Phosphorescent Manganese(II) Complexes and Their Emerging Applications

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Phosphorescent manganese(II) complexes are emerging as a new generation of phosphorescent materials with great potential in many applications, owing to their unique features including highly efficient phosphorescence, flexible molecular design and ease of synthesis, structural diversity, rich physical properties (*e.g.* triboluminescence, stimuli-responsivity, *etc*), high abundance and low cost. The research on phosphorescent manganese(II) complexes is just in its infancy but rapidly flourishing indeed, and their potential applications are also emerging in many aspects. Herein, the recent progress on the molecular design of new manganese(II) complex-based materials, mechanism of phosphorescence, photophysical properties and their representative applications is highlighted, which covers topics such as: i) structural features and photophysics of phosphorescent manganese(II) complexes; ii) molecular design strategies of phosphorescent manganese(II) complexes (*e.g.* neutral complexes, ionic complexes, coordination polymers, and other types of complexes); and iii) their emerging applications in organic light-emitting diodes, information recording and security protection, temperature sensors. Finally, some perspectives and future research focus of the field are described.

1. Introduction

In recent decades, phosphorescent transition-metal complexes (PTMCs) play an important role in the fields of advanced materials.[1-8] Quite different from the traditional fluorescent materials with the light emission from the singlet states, PTMCs are triplet emitters.[9-14] Since the first phosphorescent organic light-emitting diode (OLED) was successfully realized by S. R. Forrest and coworkers in 1998,[1] phosphorescent transition-metal complexes, especially for noble metal-based ones (e.g. iridium(III), platinum(II), *etc*.) as triplet emitters towards highly efficient organic electroluminescence, have aroused extensive attention.[15-21] These complexes could harness both singlet and triplet excitons by efficient spin-orbit coupling effect to greatly improve the device efficiency, breaking the conventional upper limit of fluorescent device efficiency. Owing to their unique properties of excited states, they also have extended their applications in other fields, for instance, catalysis, organic solar cells, organic memory devices, biological sensing and imaging, photodynamic therapy, information recording and security protection, *etc*.[22-27]

Although extensive efforts have been devoted to the design and synthesis of noble metal-based phosphorescent materials, these noble metals usually suffer from the low abundance and high cost, thereby limiting their practical applications. The relatively abundant, cheap, and less toxic phosphorescent transition-metal complexes as another important class of PTMCs, have drawn considerable interests very recently.[4,23,24,28-31] Many kinds of non-noble metal-based PTMCs such as copper(I), tungsten(VI) and manganese(II) complexes have emerged rapidly.[4,23-25,28-31] Phosphorescent manganese(II) complexes show great potential in many applications, owing to their intriguing features including highly efficient phosphorescence, flexible design in molcular structure, ease of synthesis, rich physical properties (*e.g*. triboluminescence, stimuli-responsivity, *etc*).[24,25,32-36]

Compared with the noble metals, manganese element with an atomic number of 25 has abundant reserves, is environmentally friendly and inexpensive. Moreover, it has richer valence and coordination mode, which has been widely used in the fields of catalysis, ferroelectric, and magnetic materials.[37-39] Among the various valence states of manganese ion, the divalent manganese ion having a $3d^5$ electron configuration has a $^4T_1$-$^6A_1$ radiative transition closely related to the crystal field strength. The crystal field strength in the metal complex depends mainly on the structure of the ligand and the coordination number. These features make the manganese(II) complexes having rich photophysical properties. By regulating the ligand structure, the organic counterion and the coordination number of the manganese(II) complex, the green, yellow, orange, red, or even near-infrared phosphorescence can be achieved.[23-25,36,40] It should be well noted that many phosphorescent manganese(II) complexes also exhibit interesting ferroelectric properties. In this progress report, we mainly focus on the luminescent properties and related photofunctional applications of various phosphorescent manganese(II) complexes. At present, different from the noble metal-based phosphorescent materials, the research on phosphorescent manganese(II) complexes is just in its infancy but rapidly flourishing indeed, and their potential applications are also emerging in many areas.[22-24,41] The focus here will be mainly on the molecular design of new materials, mechanism of phosphorescence, photophysical properties and their representative applications in organic light-emitting diodes, information recording and security protection, as well as temperature sensors. At last, we will present some perspectives and future research focus of this fascinating field.

2. Structural Features and Photophysics of Phosphorescent Manganese(II) Complexes

2.1. Structural Features and Mechanism of Phosphorescence

According to the charge characteristics, the manganese(II) complex can be divided into ionic complex and electrically neutral one. The ionic manganese(II) complex, for instance, $(Ph_4P^+)_2(MnBr_4)^{2-}$, is composed of an organic counter cation and manganese(II)-containing anion through the ionic bond. The neutral manganese(II) complex is formed by the organic ligand and the manganese(II) ion which are held through the coordination bond. The manganese(II) ions also can coordinate easily with certain ligand or halogen atom (such as Br, Cl) to form one-dimensional chain structures, usually known as $AMnX_3$-type (X = Br or Cl) coordination polymers. The $AMnX_3$-type coordination polymers not only exhibit bright phosphorescence but also show ferroelectricity.[35,36] Owing to the rich coordination mode of manganese(II) center, the manganese(II) complexes often show diversity in molecular structure. Due to paramagnetism in these complexes, the structural characterization of manganese(II) complexes cannot realized by the nuclear magnetic resonance spectroscopy. The most powerful analytical approach for structural determination of manganese(II) complex is to use X-ray single crystal diffraction. Most of the manganese(II) complexes are emissive, in which the photophysical process of phosphorescence can be illustrated briefly in **Figure 1**. The energy absorbed by the ligand is excited to the singlet state, and then transmitted to the triplet state of manganese(II) ion by intersystem crossing, thereby inducing the $^4T_1$-$^6A_1$ radiative transition of manganese(II) ion to generate highly efficient phosphorescence.[25]

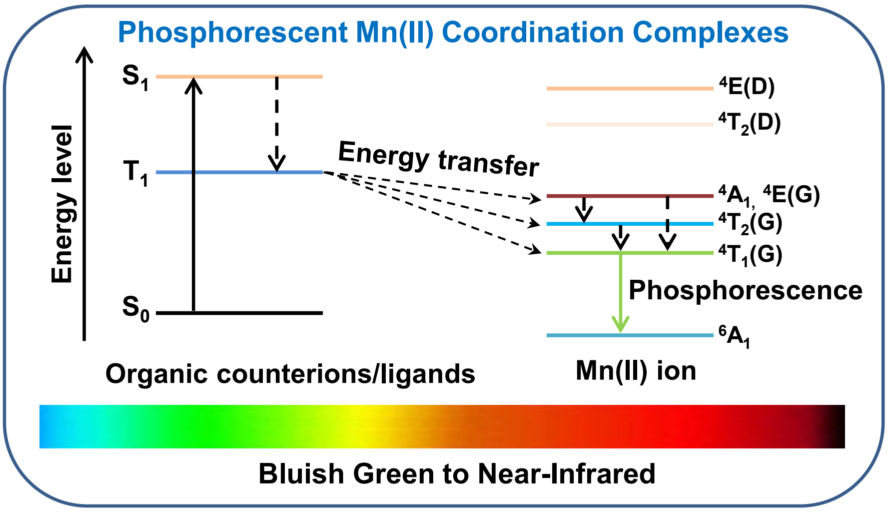


Figure 1. Representation of the energy absorption, migration and emission processes of phosphorescent manganese(II) complexes.

2.2. Factors Governing Energy Transfer from Organic Ligands or Counterions to Manganese(II) Center

2.1.1. Triplet Energy Level of Organic Ligands or Counterions

Since the manganese(II) ion in the complexes has very low extinction coefficients for absorption, the direct excitation of the manganese(II) center is quite inefficient.[42,43] Generally, indirect excitations of manganese(II) complexes by using organic sensitizers are employed to improve the photoluminescence efficiency. The triplet energy level of organic ligand or counterion is one of the important factors that govern the energy transfer from organic ligand or counterion to manganese(II) center. The energy level of organic ligands or counterions should be higher than that of the $^4A_1$, $^4E(G)$ state (23,256 cm^{-1}) of manganese(II) ion for the spontaneous energy transfer from organic ligands or counterions to manganese(II) center.[25]

2.1.2. Coordination Atom and Coordination Number

The emission of phosphorescent manganese(II) complex is originated from its excited state of manganese(II) center. The $^4T_1$-$^6A_1$ radiative transition is closely related to the crystal field strength in its excited state. The crystal field strength of the complex strongly depends on the kind of coordination atom and the coordination number. Based on the crystal field theory, if a manganese(II) ion is surrounded by four atoms to form an independent manganese(II)-containing tetrahedral unit, the weak field strength of tetrahedral coordinated manganese(II) ion exhibits typically green emission. In this case, the distance between manganese(II) ions is large enough to eliminate direct spin-spin coupling, hence its optical transition is dominated by an independent manganese(II) ion. In the octahedral coordinated complex, the manganese(II) ion surrounded by six ligand atoms face-shares to form linear chains within the crystal, in which the distance between adjacent manganese(II) ion is significantly reduced and enlarged in the orthogonal direction. This anisotropic structure supplies a confinement effect on the manganese(II) chains, which has a great effect on the d-d transition and transition energy with different sizes. Thus, octahedral coordinated manganese(II) ion with strong field strength usually exhibits a longer emission wavelength ranging from orange to near-infrared emission.

