Development of Organic Metal Halide Hybrids with Short Emission Lifetime for X-Ray Scintillation

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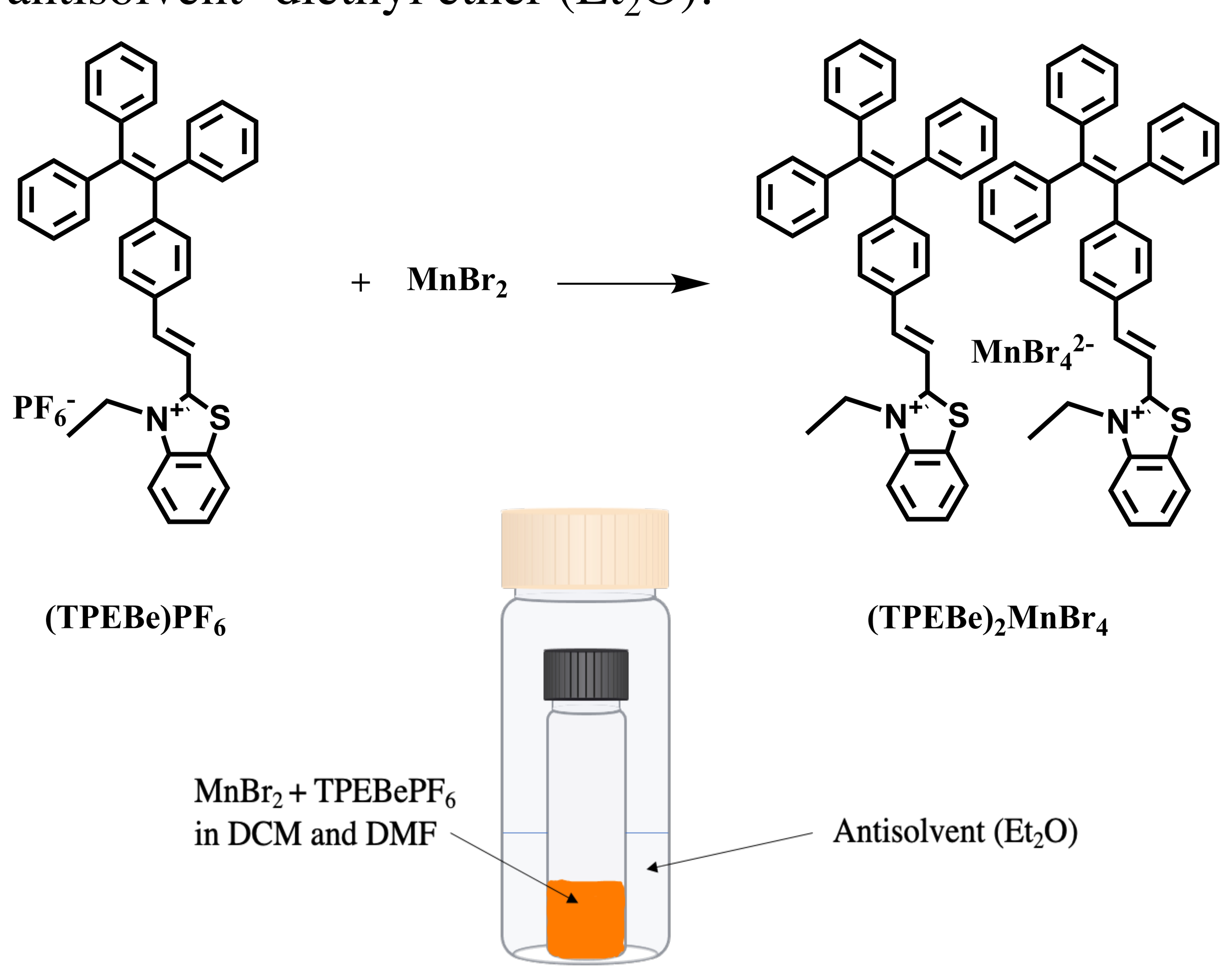
Abstract

