Tunable Emission Properties of Manganese Chloride Small Single Crystals by Pyridine Incorporation

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ABSTRACT: Pure transition-metal compounds seldom produce luminescence because of electron correlation and spin–spin coupling. The Pb-free perovskite materials, \( \text{C}_6\text{H}_{12}\text{N}_2\text{MnCl}_4 \) and \( \text{C}_6\text{H}_8\text{NMnCl}_4\cdot\text{H}_2\text{O} \), were obtained by using pyridine-implanted manganese chloride lattices. The single-crystal X-ray diffraction indicates their different crystal structures. In \( \text{C}_{10}\text{H}_{12}\text{N}_2\text{MnCl}_4 \), \( \text{MnCl}_4 \) cocoordinated with two pyridine molecules forms a lattice composed of independent mononuclear structures with paramagnetic behavior, which shows a clear emission band at 518 nm from the lowest d–d transition of a single Mn(II) ion in the octahedral crystal field. In \( \text{C}_6\text{H}_8\text{NMnCl}_4\cdot\text{H}_2\text{O} \) crystal, \( \text{MnCl}_4 \cdot (\text{H}_2\text{O})_3 \) octahedron-cocooordinated with less pyridine molecules than 2 lead to formation arris-share linear chains of Mn-ion octahedra, which give emission band at 620 nm due to the ferromagnetic Mn pair, and ferromagnetism. Pyridine incorporations in the transition-metal halide lattice provide a new channel to modulate the electron correlation and obtain materials with both luminescence and ferromagnetic properties.

1. INTRODUCTION

Halide perovskites have recently attracted great attention because of their remarkable optoelectronic properties such as long electron diffusion performance, excellent absorption coefficients, and splendid light-emitting and photovoltaic performance.\(^1\)–\(^4\) This proves that the ionic crystal also can work as the functional or photonic material. Although they have such preeminent characteristics, most of the perovskite materials involved heavy metals such as Pb element, which is poisonousness to humans and the environment. Recently, the lead-free perovskite progress has been considered out of their nonpoisonous character.

Transition-metal binary compounds seldom produce luminescence because of the electron correlation and spin–spin coupling.\(^5\) They usually exhibit antiferromagnetic behavior. The ternary transition-metal compounds such as perovskites possess rich electronic states and electronic properties but seldom luminescence except doping in semiconductors. Hence, it is astonishing to find a way to modulate the electronic structure of transition-metal compounds and transform them into a luminescent material, which will open a giant gate to rebuild the field of the optoelectronic technology.

Doping by transition metal ions like manganese makes perovskite materials show several new features: tunable luminescence, nonlinear optical molecular switching, and multiferroics, and sometimes these performances can coexist.\(^6\)–\(^10\) These remarkable properties make transition-metal-doped perovskites have potential applications in sensors, optical devices, piezoelectrics, and so forth.\(^11\)–\(^12\)

In addition, the inorganic part of inorganic–organic perovskite configuration in a certain direction separates the organic units to constitute low-dimensional folium, which provides dimensionality confinement for excitonics. That is to say, the inorganic–organic perovskite luminescence has a close-knit relationship to crystal field, originating from their polytropic structure such as \((\text{NH}_3\text{(CH}_2\text{)}_5\text{NH}_3\text{MnCl}_4)\) and \((\text{C}_6\text{H}_8\text{NMnBr}_4\text{)}\) and \((\text{C}_6\text{H}_8\text{NMnBr}_3)\).\(^13\)–\(^14\)

According to the ligand field theory, four ligands encircled an atom such as manganese and obtained an individual MnX\(_6\)\(^{2–}\) tetrahedra cluster, and the unit forms a determinant style while the around space is filled with the organic cations, so the tetrahedrally coordinated manganese ions with the infirm strength of field have an emblematic green emission.\(^15\)–\(^16\)