2.3. Triboluminescence

Triboluminescence, also called fractoluminescence or mechanoluminescence, is an optical phenomenon in which light is generated when a material is mechanically pulled apart, ripped, scratched, crushed, or rubbed. The first observation of triboluminescence was reported by F. Bacon on a hard sugar after it was scraped.[44] This intriguing phenomenon has been observed in many material systems including pure organic materials, metal-centered organic chelates, and inorganic materials, *etc*.[45] This interesting triboluminescence can also be frequently found in many phosphorescent manganese(II) complexes. Although triboluminescence has been observed for many years, there is still no well-established theory that can fully interpret the complete physical process of triboluminescence. In general, it is widely accepted that electrical potentials may be produced via charged fracture planes by the movement of charged dislocations or even via contact potential differences between the crystal and the grinding tool. In addition, impurities in the crystal can also change the crystal symmetry and charge distribution in small areas, thus inducing the triboluminescence.[45]

2.4. Stimuli-Responsivity

Smart luminescent materials that are responsive to external stimuli have received considerable interest.[32,46,47] Besides the triboluminescence observed in some phosphorescent manganese(II) complexes, many manganese(II) complexes, especially for ionic ones, also exhibit interesting stimuli-responsive property. The interaction between organic cation and emissive anion in ionic manganese(II) complex is weak, and easily influenced by external stimuli (such as solvent, temperature, pressure, *etc*.).[24,32,41,48,50] So the energy transfer from organic ligands or counterions to manganese(II) center is sensitive to solvent, temperature, pressure, making them excellent candidates for stimuli-response-related applications.

3. Molecular Design Strategies of Phosphorescent Manganese(II) Complexes

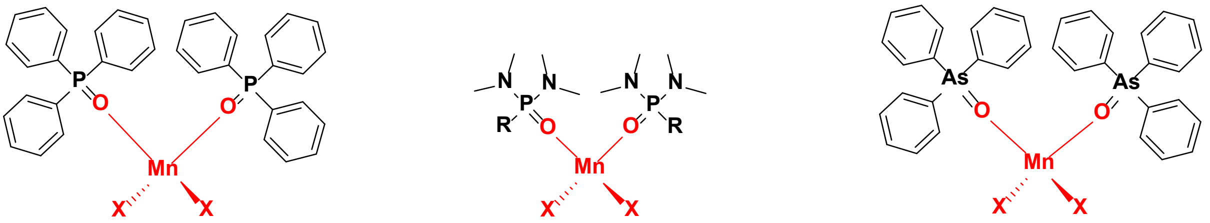
3.1. General Synthesis

As discussed in the previous section, from the structural viewpoint, the manganese(II) complex can be divided into two types, namely electrically neutral complex and ionic complex. For neutral complex, it is usually prepared by the reaction of organic ligand and MnX_2 (X = Cl, Br, I) in a stoichiometric ratio in ethanol at high temperature.[25] In the aspect of ionic complex, the tetrabromide manganese(II) complex can be prepared quantitatively by mixing organic halogen salt and MnX_2 (X = Cl, Br, I) in a stoichiometric ratio in CH_2Cl_2 at room temperature;[22] the $AMnX_3$-type coordination polymers can also be easily obtained by evaporation of an aqueous solution containing stoichiometric amounts of MnX_2, organic salt or free base, and excess of HX at room temperature.[35,36] Compared with the noble metal-based phosphorescent complex,[10-12] the synthesis of phosphorescent manganese(II) complex is much easier, and the target complex can be obtained in a high yield.

3.2. Neutral Phosphorescent Manganese(II) Complexes

3.2.1. Manganese(II) Complexes Based on Monodentate Ligands

The organophosphorus/arsenic oxygen derivatives are important class of ligands, which can successfully be used to design the monodentate ligand-based neutral phosphorescent manganese(II) complexes.[49-55] The monodentate ligand-based neutral manganese(II) complexes usually consist of two monodentate organophosphorus/arsenic oxygen ligands and another two halogen atoms (such as Cl, Br, I). Typical structures of these complexes (**1**-**3**) are shown in **Scheme 1**. The earliest examples of this kind of complexes was reported by Cotton and coworkers,[49] and due to the lack of X-ray single crystal diffraction at that time, the chemical structures of these complexes were investigated by various physical techniques and elemental analysis to support the existence of tetrahedrally coordinated manganese(II) ion in the complexes (**1**, **3**). For the organophosphorus oxygen ligand-based complex **1a**-**1c**, the complexes **1b** and **1c** show green phosphorescence and triboluminescence at room temperature.[49] However, the complex **1a** do not show any phosphorescence both at room temperature and 80 K, while its triboluminescence can be activated at 80 K. Unlike **1a**-**1c**, the organoarsenic oxygen ligand-based ones **3a**-**3c** show different emission properties. Complexes **3a**-**3c** are nonemissive both at room temperature and low temperature, but only the complex **3b** with bromine atom shows phosphorescence and triboluminescence at 80 K.[49] These results reveal that the emission properties of these manganese(II) complexes are not only influenced by the ligand but also greatly affected by the nature of halogen atoms.



1a, X = Cl
1b, X = Br
1c, X = I

2a, X = Cl, R = NMe_2
2b, X = Br, R = NMe_2
2c, X = I, R = NMe_2
2d, X = Br, R = Ph
2e, X = I, R = Ph

3a, X = Cl
3b, X = Br
3c, X = I

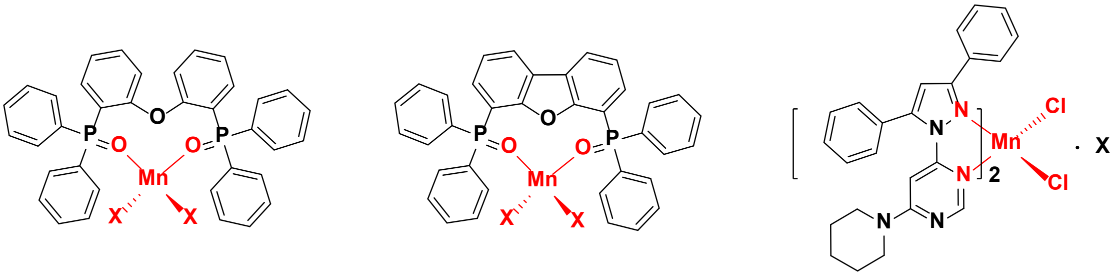
Scheme 1. Chemical structures of manganese(II) complexes based on monodentate ligands.

In addition to triphenylphosphine oxide, the phosphoramide derivatives are another class of ligands for forming neutral phosphorescent manganese(II) complexes. Jin and Bortoluzzi *et al.* reported a series of phosphoramide-based manganese(II) complexes **2a**-**2e** shown in **Scheme 1**.[52-54] Their chemical structures are fully confirmed by X-ray single crystal diffraction and are unambiguously proved to possess tetrahedrally coordinated manganese(II) ion in these complexes. Except for the chlorine-based complex **2a** with unclear emission property, these complexes show similar phosphorescence with emission peaks from 516 nm to 521 nm at room temperature, which corresponds to the characteristic $^4T_1$-$^6A_1$ radiative transition. The halogen atoms have remarkable influence both on the lifetime (τ) of emissive excited state and the luminescent quantum efficiency (Φ), and the more heavy iodine-based complexes show much shorter τ of 112-188 μs than that of bromine-based complexes (479-594 μs).[52-54] This phenomenon is the result of heavy atom effects. With the nuclear charge number increasing from Br to I, the spin-orbit coupling interactions in these complexes become larger and hence lead to a reduction in the lifetime of the excited state. However, the phosphorescence of bromine-based complexes **2b** and **2d** have a moderate quantum efficiencies of 15-19%, while iodine-based complexes **2c** and **2e** exhibit weeker phosphorescence with efficiencies of less than 1% (**Table 1**).[52-54] The quite low quantum efficiency of the iodine-based complexes may be due to the quenching effect of heavy iodine atom in the complexes.

Table 1. Summary of the photophysical properties of selected neutral phosphorescent manganese(II) complexes at room temperature.

Complex	λ_{PL}/nm	$\tau/\mu s$	Φ/%
1b	518	1,000	23
2b	516	954	19
2c	522	188	<1
2d	521	515	17
2e	518	112	<1
4a	507	2,200	32
4b	502	5,000	70
4c	528	100	64
5a	532	5,300	33.3
5b	550	1,000	81.4

3.2.2. Manganese(II) Complexes Based on Bidentate Ligands



4a, X = Cl
4b, X = Br
4c, X = I

5a, X = Cl
5b, X = Br

6a, X = H_2O
6b, X = H_2O, EtOH
6c, X = Me_2CO

Scheme 2. Chemical structures of manganese(II) complexes based on bidentate ligands.

Compared to the monodentate ligand, the bidentate ligand is more attractive in the molecular design of the manganese(II) complexes owing to its strong capability of coordination. The popular bidentate ligands for manganese(II) complex are bis(diphenylphosphine oxide and its analogues. The first example of bidentate ligand-based phosphorescent manganese(II) complex was realized by F. Zheng and coworkers.[25] Bis(2-(diphenylphosphino)phenyl)ether oxide was selected as the bidentate ligand to prepare three air-stable tetrahedral manganese(II) dihalide complexes (**4a-4c**, **Scheme 2**). As shown in **Figure 2**, these complexes were characterized by single-crystal X-ray diffraction (**Figure 2c**), revealing that they crystallized in centrosymmetric space groups and featured an isolated mononuclear structure with manganese(II) ion in a tetrahedral environment. These complexes show intensive green phosphorescence (507-528 nm) in the solid states with the lifetimes in the millisecond scale (100-2,200 μs) and the quantum yields of 32-70% (**Figure 2a**, **Table 1**). Notably, by rubbing the manganese(II) complexes, intense green flashes of light could also be observed by the naked eye, indicating the presence of triboluminescence in these complexes. Similar to the monodentate ligand-based ones in terms of the emissive excited state lifetimes, the emission decay times of **4** dramatically decrease from Cl to Br to I, and the phosphorescence intensity tends to increase along the series. The higher photoluminescence quantum efficiency of these bidentate ligand-based complexes may be induced by the more rigid ligand structure.

