**Supporting Information**

# High-Temperature Ferroelectricity and Photoluminescence in a Hybrid Organic-Inorganic Compound: (3-Pyrrolinium)$MnCl_3$

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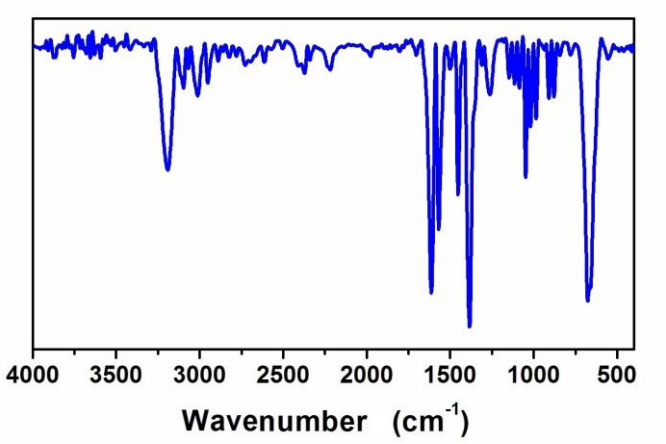


**Figure S1**. IR spectrum for (3-pyrrolinium)$MnCl_3$ (**1**).

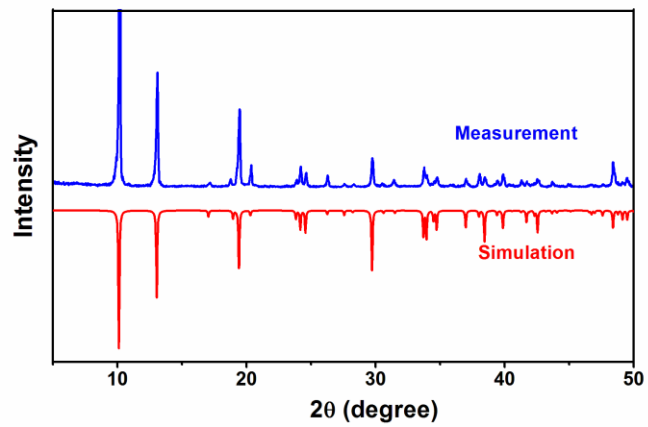


**Figure S2.** Pattern of the powder X-ray diffraction (PXRD) of (3-pyrrolinium)$MnCl_3$ (**1**), verifying the purity of the bulk phase.

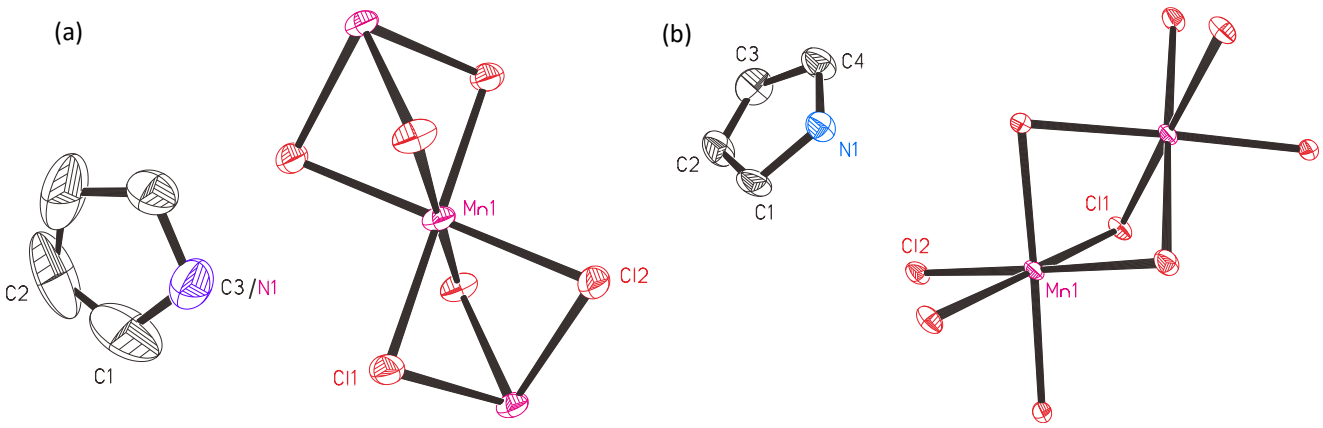


**Figure S3.** Ellipsoid drawings of symmetric units of (3-pyrrolinium)$MnCl_3$ (**1**) in (a) the HTP at 413 K and in (b) the LTP at 273 K. In (a), the site of N1/C3 is occupied equally by C and N atoms. Atoms not labeled are generated by symmetry operator. Displacement ellipsoids were drawn at 30% probability level.