In this situation, the direct interaction within Mn ions can be avoided because of the large distance between adjacent Mn ions; therefore, the individual Mn ion dominates the optical transition. Six ligands surround a Mn atom to form a MnX\(_6\)\(^{2–}\)-independent octahedral unit. The cluster obtained a linear chain crystal structure by edge-share in a certain direction, and thus the distance in adjacent Mn ions reduced in this certain direction. But in the orthogonal direction, the organic molecules implant between Mn ions, the distance is enlarged to form an anisotropic crystal structure. For the Mn-ion chains, the structure of MnX\(_6\)\(^{2–}\) provides a confinement effect and...
influences the d–d transition and transition energy of Mn ions, in
which the MnX$_6^{4-}$ octahedral structure is shown as a red
emission due to the strong field strength. In our previous
work on Mn doping in ZnSe nanobelt, the emission band
tuned in doped diluted magnetic semiconductors causes by
manganese aggregated whether it is single Mn ion or multiple
Mn ions has been observed. Like ZnSe quantum dots doped by
manganese aggregated whether it is single Mn ion or multiple
work on Mn doping in ZnSe nanobelt, the emission band
transformation may also in
majority of the situations, a n dp r e s s u r e - i n d u c ep h a s e
organic cations govern the organic metal emissions in a
been observed in our previous work. It is worth noting that, the
organic cations govern the organic metal emissions in a
C5H6NMnCl3
C5H6NMnCl3 crystal emission at 518 nm attributes to Mn ion d
varied pyridine concentrations.

The crystal structure of C10H12N2MnCl4 and C5H6NMnCl3
C10H12N2MnCl4 crystal structure: (A) structure viewed
across the a axis and (B) general view. The Mn–Mn distance is
8028(9) Å.

Figure 2. C5H6NMnCl3·H2O crystal structure: (A) structure viewed
along the b direction and (B) general view. The Mn–Mn distance is
3.65 Å.

Table 1. Crystallographic Data of C5H6NMnCl3·H2O and
C10H12N2MnCl4

| parameter | comment | comment |
|-----------|---------|---------|
| formula   | C5H6Cl3MnNO | C10H12N2MnCl4 |
| Mn, g/mol | 259.41 | 356.96 |
| crystal system | monoclinic | triclinic |
| space group | P2$_1$/n | P1 |
| a/Å | 11.404(2) | 7.6243(15) |
| b/Å | 7.2734(15) | 8.0440(16) |
| c/Å | 11.807(2) | 12.562(3) |
| α/deg | 90 | 88.72(3) |
| β/deg | 102.99(3) | 83.85(3) |
| γ/deg | 90 | 80.07(3) |
| volume/Å$^3$ | 954.3(4) | 754.5(3) |
| Z | 4 | 2 |
| ρ calc, g/cm$^3$ | 1.806 | 1.571 |

In the C5H6NMnCl3·H2O crystal structure (the Cambridge
Crystallographic Data Centre deposition number is 1899261),
every Mn atom is encircled by five Cl atoms and a crystal
water, in which two Cl atoms share the edge that bonds with
the other adjoining Mn atoms, and a crystal water links the Mn
atom by a coordinate covalent bond as shown in Figure 1. The
Mn–Cl distance ranges from 2.4934(10) to 2.5877(6) Å;
meanwhile, the Mn–O distance is 2.2262(14) Å. The bond
angles surrounding the Mn atom ranges from 88.53(2) to
177.90(3) Å. It is much less than that in C10H12N2MnCl4.
In the single-crystal structure, MnCl3·H2O octahedrons arris-
share to form linear chains along the b axis, and pyridine
molecules fill in space while it is vertical with the b axis.

In the C5H6NMnCl3·H2O compound, the Mn ion has
sixfold coordination; five Cl atoms occupy five peaks of the
octahedron, of which four Cl ions arris-share with the near Mn
ion, and crystal water occupies the last peak by a coordinate
covalent bond with Mn ions. Two Mn ions form an Mn ion
chain, and it is the opposite ligand sites of the MnCl3·H2O cluster.
The Mn in C5H6NMnCl3·H2O is six-coordinated, and
its crystal structure space group, P2$_1$/n, belongs to monoclinic.