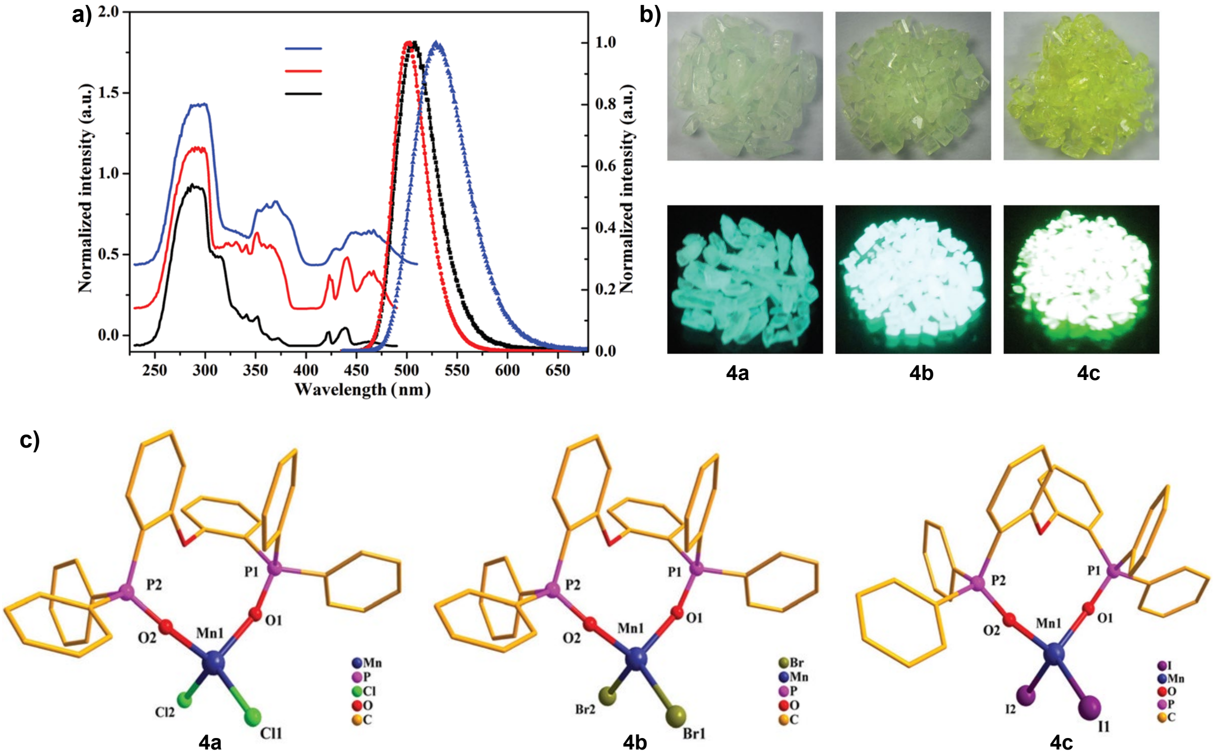


Figure 2. a) Solid-state excitation spectra (left, λ_{em} = 507, 502, 528 nm for **4a**, **4b**, **4c**, respectively) and emission spectra (right) of **4a**-**4c** measured at 298 K (λ_{ex} = 303 nm); b) photographs of crystals of **4a**-**4c** under ambient light (up) and under 365 nm UV light (down); c) single crystal structures of **4a**-**4c**. Reproduced with permission.[25] Copyright 2015, The Royal Society of Chemistry.

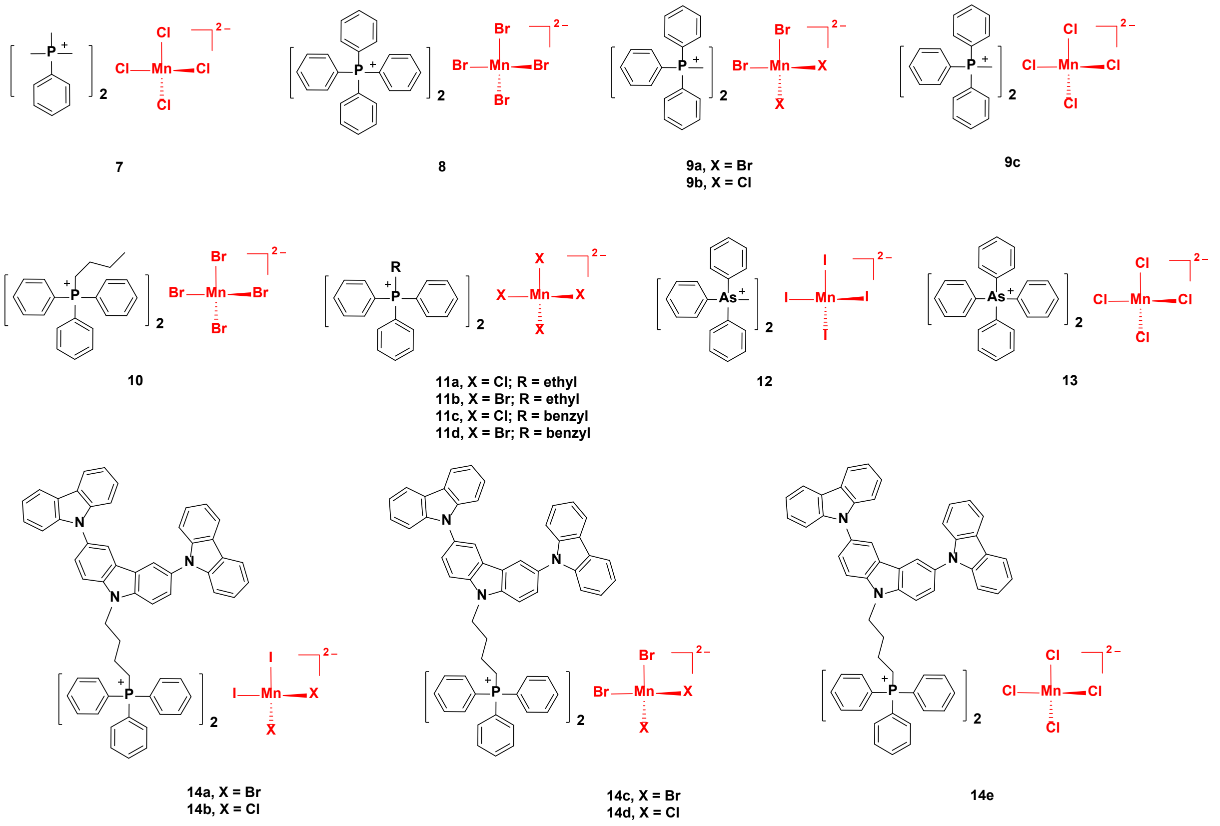
Recently, as inspired by the above mentioned examples, two bidentate ligand-based complexes **5** were also designed by incorporating 4,6-bis(diphenylphosphoryl) dibenzofuran as the bidentate ligand.[23] Owing to the rigid skeleton of ligand, these manganese(II) complexes exhibit high stability in air and intense green phosphorescence (532-550 nm) with photoluminescence quantum yields of 33.3 to 81.4%. In addition, the emissive lifetimes in the millisecond range from 1,000 to 5,300 μs confirm the phosphorescence nature of emission (**Table 1**). Unlike complex **4**, triboluminescence was not observed from these manganese(II) complexes. The application of these complexes in organic light-emitting diodes will be discussed in the section 4.1.

The *N*,*N*-type bidentate ligand is quite rare in designing phosphorescent manganese(II) complex. To the best of our knowledge, there is only one example of this type of ligand-based phosphorescent manganese(II) complex. Recently, M. Bushuev and coworkers designed a octahedral manganese(II) complex **6** with a chelating 4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine ligand.[55] This complex shows intriguing excitation wavelength-dependent emission. The emission at 495 nm with a microsecond lifetime is attributed to the d-d transitions and/or metal-to-ligand and halogen-to-ligand charge transfer. The emission behavior of this complex is also temperature-dependent, and the intensity of emission increases considerably upon cooling. This compound represents the first example of manganese(II) complexes showing excitation wavelength-dependent emission.

3.3. Ionic Phosphorescent Manganese(II) Complexes

Ionic phosphorescent manganese(II) complexes are typically made up of the organic counterions and manganese(II) ion bonded with various number of halogen atoms, which are formed by the weak electrostatic interactions. We will focus on the small molecule-based manganese(II) complex in this section, while the polymer-based ionic congeners will be discussed in section 3.4. In principle, any organic cationic species with suitable triplet energy level can be used as the counterions. For the currently reported ionic phosphorescent manganese(II) complexes, the organic counterions are phosphonium, arsonium, ammonium, pyridinium, and imidazolium type cations. The other part of the ionic complex is the emissive manganese(II)-containing anion, which is usually bonded with different number of halogen atoms. The number of halogen atoms can be tuned from 4 to 6, and the halogen atoms attached to manganese(II) ion can also be the same or different.[22,34-36,41] These features also make them more flexible in the molecular design. The photophysical properties of ionic manganese(II) complexes are closely related to the species of organic cation, halogen atom, and the coordination number.

3.3.1. Manganese(II) Complexes Based on Phosphonium or Arsonium Salts



Scheme 3. Chemical structures of manganese(II) complexes based on phosphonium or arsonium salts.

