temperature produces two effects, one is the blue shift in PL emission and the other is the PL quenching. But the PL emission intensity of Mn\textsuperscript{2+} decreases between temperatures 80 K to 143 K and then PL emission is enhanced with further increase in temperature. This phenomenon is due to the two factors: (i) thermal quenching and (ii) temperature dependent exciton to Mn ET.\[49\] The CsPbBr\textsubscript{3}@Eu-MOF nanocomposite was also used for FIR-based temperature sensing. The nanocomposite showed dual emission peaks originated from perovskite and MOF. The PL emission peak of CsPbBr\textsubscript{3} QDs decreases in intensity while PL intensity of Eu-MOF increases with increasing temperature. The two emission peaks are independent with no energy transfer. The high relative sensitivity of 3.9\% °C\textsuperscript{-1} at 20 °C was observed for CsPbBr\textsubscript{3}@Eu-MOF nanocomposite.\[85\] Recently, Zhang, et al.\[86\] synthesized the Tb\textsuperscript{3+}:CsPbI\textsubscript{3} NCs glasses by using melt quenching and used them for temperature sensing applications. The fluorescence intensity ratio of Tb\textsuperscript{3+}: CsPbI\textsubscript{3} NCs glass was measured in the temperature range of 80-480 K. The prepared glass has good water and thermal stability with excellent repeatability. Moreover, the relative sensitivity of about 1.78 % K\textsuperscript{-1} was observed. Although, superior relative sensitivity was shown by Tb\textsuperscript{3+}: CsPbI\textsubscript{3} NCs glasses, further exploration is highly required.
5. Metal halide Perovskite radiation detectors

X-rays, α-rays, β-rays, and γ-rays are high energy radiations and can have strong penetration power and high ionizing radiation energy. X-ray detectors have been used in various modern applications such as radio astronomy, crystal structure determination, security, defense, nuclear power stations and medical radiography. Likewise, β-rays have comparatively moderate penetration power and have been used for surface radiative contamination surveillance.\[[119]\] High energy radiation-based detection/imaging approaches are of two types:

a) Indirect conversion via scintillators

b) Direct conversion of X-ray photons into electrical current

X-ray detectors based on semiconductors operate under visible light photodetectors with some differences like photon absorption, charge generation and charge extraction processes. X-ray photons have much stronger penetration power, therefore thicker active layer of semiconductor is required, and charges are generated in the entire thickness of the semiconductor crystals.

5.1 Match-mismatch of MHPs for radiation detector

MHP materials show large absorption coefficient, tunable band gap, large charge carrier mobility, and long luminescence lifetime. Moreover, the scintillator light yield and material band gap are inversely proportional to each other.\[[120]\] Therefore, MHPs can be the ideal candidates for high energy radiation detectors and scintillators. Following are the properties of MHPs which match with the requirements of high energy radiation detectors and scintillators.

- **Strong stopping power:**

  The stopping power of materials is based on their atomic number and density. Common elements found in MHPs are Cs\(^+\), Ag\(^+\), Bi\(^{3+}\), Pb\(^{2+}\), Sn\(^{2+}\), I\(^-\), and Br\(^-\) ions which have atomic
numbers of 55, 47, 83, 82, 53, and 35, respectively. These atomic numbers are quite high, that matches well with the basic requirement of radiation detectors.

The density of CH$_3$NH$_3$PbI$_3$ perovskite is 4 g/cm$^3$. Owing to high atomic number and high density, CH$_3$NH$_3$PbI$_3$ perovskite shows high attenuation coefficient of 3.1 cm$^2$ g$^{-1}$ at 100 KeV X-rays, compared to CSI:Tl materials (2.0 cm$^2$ g$^{-1}$). Likewise, CsPbI$_3$ perovskite shows attenuation coefficient of 14 cm$^{-1}$. The radiation stopping power of materials depends on the mass density and not only in the mass attenuation coefficient. However, majority of MHPs have a mass density less than 4 g cm$^{-3}$. This low mass density of MHPs is due to the large volume occupied by the halide ions. Layered 2D MHPs have shown quite low mass density compared to 3D MHPs.$^{[121]}$ Moreover, the polymer matrix used to fabricate MHPs based scintillators, further reduces the mass density from 3D MHP materials. The incorporation of high atomic number elements in double perovskites is possible making them more suitable for high energy radiation.$^{[122]}$ To overcome the problem of mass density in lower dimensioned MHPs, almost the double amount of materials is required for the scintillator.$^{[123]}$ On the other hand, β-rays detection is favored by the low mass density materials due to the high capture efficiency of β-rays.$^{[124]}