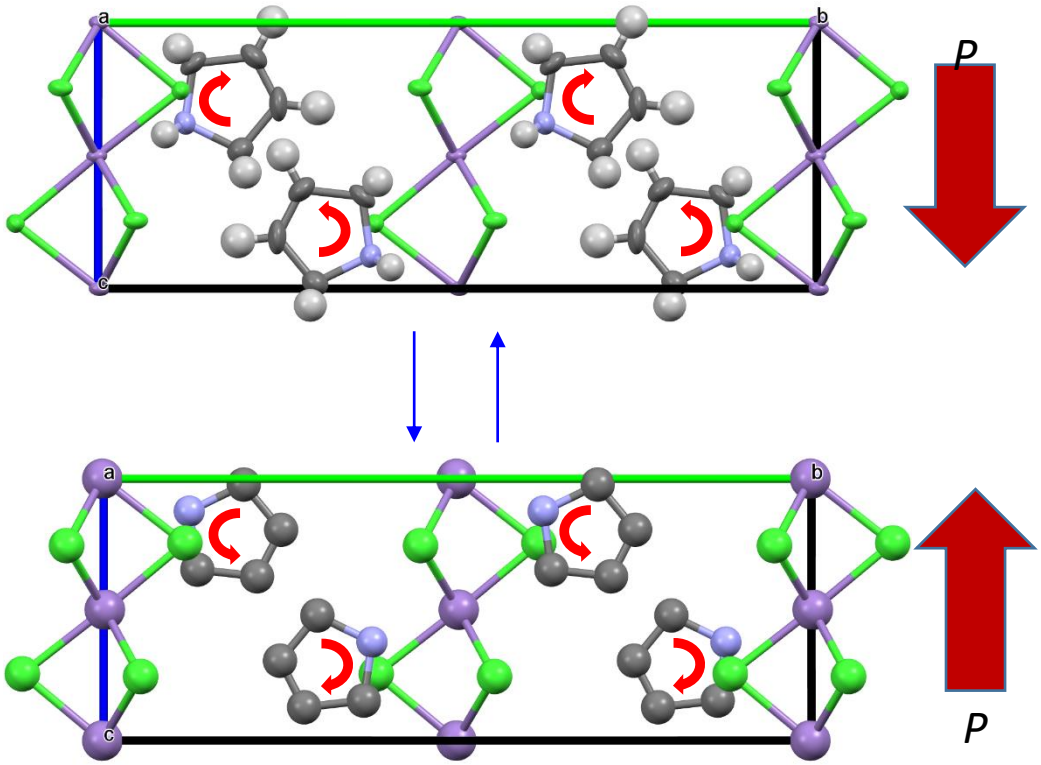


**Figure S4.** Schematic drawing of the realization of polarization reversal in (3-pyrrolinium)$MnCl_3$ (**1**).

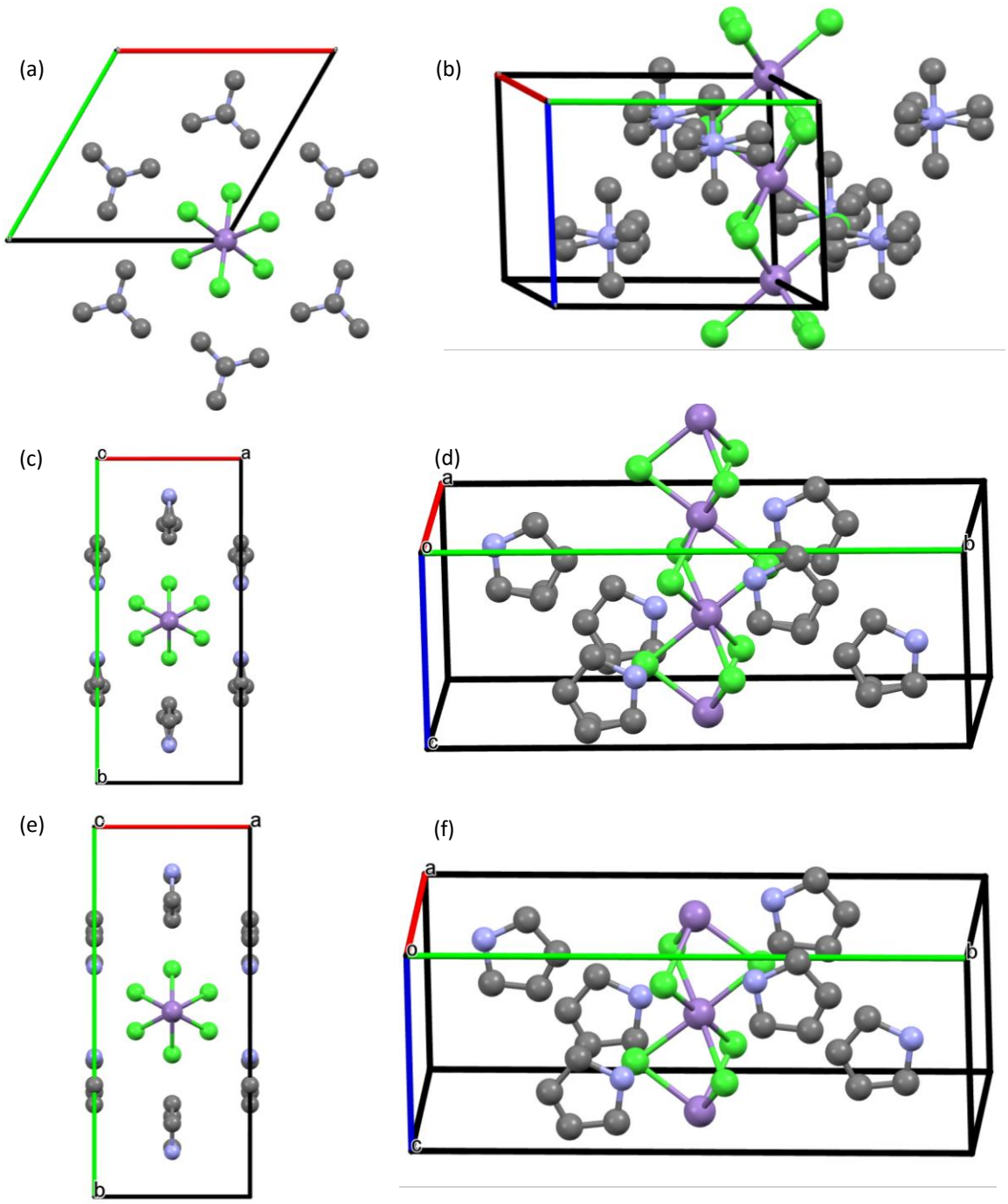


**Figure S5.** Comparison of crystal structures of (tetramethylammonium)$MnCl_3$ (a,b), (pyrrolidinium)$MnCl_3$ (c,d) and (3-pyrrolinium)$MnCl_3$ (**1**) (e, f). H atoms were omitted for clarity.