Quaternary phosphonium cations are the most useful counterions for the design of ionic manganese(II) complexes. The currently used quaternary phosphonium cations are mainly based on the phenyl-containing compounds, and they may contain one, three and four phenyl group(s) directly bonded to the phosphorus atom, as shown in **Scheme 3**. The early researches on the photophysical properties of this kind of complexes were also carried out by Cotton and coworkers.[49,56] Complex **8** with tetraphenylphosphonium cation is a representative one,[22] in which the solid-state UV-vis spectrum of **8** shows an intense band centered at 280 nm together with two absorption peaks at 350 and 460 nm. Upon irradiation at $\lambda_{ex} > 250$ nm, crystals, powder, and poly(methyl methacrylate) (PMMA) film display brilliant green luminescence with featureless emission bands centered at 516, 522, and 518 nm and emissive lifetimes of 355, 317, and 338 μs, respectively. The emissive quantum yields in crystals and PMMA films are as high as 0.98 and 0.71, respectively. The strong green emission is ascribed to the $^4T_1$-$^6A_1$ transition of the manganese(II) ion with a tetrahedral coordination geometry. The microsecond range of the emissive lifetimes together with the large Stokes shifts is indicative of a triplet excited state. Recently, Natarajan and coworkers demonstrated the triboluminescence and vapor-induced phase transitions in the solids of complexes **9a** and **9b** (**Scheme 3** and **Figure 3**).[32] They show interesting solvent-dependent triboluminescence (**Figure 3b**). These complexes synthesized in aprotic solvents such as acetone and monoglyme are stable in dry air and exhibit a bright green light upon grinding. However, they underwent phase transformations while exposed to vapors of the protic solvents such as methanol, ethanol, isoamyl alcohol, and water. After the transformation, the color changed from bright green to faint green, and the TL emission dropped (**Figure 3c**). These results may provide potential applications in organic vapor sensing.

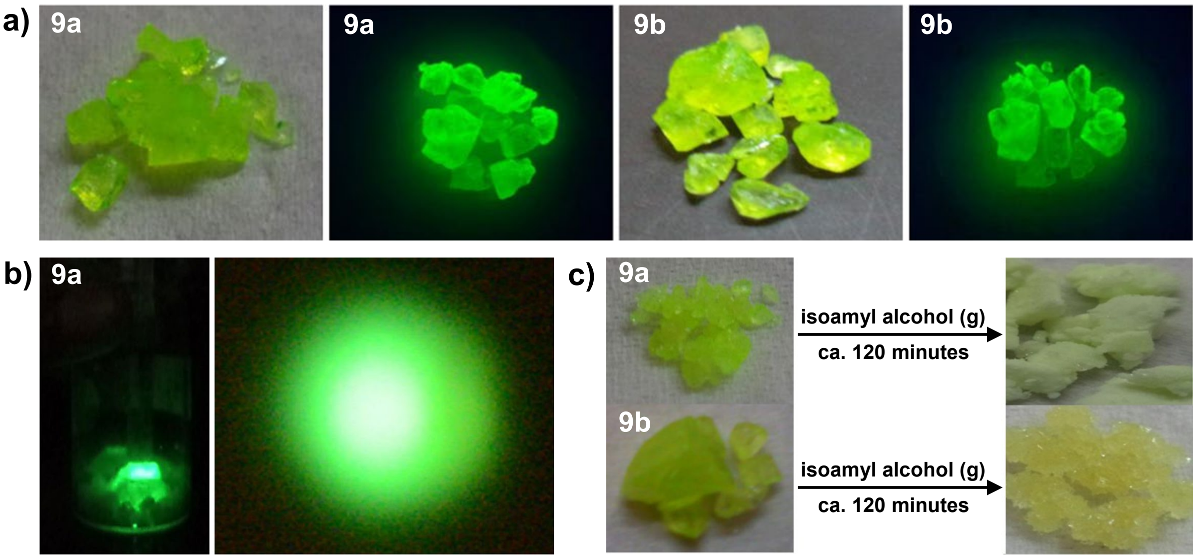


Figure 3. a) Photographs of crystals of **9a** and **9b** under ambient light (left) and under UV light (λ = 365 nm) (right) at room temperature; b) photographs of the TL light captured from crystals of **9a** upon grinding with a glass rod (left) and a drop tower (right) at ambient conditions; c) photographs of the solids of **9a** and **9b**, before and after exposure (ca. 120 min) to vapors of the isoamyl alcohol.[32] Copyright 2014, American Chemical Society.

Generally, the excitation wavelength of the quaternary phosphonium-based complex is in the ultraviolet region (for example, λ_{ex} of **11a** is below 340 nm) due to the limited conjugation length of quaternary phosphonium moiety, which may hinder their potential applications.[24] Thus, extending the absorption domain of the manganese(II) complex is necessary. Very recently, by incorporating tercarbazole possessing the larger degree of conjugation into the quaternary phosphonium cation, a series of ionic manganese(II) complexes (**14**) with various halide ions around the manganese(II) center were designed,[24] which result in significant variations in their photophysical properties owing to the remarkable differences in the heavy atom and ligand field effects. Compared to the complex **11a**, the excitation range for complex **14e** bearing tercarbazole moiety can be extended to 430 nm. The solid form of these manganese(II) complexes showed intense green emissions from 518 nm to 526 nm under excitation at 365 nm. More interestingly, as shown in **Figure 4**, the luminescence lifetimes of these manganese(II) complexes in the solid state are significantly increased from 115 to 511 μs in the order **14b** < **14a** < **14c** < **14d** < **14e** (**Table 2**). The differences in the heavy atom and ligand field effects for various halide ions are responsible for the wide tuning range of the emission lifetimes of these manganese(II) complexes. In addition, the phosphorescence of these complexes also shows high sensitivity to polar solvents because of their inherent ionic structure. These rich photophysical properties make them excellent candidates for information recording and security protection, which will be discussed further in Section 4.2.

Table 2. Summary of the photophysical properties of selected ionic phosphorescent manganese(II) complexes at room temperature.

Complex	λ_{PL}/nm	τ/μs	Φ/%
8	516	355	0.98
9c	505	-	-
10	522	-	-
12	523	36.5	
13	515	2050	
14a	518	175	-
14b	526	115	-
14c	522	234	-
14d	520	373	-

14e	524	511	-
15e	515	-	-
16a	514	-	72.3
17a	525	715	79.4
17d	520	358	81
18a	611	156	1.27
18b	527	361	55
19	520	390	3.31
20	525	-	13.1
21	530	1,540	92.3
22	620	290	4.83

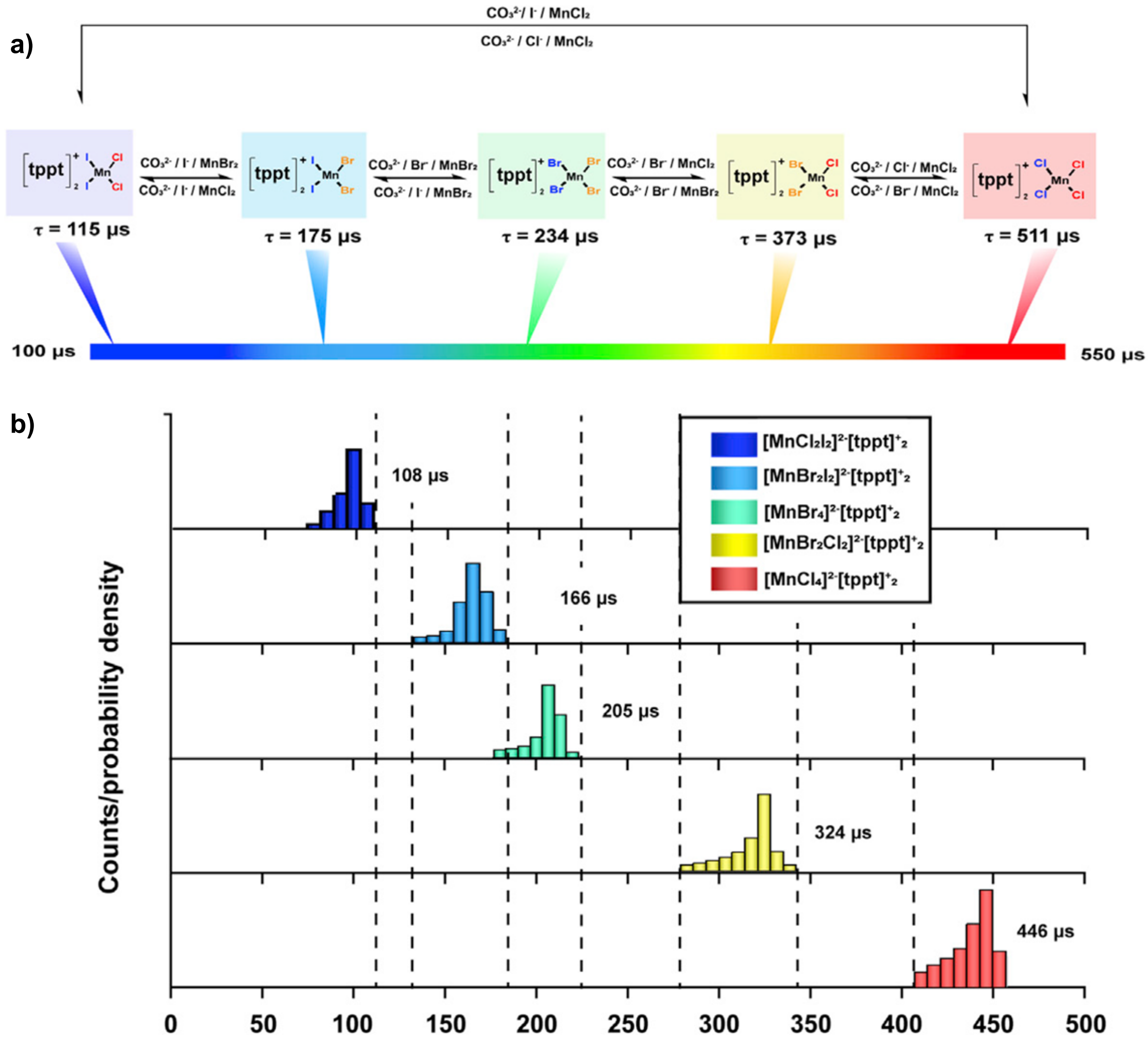
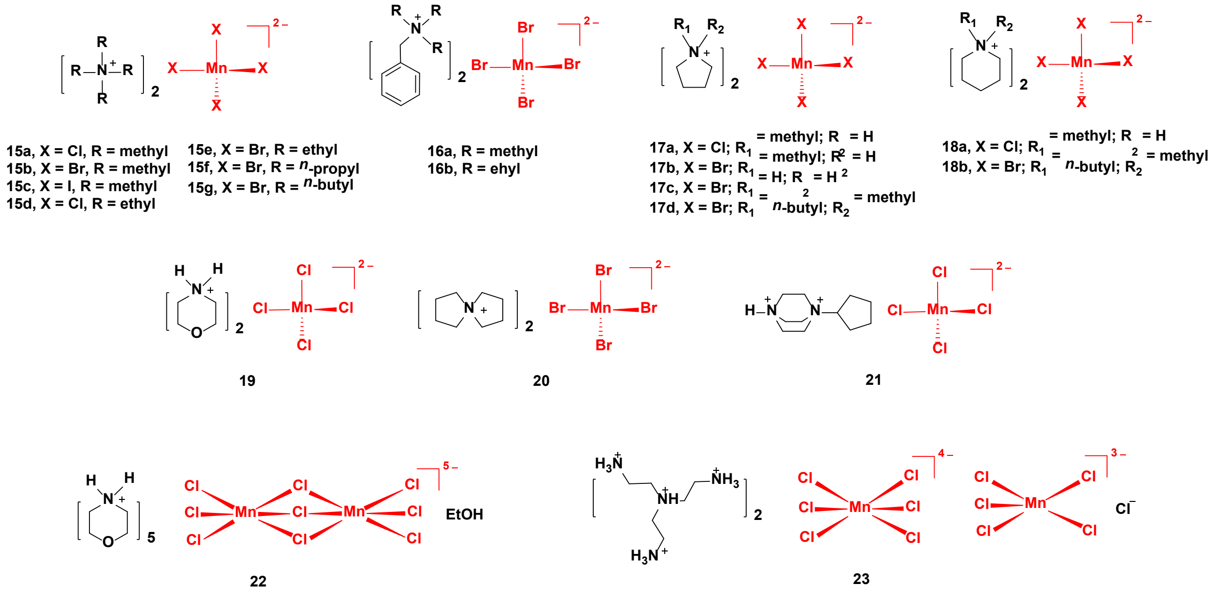