To enhance the dosage of pyridine, we acquire the
C10H12N2MnCl4 structure (the Cambridge Crystallographic
Data Centre deposition number is 1899261),
every Mn atom is encircled by five Cl atoms and a crystal
water, in which two Cl atoms share the edge that bonds with
the other adjoining Mn atoms, and a crystal water links the Mn
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every Mn atom is encircled by five Cl atoms and two pyridine molecules; it forms a unit octahedral cluster
structure of C10H12N2MnCl4, as shown in Figure 1. The Mn–
Cl distance ranges from 2.3532(10) to 2.3711(9) Å. The band
angles around the Mn atom change from 105.08(4)° to
112.68(3)°. These octahedral structures are layout directed at
the $a$ axis, which are different from the $C_{10}H_{12}NMnCl_3·H_2O$ structure, and the pyridine molecules fill up the space among the 2D structure along the plane of $c$ axis. Thus, Mn ions are kept sixfold coordinated with four Cl ions and two pyridines, and the adjacent Mn ions did not have direct Mn–Mn coupling. The crystal structure space group of the Mn 6-coordinated cluster is triclinic $P1$. These octahedra separated by pyridines in the crystal structure lead to a Jahn–Teller effect, making Mn ions show clear emission related to the allowed $d$–$d$ transition. The related single-crystal XRD data are shown in Figure 3.

![Figure 3](Image)

Figure 3. Simulated single-crystal structure XRD patterns of $C_{10}H_{12}NMnCl_3$ and $C_{10}H_{12}NMnCl_4·H_2O$.

Comparing the $C_{10}H_{12}NMnCl_3·H_2O$ and $C_{10}H_{12}NMnCl_4·H_2O$, the closest Mn–Mn distance in the $C_{10}H_{12}NMnCl_4·H_2O$ (7.6243(19) Å) structure is more than twice the Mn–Mn distance observed in $C_{10}H_{12}NMnCl_4·H_2O$ (3.6484(9) Å), and it has pointed out the distorted crystal fields are coordinated by Cl atoms and organic ligands, which also lead to Jahn–Teller distortion in the $C_{10}H_{12}NMnCl_4$ lattice. Moreover, direct Mn–Mn magnetic coupling shows up in $C_{10}H_{12}NMnCl_4·H_2O$, as shown in Figure 6B.

### 2.2. Optical Properties of $C_{10}H_{12}NMnCl_4$ and $C_{10}H_{12}NMnCl_4·H_2O$

In this work, we obtained the two single crystals ($C_{10}H_{12}NMnCl_4$ and $C_{10}H_{12}NMnCl_4·H_2O$); they can show different luminescence bands with different pyridine amounts incorporated in the MnCl$_2$ lattice. A pyridine molecule can occupy one site of Cl ions as the coordination ligand. Based on Reinhardts’s empirical rule, the most effective intersystem-crossing process needs the energy gap $\geq$5000 cm$^{-1}$. About the pyridine molecule, the ground state is $^4$A$_1$, a triplet state is located at 33 001 cm$^{-1}$, 3.68 eV, and it is higher than $^4$A$_1$ and $^4$E$_u$ states (23 256 cm$^{-1}$) of Mn$^{2+}$. In this situation, the ligand–metal ion energy transfer could occur, depending on their energy locations. Therefore, the absorbed photon energy by pyridine can transfer to the Mn$^{2+}$ ion effectively in the lattice. In another word, the singlet state of pyridine that is higher than the low-lying triplet state can transfer energy to the triplet state by nonradiative intersystem crossing, according to the empirical rule, after which the energy of the triplet state can transfer to Mn$^{2+}$ ion’s $^4$A$_1$ state, and in this distorted octahedral crystal field, the $d$–$d$ transition selection rule was relaxed, leading to an high-efficient luminescence out of the $d$–$d$ radiation transition of the Mn(II) ion when no neighboring Mn ions are coupled with absorbing Mn ions.