- **Large charge carrier mobility ($\mu$)–charge carrier lifetime ($\tau$) product ($\mu\tau$):**

MHPs shows large $\mu\tau$ product. For example, the CH$_3$NH$_3$PbI$_3$ single crystals of 3 mm thickness shows the 100% charge collection efficiency which indicate the long charge carrier diffusion length with $\mu\tau$ product of $3.9 \times 10^{-7}$ cm$^2$ V$^{-1}$.$^{[125]}$ Likewise, CH$_3$NH$_3$PbBr$_3$ single crystals shows the $\mu\tau$ product of $1.2 \times 10^{-2}$ cm$^2$ V$^{-1}$.$^{[125]}

- **Large bulk resistivity:**
To achieve small dark current and noise, large bulk resistivity of the material is important. In this context, the major challenge is the difficulty in doping. But, still it can undergo some self-doping.\[126\] The partial or integral replacement of I\(^-\) ions by Cl\(^-\) ions can reduce the intrinsic charge carrier concentration due to band gap increase. The CH\(_3\)NH\(_3\)PbI\(_3\) perovskite has 10\(^7\) \(\Omega\)cm resistivity at room temperature,\[127\] whereas, CH\(_3\)NH\(_3\)PbBr\(_3\) perovskite has 10 times higher resistivity.\[128\]

- **Radiation hardness:**
  MHPs show relatively better defect tolerance and thus long electron-hole diffusion length\[129\] and radiation damage tolerance in the form of crystals.\[130\] For example, continuous irradiation of an MHP solar cell with gamma rays for 1500 h at 23 kGy dose does not significantly effects its PEC.\[131\]

- **Cost effective:**
  MHPs are low cost due to the natural abundance. The material cost of MHPs is 3 to 4 times lower than CZT crystals.\[122\]

- **Light yield:** MHPs can show exciton decay time less than nanoseconds due to the absence of transfer step, which make these materials much brighter than traditional extrinsic emission materials.\[123\] However, detail investigations are still missing.

- **Speedy response:** speedy response results in fast applications. MHPs scintillators have shown rapid response. For example, CsPbBr\(_3\) NCs based scintillator presented a short decay time of 44.6 ns under gamma radiations, 5 ns for UV radiation.\[123, 132\]

- **Stability:** Although, MHPs are found unstable in various device applications like photovoltaics, in the field of scintillators, MHPs have shown promising stability. Higher radiation doses for prolonged time did not produce energy losses in the MHPs scintillators.
A detailed investigation is highly required to understand the stability performance of MHPs scintillators. It has been observed that gamma radiation dose results in small short-circuit current ($J_{sc}$) losses due to phase segregation in mixed halide perovskite systems.[133]

- **Processability**: MHPs allow fabrication of scintillors at low temperature from solution and retain exceptional optoelectronic properties. Low temperature fabrication also makes them compatible with flexible device fabrication. However, large area device fabrication remains a challenge. Moreover, in flexible systems, the increase in MHPs thickness causes the decrease in device flexibility.[134]

To collect the generated charge, the product of charge carrier mobility and charge carrier lifetime needs to be large. The atomic number controls the attenuation coefficient ($\alpha$) of X-ray (stopping power). The relationship between attenuation coefficient ($\alpha$) and atomic number ($Z$) is as follows.

$$\alpha \propto \frac{Z^4}{E^3}$$

Where, $E$ is the X-ray photon energy.

MHPs have gained enormous attention for the X-ray detection application due to their large atomic number and density. Moreover, the linear attenuation coefficient of CH$_3$NH$_3$PbI$_3$ is 10-times higher than to $\alpha$-Si for 120 KeV X-rays. In contrast, CH$_3$NH$_3$PbBr$_3$ has lower X-ray stopping power but have been widely used for X-ray detection due to its cubic crystal lattice, larger band gap, facile single crystal growth, and reduced ion migration. CH$_3$NH$_3$PbBr$_3$ single crystals have shown highest $\mu\tau$ product of $1.4 \times 10^{-2}$ cm$^2$ V$^{-1}$.[135]
Scintillators convert high energy radiations like X-rays and gamma rays into low energy visible radiation. Scintillators can be used for application in the fields of medical imaging, space exploration and non-destructive testing.