Figure 4. a) Dynamic manipulation of emission lifetime process for complexes **14a-14e**; b) luminescence lifetime distributions of PLIM imaging of **14a-14e** with different halide ions. Reproduced with permission.[24] Copyright 2019, Elsevier Inc.

So far, there are only two reported examples (**12** and **13**) of ionic manganese(II) complex based on quaternary arsonium cation.[43] Both two complexes are emissive at 298 K and 77 K. Complex **12** shows green phosphorescence (523 nm with 36.5 μs at 298 K, 529 nm with 44 μs at 77 K), and complex **13** also shows green phosphorescence (515 nm with decay time of 2,050 μs at 298 K, and 523 nm with decay time of 3,100 μs at 77 K). The variation trend of emission lifetime of excited state of these two complexes is consistent with the quaternary phosphonium-based analogues.

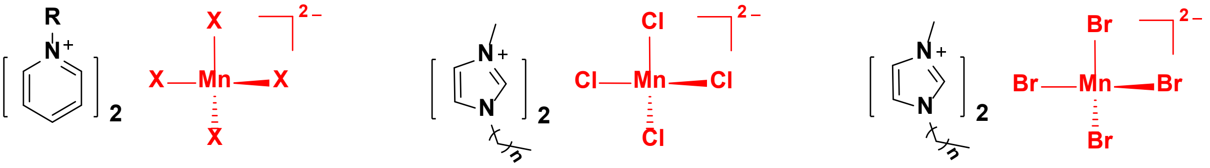
3.3.2. Manganese(II) Complexes Based on Ammonium Salts



Scheme 4. Chemical structures of manganese(II) complexes based on ammonium salts.

Ammonium-based manganese(II) complexes represent another important class of ionic manganese(II) phosphors. As the analogues of quaternary phosphonium-based complexes, they share similar photophysical properties. The typical structures of this class of complexes are shown in **Scheme 4**. For the MnX_4^{2-}-type ones (**15-21**), various ammonium-based organic cations have been adopted as counterions. These complexes also show intensive green phosphorescence with the decay time in microseconds (**Table 2**).[26,34,41,50,51,56-66] In addition to the MnX_4^{2-}-type complexes, other type of ammonium-based complexes have also been designed. Recently, Zang and coworkers prepared a novel binuclear red-emissive manganese cluster crystal (**22**) by using morpholine as the organic counter cation.[26] Interestingly, upon heating, crystals of **22** can be structurally transformed fast *in situ* into the crystalline states of **19** with green phosphorescence. By the crystal structural analysis, it is found that the manganese dimer in octahedral coordination decomposed into mono manganese species in the tetrahedral mode. Fu and coworkers designed an unusual ionic manganese(II) complex (**23**) containing two different species ($MnCl_6^{4-}$ and $MnCl_5^{3-}$), and this complex shows red emission at 617 nm attributed to the $MnCl_6^{4-}$ octahedron.[41]

3.3.3. Manganese(II) Complexes Based on Pyridinium or Imidazolium Salts



24a, X = Cl, R = H
24b, X = Br, R = H
24c, X = Br, R = benzyl

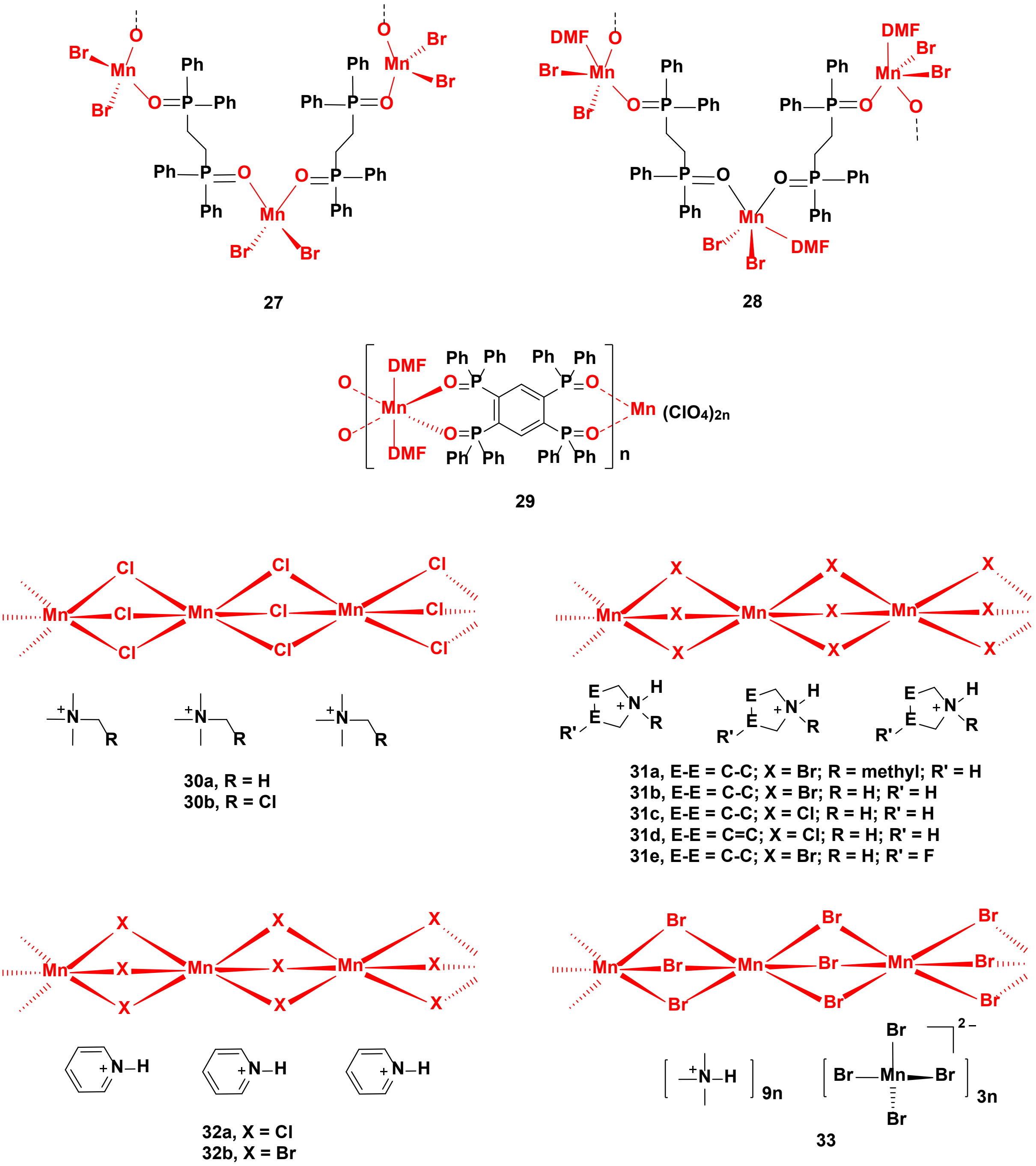
25a, n = 1
25b, n = 2
25c, n = 3
25d, n = 5

26a, n = 1
26b, n = 2
26c, n = 3
26d, n = 5

Scheme 5. Chemical structures of manganese(II) complexes based on pyridinium or imidazolium salts.