Figure 4A–D illustrates the absorption and related emission spectra at ambient conditions of the $C_{10}H_{12}NMnCl_4$ and $C_{10}H_{12}NMnCl_4·H_2O$ structures. The absorption spectra contain three components: charge transfer between M–ν, $n$–$\pi$ transition, and $\pi$–$\pi$ transition in pyridine and the $d$–$d$ transition of the Mn ion in the as-formed crystal. Both of the absorption spectra show the similar electronic migration from the low-lying state $^6$A$_1$ to other excited states of Mn$^{2+}$ ions in the MnCl$_4$ cluster, which form the $C_{10}H_{12}NMnCl_4$ and $C_{10}H_{12}NMnCl_4·H_2O$ structure, and there are two disparate groups of the band in the spectra for these compounds: G-terms and D-terms. In $C_{10}H_{12}NMnCl_4$ crystal absorption spectra, the strong absorption bands at 351 and 366 nm belong to transitions of the D-terms $^6$A$_1 \rightarrow ^6$E (D) and $^6$A$_1 \rightarrow ^4$T$_2$ (D). The other three bands belong to the G-term transitions $^6$A$_1 \rightarrow ^4$A$_2$ $^2$E (G) (417 nm), $^6$A$_1 \rightarrow ^4$T$_2$ (G) (451 nm), and $^6$A$_1 \rightarrow ^4$T$_1$ (G) (531 nm). The luminescence band of $C_{10}H_{12}NMnCl_4$ is at 518 nm because of the $d$–$d$ transition for the single Mn ion in its crystal field. For the $C_{10}H_{12}NMnCl_4·H_2O$ crystal, the absorption has a very close profile, for its similar symmetry mainly formed by Cl ions. The two intense absorptions belong to transitions of the D-terms $^6$A$_1 \rightarrow ^6$E (D) and $^6$A$_1 \rightarrow ^4$T$_2$ (D) and the other bands are attributed to G-term transitions $^6$A$_1 \rightarrow ^4$A$_2$ $^2$E (G) (418 nm), $^6$A$_1 \rightarrow ^4$T$_2$ (G) (450 nm), and $^6$A$_1 \rightarrow ^4$T$_1$ (G) (544 nm). The lowest $^6$A$_1 \rightarrow ^4$T$_1$ transition has a red shift from 531–544 nm to 620 nm. Because the charge transfer between Mn and pyridine contributes minor to band red shift of the Mn $d$–$d$ transition, the observed giant shift of $^6$A$_1 \rightarrow ^4$T$_1$ in $C_{10}H_{12}NMnCl_4·H_2O$ is hard to explain for the less pyridine coordination number than $C_{10}H_{12}NMnCl_4$. The $C_{10}H_{12}NMnCl_4$ crystal gives green emission at 2.39 eV, while the $C_{10}H_{12}NMnCl_4·H_2O$ structure has emission at about 2.00 eV, far less than the Mn$^{2+}$ $d$–$d$ transition ($E_{546} = 2.15$ eV). Therefore, it is suggested that for the similar crystal field, there is another cause for the shifted $d$–$d$ transition.

With the different concentrations of pyridine in the lattice, the MnCl$_4$ cluster has different ion distributions in space, and it may play an important role in influencing the Mn–Mn couplings and therein its photoluminescence (PL). In $C_{10}H_{12}NMnCl_4$, the Mn–Mn distance is 7.64 Å and the direct spin coupling between the Mn ion and neighboring resonant energy transfer between Mn ions is almost negligible, so the lifetime of the $d$-state increased. Then, its radiation $d$–$d$ transition can happen together with the relaxed selection rule.

In contrast to $C_{10}H_{12}NMnCl_4$, the Mn–Mn distance is 3.65 Å in $C_{10}H_{12}NMnCl_4·H_2O$ and the MnCl$_4$ octahedron forms linear chains by edge-sharing. These linear chains are separated by the pyridine molecules with higher levels, which supply a spatial confining barrier for the electron state in the Mn ion chains, which at least reduced two directional electronic quenchings in the lattice. In a previous report, we have found that the ferromagnetic coupling between Mn ions in a semiconductor lattice can lead to a red-shifted $d$–$d$ transition, even in ionic crystal MnBr$_2$. Therefore, the $d$–$d$ red-shifted emission band has a similar origin out of the ferromagnetically coupled pair in the $C_{10}H_{12}NMnCl_4·H_2O$, and we need to verify if $C_{10}H_{12}NMnCl_4·H_2O$ with the emission band at 620 nm has ferromagnetic behavior.
2.3. Transition State from the C_{10}H_{12}N_{2}MnCl_{4} Crystal to the C_{5}H_{6}N MnCl_{3}·H_{2}O Crystal. To control the pyridine dosage of the C_{10}H_{12}N_{2}MnCl_{4} crystal and C_{5}H_{6}N MnCl_{3}·H_{2}O crystal, a transition state between them was obtained, and it has dual-emitting bands as shown in Figure 5. In this crystal,

Figure 4. Emission spectra and excitation spectra of C_{10}H_{12}N_{2}MnCl_{4} (B,D) and C_{5}H_{6}N MnCl_{3}·H_{2}O (A,C). Emission spectra excited by the 365 nm UV lamp.