**Scintillation mechanism** can be divided into three steps:

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**Conversion** step depends on the energy of incident photons and the photon interaction with the scintillator lattice via photoelectric effect, where the effective atomic number and density of the materials are important parameters. Likewise, another photon interaction phenomenon that takes place during the conversion step is Compton scattering and pair production.\[^{136}\] After absorption, the high energy incident photons generate deep holes and hot electrons. Afterwards, hole and hot electron multiplication takes place through various processes including inelastic electron-electron scattering, radiative and non-radiative decay. Hole and hot electron thermalization to the top of the valence band and the bottom of the conduction band occurs. The conversion stage is completed within few ps duration.\[^{136-137}\]

**Transport:** Hot electrons and holes have to be transported to the emission centers. These hot electrons and holes can be trapped during migration at trapping levels due to lattice defects. The scintillation process depends on the properties of the energy carriers.\[^{138}\]

**Luminescence:** At the emission center, the excited hot electrons and holes undergo trapping and radiative recombination.\[^{136, 138}\]
The most important figure of merit for the scintillators is the light yield which determines the X-ray conversion efficiency and detection contrast. MHPs scintillators have lower light yield than more traditional scintillators as Lu$_{1.8}$Y$_{0.2}$SiO$_5$-Ce (33200 photons/MeV), CsI-Tl (54000 photons/MeV)$^{[139]}$ and Gd$_2$O$_2$S-Tb (60000 photons/MeV)$^{[140]}$. To achieve high light yield, large Stokes shift and high photoluminescence quantum yield is required. In the case of MHPs, the small Stokes shift results in self-absorption that limits their light outcoupling efficiency both in thin-films and crystals.

### 5.2 Basic requirements for scintillators

The requirements for the scintillation applications includes

- Fast response < 100 ns
- Scintillation efficiency
- High yield > 40000 photons/ MeV
- High energy resolution < 3%
- High density > 6 g cm$^{-3}$
- Large high-quality crystals > 1 cm$^3$
- Radiation resistance
- Price, low cost/cm$^3$

### 5.3 X-Ray Detection

Stoumpos et al. introduced X-ray detection using single crystal of CsPbBr$_3$ grown by melt method that could resolve K$_\alpha$ and K$_\beta$ peaks.$^{[141]}$ The direct conversion of X-ray photons into electric current by solution processed CH$_3$NH$_3$PbI$_3$ perovskite thin film device with 60 µm thickness was also
achieved. This thickness of a film was able to achieve highly sensitive photoconduction operating in the UV-visible, near infrared and soft X-rays (8 KeV) regions. CH$_3$NH$_3$PbI$_3$ has sensitivity of 1.1 µC Gy$^{-1}$ air cm$^{-2}$ and responsivity of 1.9 × 10$^4$ carriers/photon.$^{[142]}$ The suitability of MHPs for X-ray detection is due to their strong X-ray attenuation. But polycrystalline thin films of perovskite have shown a small charge carrier mobility (µ)–charge carrier lifetime (τ) product of 2 × 10$^{-7}$ cm$^2$ V$^{-1}$, which is five times less than state of art X-ray detector materials like CdZnTe.$^{[143]}$ Likewise, incomplete attenuation of X-rays was observed for the perovskite films.$^{[142]}$ Higher µτ product was achieved by using high quality single crystal CH$_3$NH$_3$PbBr$_3$. These MHP single crystals have high X-ray sensitivity with low detectable dose rate.$^{[144]}$