The organic cations containing *sp*^{2}-hybridized nitrogen atom (such as pyridinium, and imidazolium derivatives) are also promising candidates for ionic manganese(II) complexes. Recently, Zou and coworkers designed the tetrahedral ionic manganese(II) complexes with anion MnX_4^{2-} (X = Cl, Br) (**24a**, **24b**) by selecting protonated pyridine as the cation (**Scheme 5**).[67,68] The complexes **24a** and **24b** both show green phosphorescence (518 nm for **24a** and 523 nm for **24b**) with the lifetime of several hundred microseconds at room temperature. Complex **24b** also shows interesting temperature-dependent photoluminescence. When the temperature is below 80 K, the PL spectrum exhibits a new emission peak at 493 nm, originating from its vibronic state at low temperature. Recently, a 1-benzylpyridinium-based ionic manganese(II) complex **24c** was also reported,[57] which was found to show bright green phosphorescence with the lifetime of microseconds. In addition to the pyridinium-based manganese(II) complexes, Mudring and coworkers further developed a series of manganese(II) complexes (**25**, **26**) by incorporating *n*-alkyl-methylimidazolium cations with different chain length.[69] Owing to the presence of alkyl chains in the organic cations, these complexes exhibit unique luminescent properties in the ionic liquid state. These complexes are ionic liquids with melting points below 100 °C. Except for complexes **25d** and **26d** with hexyl group, all the complexes are solids at room temperature with the emission maximum ranging from 510 nm to 524 nm. However, due to thermal collision deactivation, the phosphorescence is quenched completely when the solid complexes are melted. Interestingly, at both room temperature and -196 °C, the emission wavelength and the lifetime of excited states of complexes with the same anion can be finely tuned by the length of alkyl chains. The lifetime of excited states of complexes with anion $MnBr_4^{2-}$ (**26**) is much shorter than that of $MnCl_4^{2-}$-based ones (**25**). Notably, these complexes in the solid states also show triboluminescence. Compared to the ionic manganese(II) complex based on phosphonium or ammonium salt, the pyridinium or imidazolium-based manganese(II) complexes are still quite limited.

3.4. Manganese(II) Complex-Based Coordination Polymers



27

28

29

30a, R = H
30b, R = Cl

31a, E-E = C-C; X = Br; R = methyl; R' = H
31b, E-E = C-C; X = Br; R = H; R' = H
31c, E-E = C-C; X = Cl; R = H; R' = H
31d, E-E = C=C; X = Cl; R = H; R' = H
31e, E-E = C-C; X = Br; R = H; R' = F

32a, X = Cl
32b, X = Br

33

Scheme 6. Chemical structures of coordination polymers based on manganese(II) complexes.

Owing to the rich coordination mode of manganese(II) center, the manganese(II) ions can easily coordinate with certain ligands or halogen atoms (such as Br and Cl) to form one-dimensional chain structures. Chen and coworkers reported a neutral one-dimensional coordination polymer (**27**) composed of manganese(II) ions linked by bridging ethane-1,2-diylbis(diphenylphosphine oxide) to form tetrahedral coordination geometry (**Scheme 6**).[33]

Interestingly, upon exposure of **27** to *N*,*N*-dimethylformamide vapor, the green emission centered at 510 nm is converted to red luminescence peaking at 630 nm, ascribed to the formation of DMF coordinated polymer (**28**) with a trigonal-bipyramidal ligand field, as demonstrated by X-ray crystallography. Moreover, red-emitting polymer (**28**) could be reverted to the original green-emitting polymer (**27**) with a tetrahedral ligand field upon heating at 160 °C, and such a reversible conversion could be perfectly repeated for several cycles. Recently, Artem'ev *et al.* also designed an ionic one-dimensional coordination polymer (**29**) by the reaction of $Mn(ClO_4)_2{\cdot}6H_2O$ with 1,2,4,5-tetrakis(diphenylphosphinyl)benzene in DMF.[70] At the temperatures below 200 K, the polymer (**29**) shows temperature-dependent red phosphorescence with emission peak at 660 nm and lifetimes of 1,500-4,500 μs. The absence of exchange interactions between the high-spin state of the manganese(II) ions in this polymer was confirmed by electron paramagnetic resonance spectroscopy.

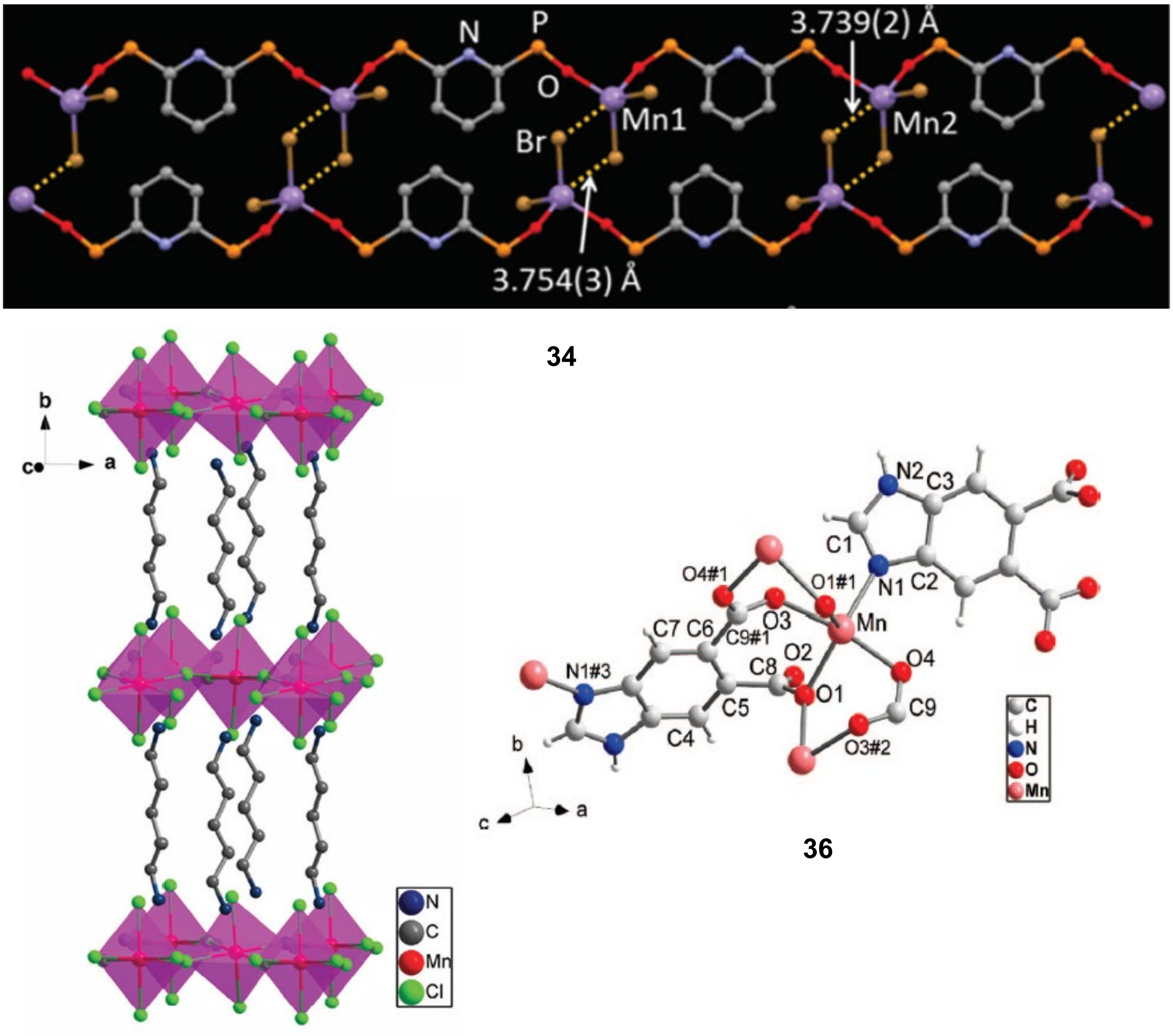
The hybrid hexagonal stacking perovskite-type compounds with general formula $AMnX_3$ (A is an organic cation, X is Br or Cl) usually emit brightly. As demonstrated by Xiong and coworkers, this class of manganese(II)-based coordination polymers not only exhibit bright phosphorescence but also show ferroelectricity.[35,36] The $AMnX_3$-type coordination polymers usually consist of infinite columns of *face*-sharing MnX_6 octahedra and organic counterions. The Br or Cl atom often serves as the bridging halogen atom in *face*-sharing MnX_6 octahedron. The cavities between the octahedral columns are occupied by organic cations. So far, many $AMnX_3$-type coordination polymers (**30**-**33**) have been designed by selecting different kinds of organic cations,[35,36,38,48,66,67,71-73] as shown in **Scheme 6**. The frequently used organic cations are organic ammonium and pyridinium salts. In the polymers **31**-**33**, there exists N-H···X hydrogen-bonding interactions between the columns of *face*-sharing MnX_6 octahedra and organic counterions.[35,36] Upon heating or cooling, the $AMnX_3$-type coordination polymers also show reversible structural phase-transition process, which is caused by the orientation variations of the organic cation. The phase-transition temperature (T_c) is closely related to the type of organic cation. These polymers show typical red phosphorescence from octahedral manganese(II) center (**Table 3**) The emission wavelengths of these polymers lie in the range of 609-650 nm with high photoluminescence quantum yields of 28 to 56%. The decay times of these polymers are in the range of 157-515 μs, implying the phosphorescent nature of the emission.