Figure 5. Excitation spectra of penetration twin construction (A). Emission spectra excited by the 300 nm UV lamp (B). Emission spectra excited by the 365 nm UV lamp (C).

we assume that the C_{10}H_{12}N_{2}MnCl_{4} and C_{5}H_{6}N MnCl_{3}·H_{2}O structure was formed with a penetration twin construction, so a mixed crystal forms and produces the dual emission bands at 531 and 644 nm. Figure 5A–C illustrates the emission spectra and related absorption spectra. It has absorption spectra similar to C_{10}H_{12}N_{2}MnCl_{4} and C_{5}H_{6}N MnCl_{3}·H_{2}O. It is interesting that when we excite the mixed crystal with 365 nm UV-light, it shows prominent dual emission, while it only has an emission band at 525 nm when it is excited by 300 nm UV-light. This indicates that the absorption bands for the lattice containing the aggregated Mn ions or the individual Mn ion have some
difference, while the one with aggregated Mn ions has a red-shifted band even at high levels.

2.4. Magnetic Properties of C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ and C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O. To ascertain the relationship of the Mn–Mn-coupled pair and ferromagnetism and the red-shifted emission band, we measured the C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ and C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O magnetic hysteresis loops at room temperature by using a vibrating sample magnetometer (VSM), and the results are shown in Figure 6. The magnetic hysteresis loops of both samples were measured in a magnetic field at about ±1 T. C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ proves a paramagnetic profile, while C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O shows strong ferromagnetic peculiarity, as shown in Figure 6, and the saturation magnetization value is 0.252 × 10$^{-3}$ emu, measured coercivity is 861.75 Oe (0.86 kOe), and the remanence is 8.71 × 10$^{-3}$ emu. This result unambiguously demonstrates the ferromagnetism, which can only be induced by the Mn–Mn ferromagnetic coupling among Mn ions in C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O, which means that the Mn–Mn coupled pair or cluster rather than the single Mn ion d–d transition modifies crystal structure and crystal field generates the red emission at 620 nm.

2.5. PL Decay Lifetime of C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ and C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O. We used an fs laser to measure the PL emission lifetimes of C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ (A) and C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O (B). The curves are shown in Figure 7, and the decay was well fitted with single exponential function $Y = Y_0 + A \times \exp(-x/t_1)$, and the fitting lifetime of C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ is 2.14 ns; while the C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O crystal lifetime is 1.49 ns, this is far less than the common lifetime in the bulk which is milliseconds for the d–d transition in the solid lattice. In the C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ crystal, the large distance between Mn ions (7.6243(19) Å) forbids the Mn–Mn coupling, and d–d transition dominated the PL lifetime by fs excitation. However, in C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O, the Mn–Mn distance (3.6484(9) Å) is closer to generate Mn–Mn spin coupling. Because of the inefficiency spin coupling and quenching by water molecules in the lattice, the PL lifetime of the Mn pair in the C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O crystal is less than C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$. In the CdS/Mn nanobelt, the aggregated ferromagnetically coupled Mn pair often has a longer lifetime than the single Mn ion because of the strong sp–d hybridization and spin–spin coupling, but for this halide compound, this effect is strongly reduced because of the ionicity nature and water remanence. Therefore, the lifetime for the d–d transition of the Mn aggregate is reduced as compared to the single Mn radiation emission.

In the transition-metal compound, the local exciton formed from the local d-state is often quenched by the resonant energy transfer between transition ions via the hopping model. This relaxation mechanism causes a giant loss for the new luminescence material development for they cannot show luminescence. Moreover, these materials usually form antiferromagnetic properties like the MnCl$_{2}$·H$_{2}$O crystal. Here, our technique by pyridine molecule incorporation may supply a new technique to confine the Mn ion or Mn ion aggregation, reduce the efficient quenching between Mn ions and the antiferromagnetic coupling between ferromagnetic layers, then tune their optical and magnetic properties, and finally find new luminescence materials and ferromagnetic materials.