To achieve high image resolution and sensitivity, flat panel detectors (FPDs) were developed. In FPDs, the materials are integrated onto pixelated readout electronics. A solution grown CH$_3$NH$_3$PbBr$_3$ single crystal device permits 15-20 times lower dose exposure than required for the medical application as compared to α-Si based X-ray imaging. This system achieved 2.1×10$^4$ µC Gy$^{-1}$ air cm$^{-2}$ sensitivity under 8 KeV X-ray irradiation. $^{[145]}$ Single crystal X-ray detectors are in high demand for upscaling. Likewise, X-ray detectors should permit high sensitivity and high-resolution images. To develop large area detectors, polycrystalline sintered CH$_3$NH$_3$PbI$_3$ wafers were fabricated. These polycrystalline perovskite-based devices show 2527 µC Gy$^{-1}$ air cm$^{-2}$ conversion efficiency under 70 kV$_p$ X-rays. This high sensitivity is due to the high ambipolar µτ product of 2×10$^{-4}$ cm$^2$ V$^{-1}$.$^{[146]}$ On a similar note, a CsPbBr$_3$ quasi-monocrystalline film fabricated by hot pressing method had 55684 µC Gy$_{air}^{-1}$ cm$^{-2}$ sensitivity, which was higher than the previous system.$^{[146-147]}$ Likewise, a disruptive polycrystalline CH$_3$NH$_3$PbI$_3$ photoconductor was printed on TFT for X-ray detection. This CH$_3$NH$_3$PbI$_3$ system has a µτ product of 1.0 x 10$^{-4}$ cm$^2$ V$^{-1}$ and sensitivity of 11 µC mGy$_{air}^{-1}$ cm$^{-2}$. The sensitivity was 10 times higher than with a-Se imagers,
but the device also has higher dark current.\[148\] Moreover, CH$_3$NH$_3$PbX$_3$ single crystals were fabricated and $\mu\tau$ product of $1.0 \times 10^{-2}$ cm$^2$ V$^{-1}$ was measured. The CH$_3$NH$_3$PbBr$_3$ perovskite single crystal device with a thickness of 2-3 mm has 16.4% detection efficiency under 50 KeV X-rays, a 0.5 $\mu$Gy$^{-1}$ dose rate and 80 $\mu$C Gy$^{-1}$ air cm$^{-2}$ sensitivity.\[144\]

Indirect conversion was achieved with scintillators fabricated using various MHPs based on their intrinsic and extrinsic luminescence properties. The light output of CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbBr$_3$ and (EDBE)PbCl$_4$ single crystals was measured in 10-300 K range. It was observed that CH$_3$NH$_3$PbBr$_3$, and CH$_3$NH$_3$PbI$_3$ show a light output of 150000 photons/MeV at 10 K, whereas, (EDBE)PbCl$_4$ perovskite show a light output of 120000 photons/MeV at 130 K.\[149\] CH$_3$NH$_3$PbBr$_3$ crystals exhibit narrow emission at 560 nm under X-rays excitation with high temperature dependence: its light yield is 90000 ± 18000 phonon/MeV at 77 K and 116 000 ± 23000 photons/MeV at T = 8 K, its decay time is 0.1 ns.\[150\]

All inorganic MHPs demonstrated high carrier mobilities, enhanced stability and low ionic migration compared to the hybrid MHPs. Therefore, high sensitivity can be observed in all inorganic MHPs based X-ray detector.\[141\] The X-rays can interact directly with CsPbBr$_3$ QDs to produce a radioluminescence (RL) effect. A CsPbBr$_3$ QD solution in toluene and n-hexane has a linear response to the X-rays from a 20-60 kV beam current, showing promising scintillation characteristics for X-ray imaging.\[151\] Later on, CsPbBr$_3$ NCs were also used for indirect X-ray detection due to high PL quantum yield of over 95%. The indirect scintillation film was fabricated by photopolymerization of a mixture of perovskite NCs and methyl methacrylate with a photoinitiator. A light yield of 177000 photons/MeV was observed for CsPbBr$_3$ NCs scintillator which is much higher than a GOS scintillator under the same conditions.\[148\] Similarly spatial resolution of a CsPbBr$_3$ NCs scintillator was found to be 6.2 lp mm$^{-1}$ with faster response time of 200 ns and
high stability under >40 Gy\textsubscript{air} s\textsuperscript{-1} of X-ray exposure\textsuperscript{[152]} The dose rate of X-ray detection was further dropped to 13 nGy s\textsuperscript{-1} for CsPbBr\textsubscript{3} NCs\textsuperscript{[153]} which is 420 times lower than with typical X-ray diagnostic devices (5.5 µGy s\textsuperscript{-1})\textsuperscript{[135]} Moreover, this scintillator has fast response with a scintillation decay time of 44.6 ns. X-ray phase-contrast imaging was assessed by implanting metal needles in the green scarab beetle with background substrates made of CsPbBr\textsubscript{3} NCs. 2.0 line pairs per millimeter spatial resolution was observed to\textsuperscript{[153]} The CsPbBr\textsubscript{3} NCs show high photoluminescence quantum yield and 20 fold accelerated radiative decay time compared to various other colloidal QDs\textsuperscript{[153-154]}

Lead free double perovskite Cs\textsubscript{2}NaEuCl\textsubscript{6} shows a light yield of 46600 photons/Me under 50 KeV X-ray photon energy with 3.45 m Gy\textsubscript{air} s\textsuperscript{-1} dose rate. However, this material has long afterglow lifetime and thermally quenched photoluminescence. Moreover, the light yield was low compared to CsPbBr\textsubscript{3} based scintillators\textsuperscript{[155]}