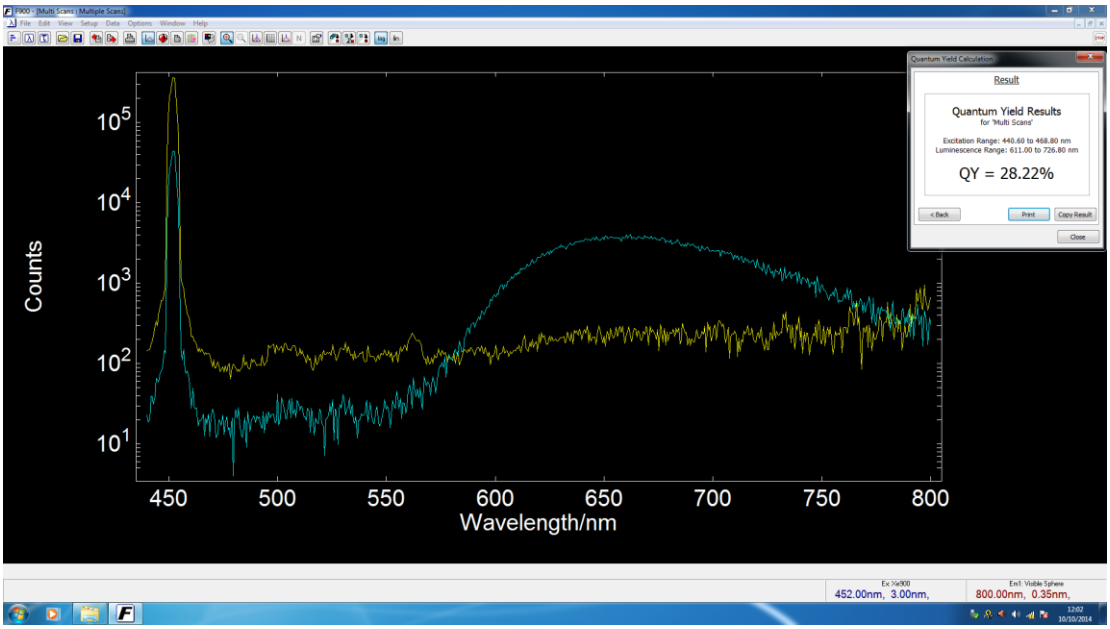


**Figure S6**. The quantum yield measurement of (3-pyrrolinium)$MnCl_3$ (**1**), giving a quantum yield of 28.22%.

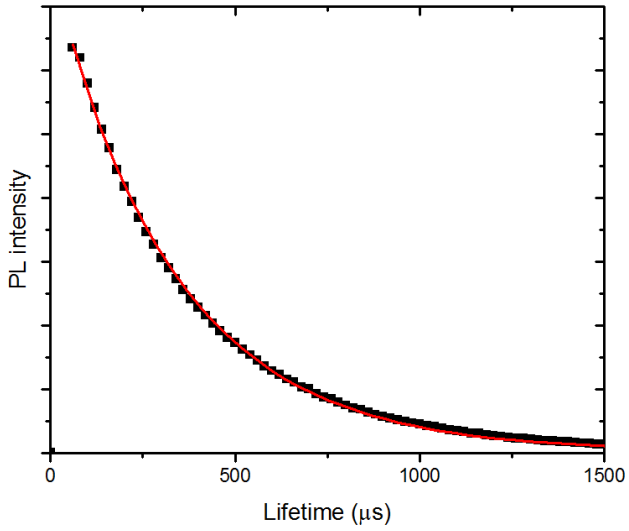


**Figure S7**. The lifetime measurement of (3-pyrrolinium)$MnCl_3$ (**1**). The fitted lifetime is 333.6 μs.

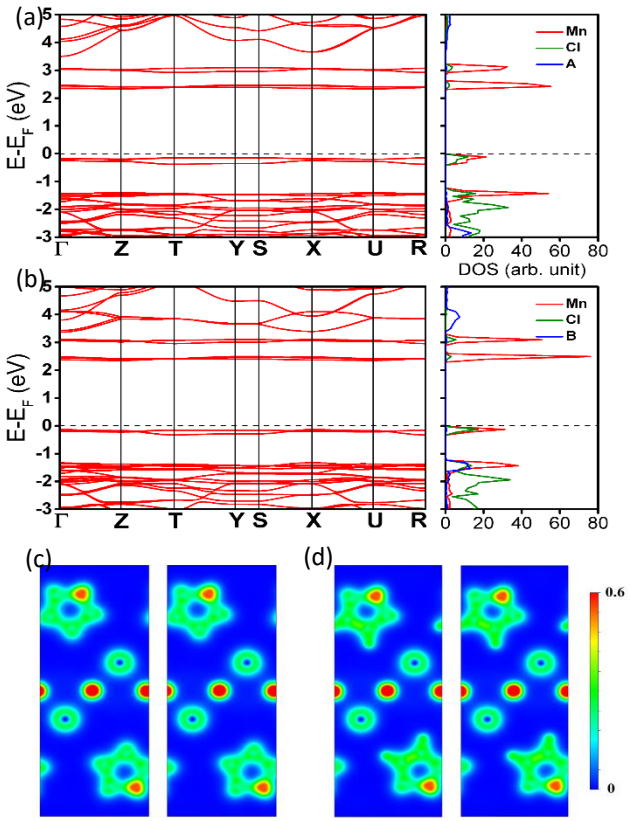


**Figure S8.** The band structure and corresponding density of states (DOS) of (a) $AMnCl_3$ and (b) $BMnCl_3$. Highest occupied band and lowest unoccupied band of (c) $AMnCl_3$ and (d) $BMnCl_3$. The unit of the scale is e/bohr$^3$. A = (pyrrolidinium), B = (3-pyrrolinium).

**Table S1.** Fitted Curie constants at different frequencies.

| Frequence | $C_{para}$ (K) | $C_{ferro}$ (K) | $C_{para}/C_{ferro}$ | $T_0$ (K) |
|---|---|---|---|---|