Table 3. Summary of the photophysical properties and phase-transition temperature (T_c) of some typical $AMnX_3$-type coordination polymers.

Polymer	λ_{PL}/nm	τ/μs	Φ/%	T_c/K
30b	-	-	-	406
31a	640	-	36.76	325
31b	640	157	28.5	219
31c	640	515	56	295
31d	635	334	28.2	376
***S*-31e**	650	-	28.13	273
***R*-31e**	650	-	32.46	273
32a	620	-	-	-
32b	650	-	-	219
33	507, 609	282	41.96	458

Materials with circularly polarized luminescence (CPL) property may have great potential applications. Very recently, Fu and coworkers demonstrated the first example of a $AMnX_3$-type polymer (**31e**) with CPL property by incorporating (*R*)- and (*S*)-3-(fluoropyrrolidinium) cation.[73] The dissymmetry factors (g_{PL}) of the two enantiomers are of $\pm 6.1\times10^{-3}$, which are comparable with the previously reported chiral 2D perovskites. This will give us inspirations for the further research in the molecular design on novel $AMnX_3$-type polymer materials toward new optoelectronic devices.

3.5. Other Types of Manganese(II) Complexes



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35

36

Figure 5. Chemical structures of coordination polymers based on manganese(II) complexes (**34-36**). Reproduced with permission.[74] Copyright 2018, The Royal Society of Chemistry. Reproduced with permission.[75] Copyright 2016, The Royal Society of Chemistry. Reproduced with permission.[40] Copyright 2008, American Chemical Society.

In addition to the above mentioned examples of phosphorescent manganese(II) complexes, many other types of phosphorescent manganese(II) complexes have also been reported owing to the rich coordination mode of manganese(II) center (**Figure 5**). Chen and coworkers reported a one-dimensional chain manganese(II) complex (**34**) exhibiting thermochromic luminescence from sky-blue (502 nm) to red (617 nm) emission in a wide range of temperatures, which can be ascribed to the conversion of a tetrahedronal to a trigonal bipyramidal ligand field by two-step single-crystal to single-crystal transformations.[74] Zhang *et al*. developed a novel kind of layered structure (**35**),[75] in which the 1,5-diaminopentane cation occupies the space enclosed by the $MnCl_6$ octahedra. This complex shows orange emission at 581 nm under ultraviolet excitation, which is ascribed to the octahedral manganese(II) ion. Wu and coworkers prepared a five-coordinated manganese(II) polymer (**36**) possessing abundant hydrogen bonds and π-π stacking interactions,[40] and this polymer shows intense near-infrared phosphorescence (λ_{max} = 726 nm) with a decay time of 300 μs. The materials containing different emissive center is much more attractive. Recently, Xia and coworkers designed a lead(II)- and manganese(II)-containing polyhedron (**37**) by a solution-grown method.[27] As shown in **Figure 6**, this complex shows dual-emission with high PLQY of 49.8%, which arises from the self-trapped excitons formed on lead-halide units and from d-d transitions in manganese(II) ions. The spectral behavior of these emission bands can be adjusted by changing the temperature and the excitation wavelength.

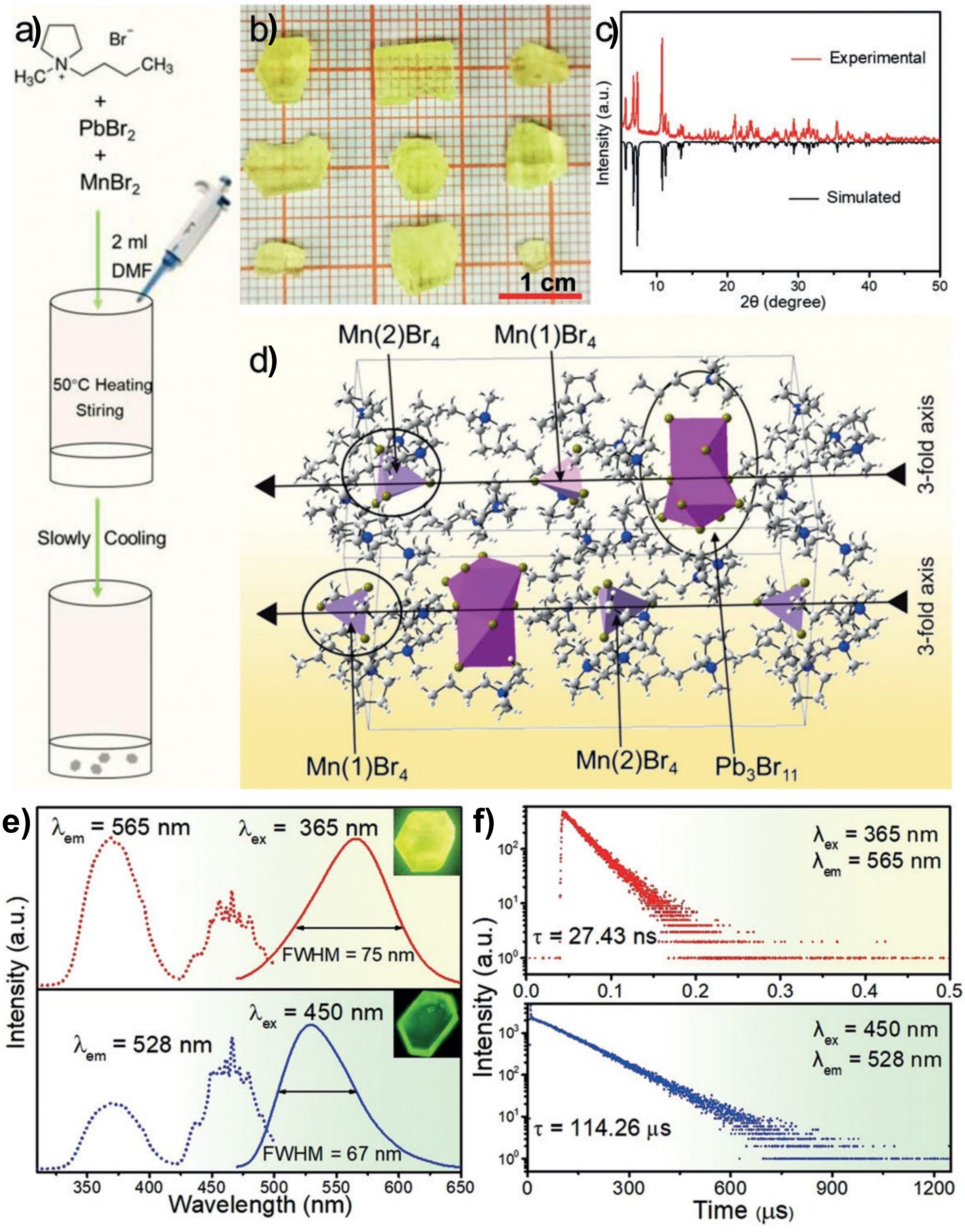

Figure 6. a) Schematic diagram showing the crystal growth of **37** ($(C_9NH_{20})_9(Pb_3Br_{11})(MnBr_4)_2$); b) optical photographs of as-grown crystals of **37** under daylight; c) the simulated and experimental X-ray powder patterns of **37**; d) the asymmetric part of the unit cell and the marked polyhedrons; e) room-temperature PL and excitation spectra of **37** at different excitation wavelengths and emission wavelengths; f) room-temperature PL decay curves. Reproduced with permission.[27] Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

4. Emerging Applications

Current research on phosphorescent manganese(II) complexes is mainly focused on the molecular design, photophysical properties, and their structure-property relationships. Very recently, by rational utilization of their unique properties such as highly efficient phosphorescence, stimuli-responsive emission properties, and tunable excited state lifetimes, several attempts on finding the potential applications of these manganese(II) complexes in organic light-emitting diodes, information recording and security protection, and temperature sensors were successfully realized.

4.1. Organic Light-Emitting Diodes

Since the reported of the first phosphorescent OLED,[1] such devices could harness both triplet and singlet excitons by efficient spin-orbit coupling effect to greatly improve the device efficiency, and break the conventional upper limit of device efficiency in the fluorescent devices which promotes the commercialization of OLEDs. Many efforts have been devoted to the design and synthesis of noble metal-based PTMCs for highly efficient OLEDs.[76-81] So far, many commercialized emitters are based on these phosphors (such as iridium(III) complex).[82-87] However, these noble metals suffer from the low abundance and high cost. The exploration of relatively abundant, low-cost, and less-toxic phosphorescent manganese(II) complexes could be the key to solve this problem.

The pioneering work on the utilization of phosphorescent manganese(II) complex in the fabricateion of OLEDs was made by Chen and coworkers in 2017.[22] As shown in **Figure 7**, they reported the first attempt on the use of green light emissive ionic manganese(II) complex $(Ph_4P^+)_2(MnBr_4)^{2-}$ (**8**) to fabricate nondoped and doped OLEDs through wet process due to its ionic nature. In the process of spin-coating, the orthogonal solvents that could not dissolve the underneath films were carefully selected to fabricate multiple layers of organic thin film. For the nondoped device, CH_3OH was selected as the solvent to dissolve the ionic complex **8**. The atomic force microscopy images show that the surface roughness of $(Ph_4P^+)_2(MnBr_4)^{2-}$ light-emitting films is 0.63 nm, demonstrating that the ionic complex **8** shows an excellent film formation ability. The maximum current efficiency (CE), power efficiency (PE), and external quantum efficiency (EQE) for the nondoped OLEDs based on **8** are 25.4 cd/A, 18.3 lm/W, and 7.2%, respectively, and the nondoped OLEDs also show a low turn-on voltage of 3.5 V. The relatively low device efficiency of the nondoped OLEDs may be caused by the poor charge transporting ability in the neat film of complex **8**. In order to increase the device efficiency, the doped device was further optimized. It was demonstrated that the blended host materials composed of 4,4′,4″-tri(9-carbazoyl)tripheylamine (TCTA) and 2,6-bis(3-(9H-carbazol-9-yl)phenyl) pyridine (26DCZPPY) doping with complex **8** as an emitting layer gives superior electroluminescence owing to the more balanced charge transporting ability. After optimizing the ratios of the three functional materials, the best device performance with the peak CE of 32.0 cd/A, PE of 16.2 lm/W, and EQE of 9.6% can be achieved. Notably, the EL spectra of complex **8** in nondoped and doped devices overlap well with the corresponding PL spectra of **8** in the pure and doped emitting layers, clearly indicating that the EL emission is originated from complex **8**.