Lead free MHPs were also used for scintillator applications. Zhao et al.\textsuperscript{[156]} reported a lead free Ru\textsubscript{2}CuCl\textsubscript{3} perovskite scintillator. With lower mass density, Ru\textsubscript{2}CuCl\textsubscript{3} has lower absorption and light yield of 16600 photons per MeV and large flicker response (48.6 nGy\textsubscript{air} s\textsuperscript{-1} - 15.7 nGy\textsubscript{air} s\textsuperscript{-1}). The detection limit is about 88.5 nGy\textsubscript{air} s\textsuperscript{-1} which is quite lower and has potential for medical and safety applications. Rb\textsubscript{2}CuBr\textsubscript{3} 1D perovskite has high light yield of 91056 photons/MeV. This high light yield in 1D lead free perovskite is due to high carrier confinement, 98.6% PLQY in violet region with negligible self-absorption from self-trapped exciton emission and strong X-rays absorption capacity\textsuperscript{[157]}

2D MHPs show good stability under ionizing radiations. Moreover, the presence of lead and iodine in the MHPs allow high mass density to efficiently absorb X-rays\textsuperscript{[155, 158]} Thus, scintillators based on 2D MHPs show reduced energy loss and slow response time due to self-absorption. Cao et
al.\textsuperscript{[159]} reported the fabrication of \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{SnBr}_4\) based scintillator with almost 100\% quantum yield and long decay time of around 3.34 \(\mu\)s. The CCD camera device has a sensitivity of 104 nGy\textsubscript{air} s\textsuperscript{-1}.

### 5.4 Gamma-Ray Detection

Gamma rays have strong penetration power owing to high energy compared to X-rays. MHPs show strong stopping power to incident gamma rays with attenuation coefficients around 0.09 cm\textsuperscript{-1} at 662 KeV.\textsuperscript{[160]} Besides this intrinsic stopping power for gamma rays, the facile growth of up to centimeter size single crystals can be achieved.\textsuperscript{[122]} The first gamma ray detector based on MHPs was a FAPbI\textsubscript{3} (Formamidinium lead triiodide) single crystal.\textsuperscript{[161]} This MHPs based single crystal has high \(\mu\tau\) product of 1 \(\times\) 10\textsuperscript{-2} cm\textsuperscript{2} V\textsuperscript{-1}. The designed device shows considerable response to 59.6 KeV gamma rays.\textsuperscript{241} But the FAPbI\textsubscript{3} single crystal was thermodynamically unstable at room temperature. Moreover, large crystal size and high bulk resistivity is required for strong gamma ray stopping power and small dark current. Therefore, the high energy gamma ray spectrum cannot be attained using FAPbI\textsubscript{3} crystals.\textsuperscript{[161]}

The polarization effect is unfavorable for good gamma ray detection. This effect also explains the dark current drift.\textsuperscript{[162]} Ion migration has been associated with the polarization effect in gamma ray detecting materials.\textsuperscript{[163]} Thus, energy spectrum and dark current stability of the devices can be monitored by the degree of polarization.\textsuperscript{[164]} In the case of MHPs, ion migration has been observed through grain boundaries in polycrystalline films.\textsuperscript{[165]} Moreover, ion migration can also occur in single crystals depending on the quality, composition of crystals and applied field. For, example, the iodide based MHPs shows more ion migration than the bromide based MHPs. To achieve less ion migration, a FAPbI\textsubscript{3} single crystal was alloyed with Cs\textsuperscript{+} and Br\textsuperscript{-} ions to get mixed composition.
The resultant mixed composition single crystal results in the stabilization of black phase and has a \( \mu \tau \) product of \( 1.2 \times 10^{-1} \text{cm}^2 \text{V}^{-1} \).[166]

The resistivity of MHPs can be increased by dopant composition. The alloying of \( n \)-type \( \text{CH}_3\text{NH}_3\text{PbCl}_3 \) into \( p \)-type \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) perovskite to achieve a mixed halide composition in perovskite single crystal reduces the self-doping level. The increase in Cl\(^-\) ion in the mixed halide perovskite changes the \( p \)-type character into \( n \)-type. The perovskite single crystal with \( \text{CH}_3\text{NH}_3\text{PbBr}_{2.94}\text{Cl}_{0.06} \) composition has the lowest charge carrier concentration. The \( \mu \tau \) product was improved from \( 1.2 \times 10^{-2} \) to \( 1.8 \times 10^{-2} \text{cm}^2 \text{V}^{-1} \). A bulk resistivity of \( 3.6 \times 10^9 \ \Omega \text{cm} \) was also observed for \( \text{CH}_3\text{NH}_3\text{PbBr}_{2.94}\text{Cl}_{0.06} \) perovskite single crystals.[128]