- Scintillator materials, which can emit light under X-ray excitation, have gained a lot of research attention due to their wide range of applications, such as medical imaging via PET scans and X-rays as well as security applications through radiation detectors and X-ray scanners.
- Recent organic metal halide hybrids, such as tetraphenylphosphonium manganese (II) bromide ($(C_{24}H_{20}P)_2MnBr_4$), have been found to be excellent scintillator materials.
- Their relatively long lifetime is not desirable for many applications. This lifetime can be shorted by the synthesis of a material that replaces the tetraphenylphosphonium ($C_{24}H_{20}P^+$) cation with low band gap cations, such as benzothiazolium-functionalized tetraphenylethene ($C_{37}H_{30}NS^+$) ($TPEBe^+$).
- The antisolvent diffusion approach is used to synthesize $(TPEBe)_2MnBr_4$, which is found to exhibit orange emission with a short lifetime, thus exhibiting more useful properties for scintillator applications.

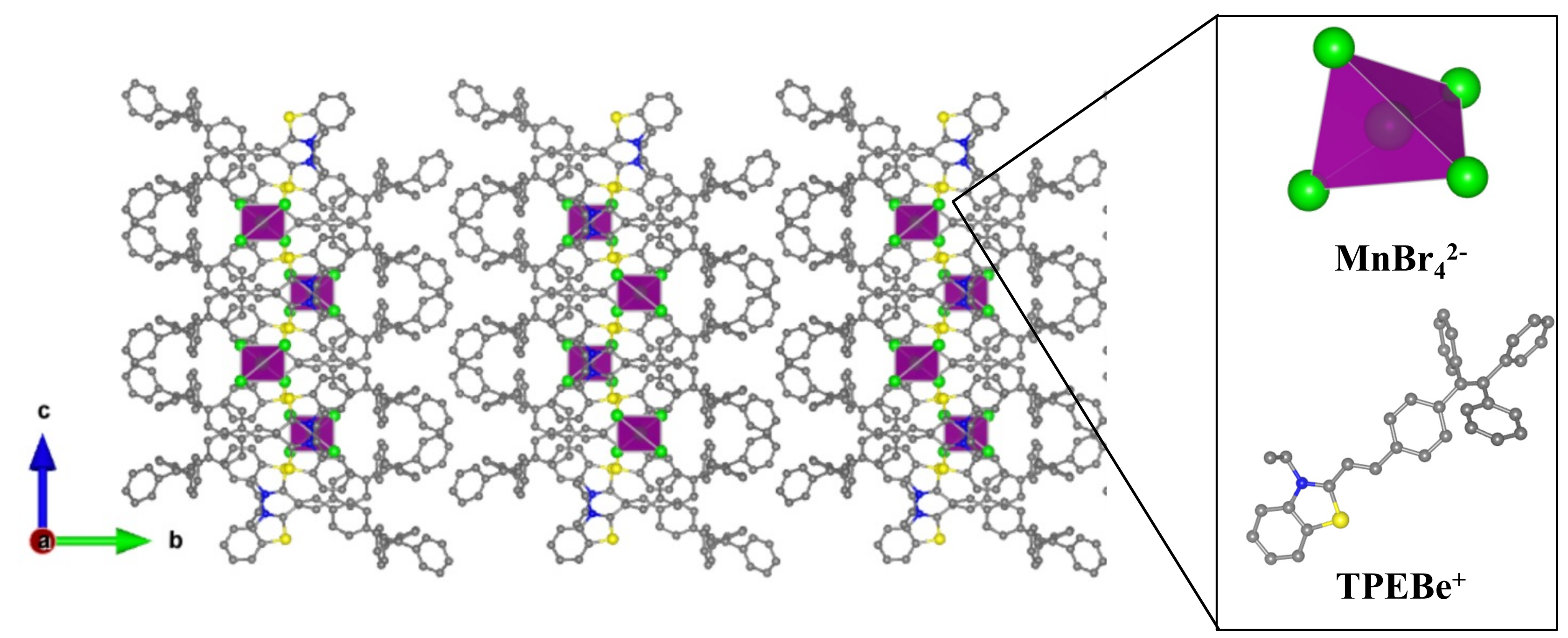
Methods

The synthesis of $(TPEBe)_2MnBr_4$ crystals is carried out using vapor diffusion which is a common crystallization technique involving the diffusion of an antisolvent into the dissolved reactant solution (see image below). For this reaction, 20mg $(TPEBe)PF_6$ is dissolved in 1.5mL of dichloromethane (DCM) in a small vial. Then, a stock solution of $MnBr_2$ is prepared by dissolving 33mg of $MnBr_2$ in 1mL dimethylformamide (DMF), of which 200μL is added to 1.5mL of the DCM solution. The solution is mixed, and the small vial is placed in a larger vial with 5mL antisolvent- diethyl ether (Et_2O).