| 1 MHz | 4086 | 1614 | 2.53 | 374.2 |
| 100 kHz | 4953 | 2000 | 2.48 | 374.6 |
| 10 kHz | 5906 | 2418 | 2.44 | 375.3 |
| 5 kHz | 6134 | 2578 | 2.38 | 375.5 |
| 1 kHz | 6706 | 3163 | 2.12 | 376.1 |
| 500 Hz | 7085 | 3374 | 2.10 | 376.3 |

**Table S2.** Comparison between ground state of **(**pyrrolidinium**)**$MnCl_3$ and **(**3-pyrrolinium**)**$MnCl_3$.

| Property | **(**pyrrolidinium**)**$MnCl_3$ | **(**3-pyrrolinium**)**$MnCl_3$. |
|---|---|---|
| Cation | pyrrolidinium | 3-pyrrolinium |
| a / Å | 7.65 | 7.36 |
| b / Å | 17.25 | 17.49 |
| c / Å | 6.48 | 6.47 |
| Magnetic order | AFM | AFM |
| Magnetic moment /$\mu_B$ per Mn atom | 4.4 | 4.4 |
| $P_s$ / $\mu C \cdot cm^{-2}$ | 8.04 | 8.04 |
| Charge transfer /electron per cation | 0.81 | 0.82 |

*The cell constants are fixed to experimental value during optimization.