Energy resolution is an important feature of X-ray detection materials to get color-based information from the X-ray images. Energy resolution can be obtained in the single photon counting mode by using the direct correlation between the energy of absorbed X-ray photons and the total number of excited electron hole pairs.[167] MHPs are quite capable to provide energy resolution. High quality CsPbBr\(_3\) single crystals grown by melt method have shown a good \( \mu \tau \) product of \( 1.34 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \). This single crystal has 3.9\% energy resolution[168] which is comparable or better than the commercially available NaI(Tl) scintillator.[140]

Compared to 3D structures, the binding energy of excitons in the 2D structures is four time larger and therefore, confined excitons have faster decay and higher light yield.[169] A \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4\) single crystal based scintillator has high light yield of 14000 photon/MeV under gamma-ray irradiation and very fast decay time of 11 ns. Moreover, the light yield is proportional to the gamma-ray energy in the 122–662 KeV range. But, these \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4\) single crystals has shown low energy resolution due to the ununiform crystal and self- absorption of exciton in the inorganic layers.[170] The improved light yield and
energy resolution was observed in CH$_3$NH$_3$PbBr$_{0.05}$Cl$_{2.95}$ single crystals based scintillators fabricated on the surface of SiPM. The light yield was found to be 18000 photons/MeV with energy resolution of 10.5±0.4% under 662 KeV $^{137}$Cs gamma rays.[171]

**Beta-rays detection**

Yu et al.[124] reported the detection of β-rays using 2D layered MHP scintillator. Different organic cation-based compositions show good scintillator performance. Moreover, Mn ion doping further enhances the β-rays capturing efficiency via action as an emitting center with no self-absorption. Under higher radiation dose of 10kGy, the scintillator remains stable and hysteresis free. Likewise, the synthesized 2D layered hybrid perovskites also show water stability.

**Figure of Merit**

**Scintillation efficiency:** Scintillation efficiency of X or gamma-rays depends on the intrinsic and extrinsic characteristics of the materials. The total number of UV-Vis photons ($N_{ph}$) generated during the scintillation conversion by the incoming X or gamma-ray photons. $N_{ph}$ can be calculated as follows:

$$N_{ph} = \frac{E}{\beta E_g} \times SQ$$

Where, $E_g$ is the forbidden gap of materials, $S$ is the quantum efficiency of transport and $Q$ is the quantum efficiency of the luminescence stage, $\beta$ is a phenomenological parameter. Moreover, the relative efficiency can be calculated as:

$$\eta = \frac{E_{\text{vis}} N_{ph}}{E}$$

Where, $E_{\text{vis}}$ is the energy of produced UV-Vis photons.
The relative scintillation efficiency can be calculated by measuring the radioluminescence spectrum under gamma or X-ras excitation in steady state mode and to compare the results with a standard scintillator sample examined under the same conditions.[136, 172]

Two methods are generally adopted to measure the overall efficiency.

i) Relative method: overall efficiency of the material can be compared with a standard sample.[173]

ii) Radioluminescence spectrum: radioluminescence of the material is measured under certain X or gamma-rays excitation.[174]

**Light Yield:** light yield is the overall conversion efficiency. The light yield is always less than $N_{ph}$ given in equation 16.

To measure the light yield, a pulse of X or gamma rays excites the sample and measurements are operated in the photon counting mode. The light flash of high energy radiation is converted into electrical current by the photodetectors.

Complete absorption of the incident light is required to get the photopeak. Position of the photopeak will define the light yield and the full width half maximum (FWHM) is used to determine the energy resolution.[175] Position of the photopeak is the measure of the total number of photogenerated electrons in the photodetectors.[176]

**X-ray or gamma ray stopping power (attenuation coefficient):** the high energy radiation stopping power of materials depends on the materials density ($\rho$) and effective atomic number ($Z_{eff}$) through the relationship:

$$\alpha \propto \frac{\rho Z^4}{E^3}$$ (18)
High effective atomic number and high density of the materials is desirable for high stopping power and therefore, thin layer or a small amount of scintillator material is required.\textsuperscript{[177]}