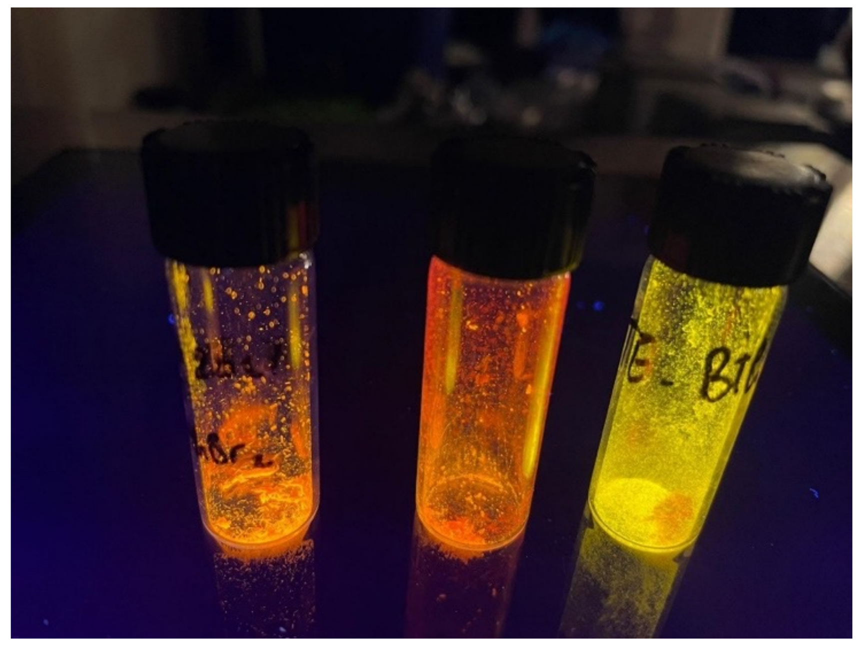
Results

Single Crystal Structure of $(TPEBe)_2MnBr_4$

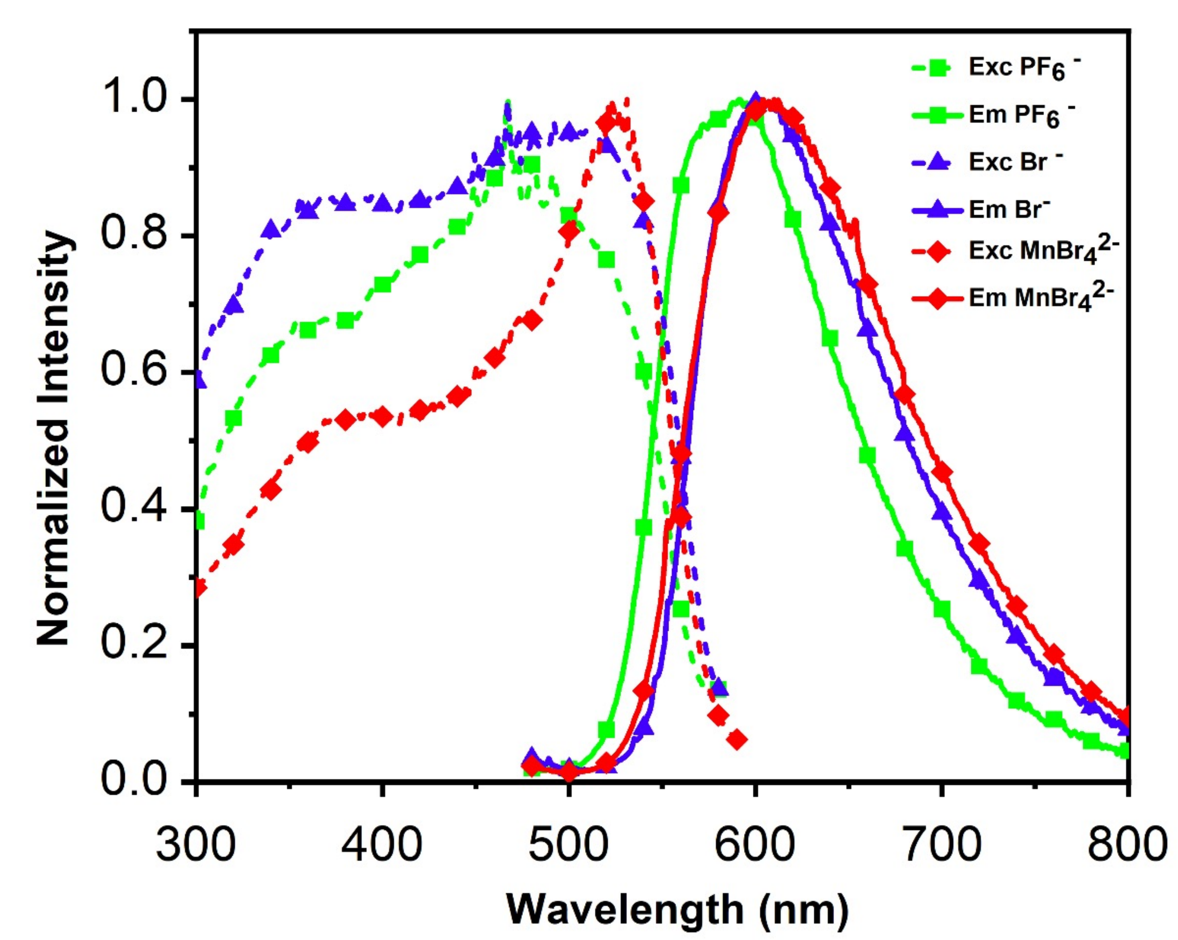


The single crystal structure of the synthesized material shows that it is composed of tetrahedral $MnBr_4^{2-}$ surrounded by photoactive organic cations. Purple: Mn, Green: Br, Grey: C, Yellow: S, Blue: N (H atoms omitted for clarity)

Image showing $(TPEBe)_2MnBr_4$, (TPEBe)Br, $(TPEBe)PF_6$ (left to right) under UV excitation (320nm)



Photoluminescence Excitation and Emission Spectra



Discussion

Summary of results:

- All materials exhibit broad featureless emissions in the orange-red region.
- The emission maxima of (TPEBe)Br and $(TPEBe)_2MnBr_4$ are at 610 nm (redshifted (λ_{max})) while that of $(TPEBe)PF_6$ is at 600 nm.
- The emission of $(TPEBe)_2MnBr_4$ is similar to that of (TPEBe)Br, as no green emission corresponding to $MnBr_4^{2-}$ anions is observed.
- The excited-state decay lifetimes of these materials range between 0.93 and 1.11 nanoseconds.
- The photoluminescence quantum efficiency (PLQE) of these materials range from 10% to 48%.
- The broad featureless emission is assigned to intramolecular charge transfer excited state.
- The nanosecond time scale indicates the fluorescence character of the emissions.
- The absence of the green emission of the $MnBr_4^{2-}$ indicates that the emission is fully quenched by the photoactive cations.

Conclusion

- Organic metal halide hybrids with short lifetimes have been synthesized and characterized.
- The complete structural and photophysical properties must be further tested.
- Future work will focus on the evaluation of their scintillating properties.

References

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