3. CONCLUSIONS

In summary, we obtained C$_{10}$H$_{12}$N$_{2}$MnCl$_{4}$ and C$_{5}$H$_{6}$NMnCl$_{3}$·H$_{2}$O crystals by using the pyridine molecule mild implant into the manganese chloride lattice. The single MnCl$_{4}$ clusters confined by the small pyridine molecule lead to Jahn–Teller...
distortion to form the C_{10}H_{12}N_{2}MnCl_{4} crystal, producing the 518 nm emission band out of the d–d radiative transition of the Mn ion. While the C_{6}H_{6}NMnCl_{3}·H_{2}O crystal possesses another conformal confinement by pyridines, the MnCl_{2} cluster chain forms and leads to the ferromagnetic coupling at the environment atmosphere, whose emission band redshifts to 620 nm. We verify that the band shift is due to Mn ions assembling in the lattice rather than the crystal field effect which contributes to their emission band shift. The above results indicate that the Mn ions maintain six-fold coordination and octahedral symmetry after pyridine implantation to form distorted similar perovskite structures (the CIF data did not match our experimental result. Therefore, we modified the crystal image which is consistent with the experimental results). Such perovskite-like structures use small molecules to confine the MX_{n} cluster as an exciton unit and then increase the lifetime of excitons in it; regardless of whether Frenkel excitons or Wannier excitons exist in the unit, their radiation lifetime of excitons in it; regardless of whether Frenkel excitons or Wannier excitons exist in the unit, their radiation results). Such perovskite-like structures use small molecules to confine the MX_{n} cluster as an exciton unit and then increase the lifetime of excitons in it; regardless of whether Frenkel excitons or Wannier excitons exist in the unit, their radiation emission were finally enhanced. This consequence demonstrates that the transition-metal ion aggregates can tune the emission band of themselves significantly by the organic molecule-confined environment. This new technique to modify the transition-metal compounds is important for the design of new luminescent and magnetic materials. Such crystals may find novel applications in the optoelectronic devices someday in the future, like lead perovskites.

4. EXPERIMENT SECTION

4.1. Materials. MnCl_{2}·4H_{2}O (manganese(II) chloride-4-hydrate, AR 99.0%, Aladdin), pyridine (analytical grade, Xilong Chemical Co., Ltd., China), hydrochloric acid (HCl, 36–38 wt % in water, Beijing Chemical Works), and ethanol (analytical grade, Beijing Tongguang Fine Chemical Co., Ltd., China) were purchased and used in this experiment when it is received without any purification.

4.2. Synthesis C_{10}H_{12}N_{2}MnCl_{4} and C_{6}H_{6}NMnCl_{3}·H_{2}O Crystals. The crystal of C_{10}H_{12}N_{2}MnCl_{4} was synthesized in the vial by slowly evaporating the mixed solution of pyridine (1 mmol) and manganese(II) chloride-4-hydrate (1 mmol); the pyridine and MnCl_{2} were dissolved in 2 mL ethanol with extra HCl for the solubilization agent. The vial was put in the heating stage for 40 °C in the atmosphere environment. A week later, after filtering the mixed reaction solution, we obtained the crystal. The crystal was preserved in n-hexane, and the largest single crystal has been observed, it can be about 1.3 cm × 1 mm (shown in Figure 8). Synthesis of the C_{6}H_{6}NMnCl_{3}·H_{2}O crystal was the same as the method mentioned above, but it needs some alterations in the mole ratio of pyridine and MnCl_{2}; the mole ratio of pyridine and MnCl_{2} was changed to 1:4 (0.25 mmol:1 mmol). The C_{6}H_{6}NMnCl_{3}·H_{2}O crystal has crystal water instead of chloridion in the crystal lattice, and the largest single crystal was obtained about 1.2 cm × 3 mm (shown in Figure 8).

4.3. Characterization. The structure of all the crystals were characterized by using the X-ray diffraction system (Saturn 724, Japan), and the power of X-ray was set at 5.4kW. UV-6100 UV-vis spectrophotometer (Shanghai Mapada instruments Co., Ltd., China) and an F-380 fluorescence spectrometer (Tianjin Guangdong Sci.&Tech. Development Co., Ltd., China) were used to obtain the UV-vis absorption spectra and photoluminescence spectra, respectively. The magnetic property was measured by using a vibrating sample magnetometer (VSM) (EZ-VSM, Micro sensor).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03661.

Crystal information of the C_{10}H_{12}N_{2}MnCl_{4} crystal (CIF)
Crystal information of the C_{6}H_{6}NMnCl_{3}·H_{2}O crystal (CIF)

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Notes
The authors declare no competing financial interest.

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