**Decay Time:** Decay time of the scintillator depends upon the transport and luminescence stages. These two stages are very slow compared to the conversion step. Moreover, the energy transfer or nonradiative quenching processes decreases the quantum efficiency (Q) and thus light yield become smaller. The emission intensity $I(t)$ is:

$$I(t) \sim \exp \left[ -\frac{t}{\tau} \right]$$ \hspace{1cm} (19)

Where, $\tau$ is the decay time. The radiative decay of Wannier excitons in direct semiconductors results in the fastest emission transitions.\textsuperscript{[177]}

Decay time can be measured by pulsed X- or gamma rays based excitation and registration of the emission decay time by time correlated single photon counting.\textsuperscript{[172, 178]} From ps to $\mu$s decay can be measured in this method.

**Spectral matching between the scintillator emission spectrum and photodetector:** The basic requirement for selection of scintillator and photodetector materials is the spectral match between the emission band of the scintillator and spectral sensitivity of the photodetector.\textsuperscript{[172]}

**Chemical and mechanical stability:** The hygroscopicity of materials is the major concern that limits the long-term operation of various materials in scintillation applications under real operating conditions. The mechanical stability of single crystals is also a major concern.\textsuperscript{[177]}

**Radiation resistance:** The performance instability caused by the induced absorption results from color center creation under material irradiation. The overlap of induced absorption with emission
spectra results in a reabsorption that lowers the light yield. Radiation resistance can be measured as:

\[
IA(\lambda) = \frac{1}{d \ln \left( \frac{T_{irr}(\lambda)}{T_0(\lambda)} \right)}
\]

(20)

Where, \(d\) is the thickness of the material, \(T_{irr}\) is the transmittance under irradiation and \(T_0\) is the transmittance before irradiation.\(^{[179]}\)

6. Conclusion and outlooks

MHPs have been explored in various application such as photovoltaics, light emitting diodes, lasers, photocatalysis due to their interesting specificities. In this review, the physical and photophysical properties of MHPs were discussed. The physical and photophysical properties of MHPs are responsible for their wide range applications in various fields. Besides aforementioned applications, MHPs have also been explored for fluorescent sensing applications from various external analytes. These analytes show various interactions with MHPs structures that result in change of fluorescence signals like enhancement/quenching or shifting.

In this review, the basics of electronic structure and origin of the optical properties of MHPs were discussed. Based on these properties, MHPs can be elaborated for fluorescent sensing applications. The underling mechanism for fluorescence quenching, enhancement and shifting was presented. Fluorescence quenching was observed in sensing studies of explosive materials, temperatures and metal ions via FRET, electron transfer and thermal quenching. Moreover, fluorescence shifting was observed in sensing of anions like chlorides and iodides via ionic exchange reactions. Likewise, structure deformation is another reason for fluorescent responsive signals.
The overview of performance of MHPs based fluorescent sensing of nitrophenols, humidity, temperature, pH, metal ions, anion, and so on shows that MHP exposure to these external factors results in reversible processes like phase change, intercalation-decalation, adsorption-desorption, and hydration-dehydration. Besides reversible process, some irreversible process like ion (cation/anion) exchange happens. With the recent upsurge in MHPs sensing applications, improvement in detection limit for all external factors with extended sensitivity and selectivity was observed. Figure of merits for the sensing application were also discussed in this section. Despite the overwhelming potential of MHPs for fluorescent sensing applications, various remaining challenges still need further exploration.

- **Stability:** Stability is one of the main challenges that limits practical applications of MHPs for sensing applications. Various strategies were adopted such as doping, surface passivation and heterostructure formation to enhance the stability of MHPs. Afterwards, these stable materials still need exploration for sensing applications. In most studies, the primary task was to explore the sensing response of MHPs rather than to determine the least value of detection limit. Moreover, lower dimension MHPs have shown enhanced stability compared to 3D MHPs without effecting sensitivity. Porous polymer composites with MHPs were also used to control the analyte exposure level and tune the sensing capability. The design and development of stable MHP based fluorescent sensors, specially in water-based systems, is in high in demand and is required for exploration.

- **Limit of detection and response measurement:** Although, MHPs have shown good LOD for various analytes, it is still lower than for various other sensing probes. The limit of detection depends on the exposure time, analyte nature and MHP composition. For example, the lead halide perovskite-based system has good emission response both in
enhancement, quenching and shifting of fluorescence signals. But the LOD is large in the case of lead-free perovskite system. Moreover, the progress in this filed is still slow and needs faster exploration and development. The MHPs fluorescence response is affected by the operational temperature. Therefore, the MHPs based system must be optimized to attain room temperature responses.

- **Mechanistic investigation**: MHP based fluorescent sensing needs detailed exploration of the underlying mechanism. Most reports lack detailed mechanistic investigation, which raises questions and difficulties for further advancement in this filed.

- **Biosensing**: fluorescent biosensing using MHPs is one of the potential fields that should be explored and developed. Therefore, attention in this filed in required to develop stable MHP fluorescent sensors. Although lead halide perovskites are performing well in fluorescent sensing applications, lead toxicity limits their application in the biological and other real-life applications. Therefore, research in the field of lead free MHP nanomaterials is highly desirable.

- **Composites**: the incorporation of matrices like polymers, metal organic frameworks etc in MHPs to develop fluorescent sensors needs more attention. Likewise, the exploration of colorimetric sensing is required.

The detection capability of MHPs for high energy X and gamma radiation was also explored. In this context, MHPs have emerged as a new generation of high energy radiation detectors. The lower detection dose rate with MHPs is still very high compared to other known materials. Thus, improvement on the lowest detection limit is still under scrutiny. One of the methods to increase charge extraction in detectors is to increase the polarization bias, but this also increases noise. MHPs show high dark current density compared to the commercially available α-Se based
detectors. The high dark current density is due to resistivity issues. Therefore, material design and compositional modifications are required in MHPs materials. Moreover, the lowest X-ray dose rate is limited by the background charge carrier concentrations. To overcome this issue, the deep mechanism of self-doping in MHPs should be better understood. Heat and moisture can degrade MHPs materials, environmental effects on high energy radiation detection applications of MHPs remain to be explored.

In case of spectroscopy applications, MHP material performance is much lower than CZT single crystal gamma-ray detectors. One of the reasons for the low energy resolution of MHPs is the lower bulk resistivity that needs to be addressed. Moreover, the size of high-quality single crystals is still not large enough. Moreover, long-term continuous operation of MHP based detectors for X and gamma-rays is another challenge due to polarization effects at room temperature. To achieve high performance in the field of scintillators, some challenges that need to be addressed are listed below.

- **Stability**: the performance of scintillators is largely affected by stability related issues. MHPs are sensitive to environmental factors like heat, humidity and incident light and undergo phase transitions that result in the formation of carrier traps under high energy radiations. Therefore, research must focus on addressing such stability issues.

- **Self-absorption and light yield**: MHP based scintillators have shown a low light yield due to small Stokes shift and self-absorption effect. Self-absorption results in low light yield and degraded energy resolution, although measures were taken to overcome this issue. For example, the scintillator can be thin and suitable halide ions reduce self-absorption effect.\[^{171}\] MHPs scintillators with high mass density can further increase the elastic scattering and energy relaxation rates to shorten the distance between holes and electrons.
Self-absorption can be decreased by shifting the emission to longer wavelength and increasing the Stokes shift. Therefore, low self-absorption, enhanced Stokes shift, and high photoluminescence quantum yield are important to improve the light yield. Self-absorption can be reduced in 2D layered MHPs scintillators. However, lower optical yield and slow response is associated with 2D layered MHPs.\textsuperscript{[170]} Thus, there can be specialties that 2D layered MHPs can perform well in radiation detection applications.

- **Scintillation performance**: with the increase of operating temperature, reduction in the efficiency of MHP scintillators is observed. Thus, the operating temperature must be below 130 K.\textsuperscript{[150]} Therefore, it is highly required to enhance device performance at higher temperatures.

- **Low resolution**: light scattering in MHP scintillators results in low device performance. Various reports focused on controlling this light scattering by controlling the grain size of the film to improve the resolution.\textsuperscript{[180]} Moreover, pixel size and light scattering result in charge trapping that also lowers the resolution.

- **Fabrication**: to improve the performance of MHPs scintillators, the fabrication of high-quality films with controlled morphology and crystallization is important. Therefore, the exploration of suitable method for the fabrication of perovskite films with large gain size and high crystallinity is crucial for achieving high performance devices.

- MHP scintillators for β-ray detection were less explored. Therefore, extensive efforts are highly required in this field.

Considering the present review of overall performance and mechanisms, it can be concluded that MHPs performances in the fluorescent sensing and high energy radiation detection both by direct
and indirect methods need further improvement which can be achieved by considering the excited properties of MHPs and the exploration of new MHPs compositions.

References