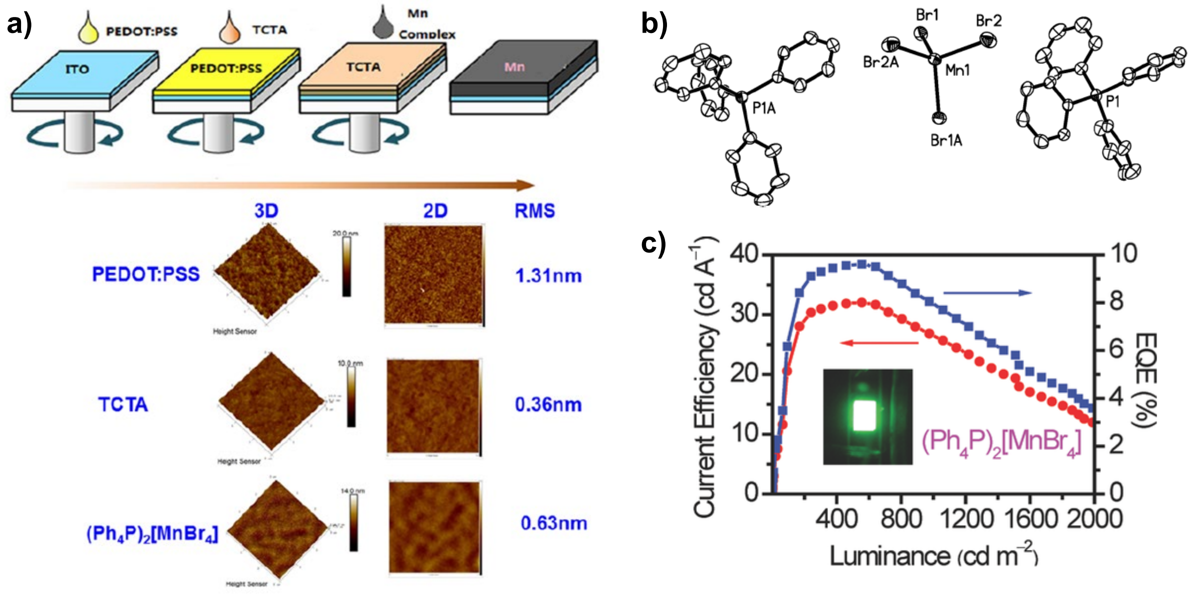

Figure 7. a) Device fabrication by solution-process and atomic force microscopy images of the surface morphology of organic layers in OLEDs; b) crystal structure of **8**; c) device efficiencies of solution-processed OLEDs based on **8**. Reproduced with permission.[22] Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

It is well known that most of the ionic manganese(II) complexes are hydrolyzed easily by water in air.[25] This may be another factor that shows a negative effect on the efficiency of the device. In contrast, the neutral ones, especially those with the greater steric bulk of ligands, are much more stable in their chemical structure, which makes them more suitable for use in the organic electroluminescence. Recently, the neutral phosphorescent manganese(II) complexes could also be used for OLEDs with higher device performance.[23] Using the newly designed neutral dibenzofuran-based phosphine oxide-based phosphorescent manganese(II) complex **5b** as the dopant, a green doped OLED with maximum CE of 35.47 cd/A, PE of 34.35 lm/W, and EQE of 10.49% can be achieved by the vacuum deposition method (**Figure 8**). More interestingly, in the optimization of device structure by varying the host materials, we found that red exciplex emission could be observed in electroluminescence, arising from the interaction between the dopant **5b** and the host materials 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBi) or (bis(2-(2-hydroxyphenyl)-pyridine)beryllium (Bepp2). The red OLED based on exciplex shows the maximum CE and PE of 18.64 cd/A and 17.92 lm/W, respectively. This exciplex-based red OLED is among the highest values to date. These preliminary results demonstrate that both ionic and neutral manganese(II) complexes attributed to their phosphorescent nature are the suitable candidates for realizing the highly efficient OLEDs.

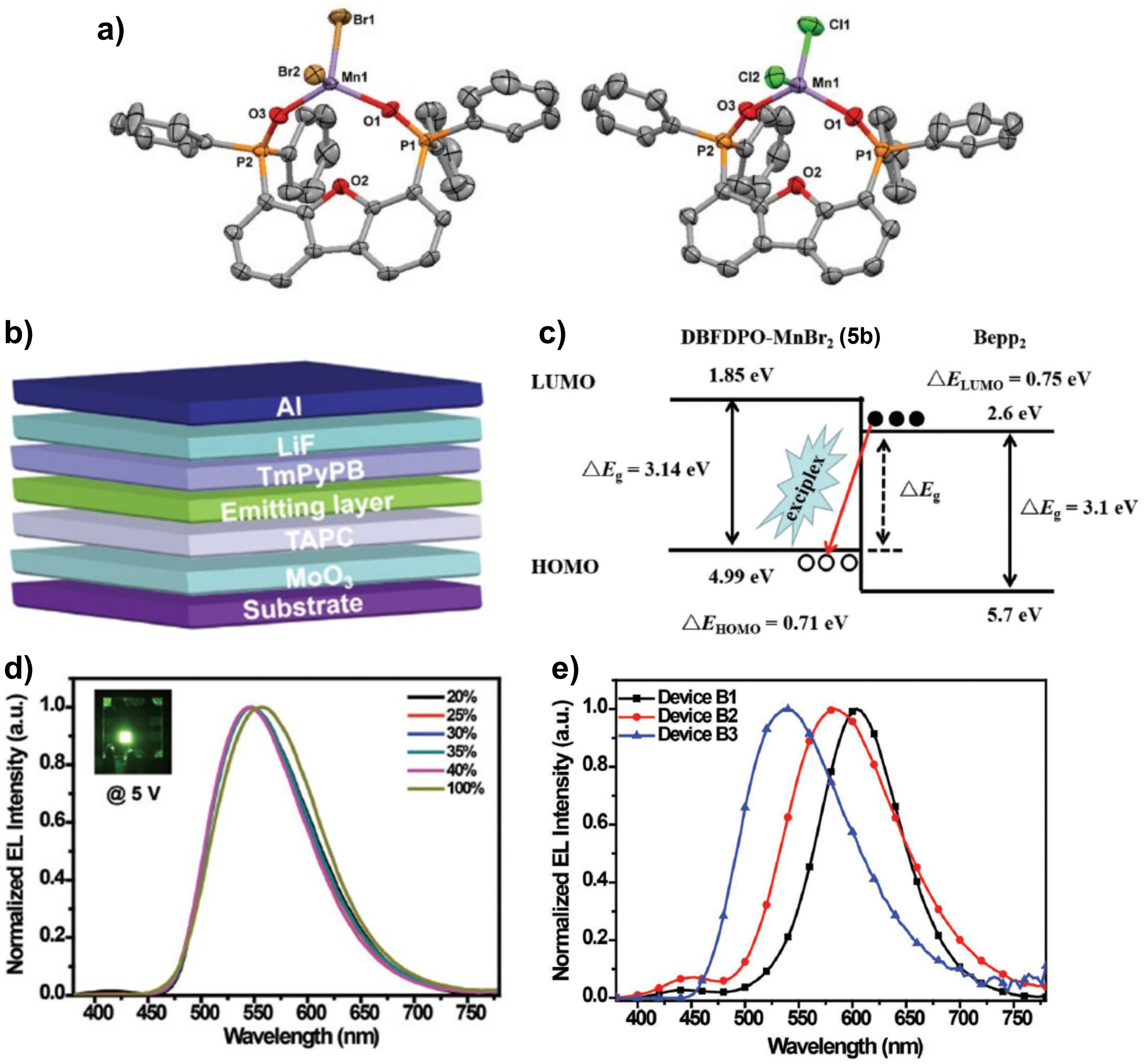

Figure 8. a) Crystal structures of **5a** (right) and **5b** (left); b) device structure of dry-processed OLEDs based on **5b**; c) the energy level diagram of the exciplex formed between Bepp$_2$ and **5b**; d and e) normalized electroluminescencent spectra of OLEDs based on **5b** with various hosts (d) TCTA, (e) Bepp$_2$, TPBi, and B$_3$PyMPM. Reproduced with permission.[23] Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2. Information Recording and Security Protection

Information recording, storage and security technologies have been widely utilized in economic and military fields as well as in our daily life.[88-92] Explorations of smart luminescent materials that are responsive to external stimuli have received considerable attention in the fabrication of optical data recording and storage devices.[93-97] Particularly, there is an increasing demand for paper document security, since paper is still the most widespread medium for information storage. Current research efforts in this field are focused on the achievement of rewritable and multi-level security printing.[98-100] For information recording and security printing on paper, the active materials for realizing this purpose should not only possess appropriate stimuli-responsive properties but should also be environmental-friendly and of low cost. Some of the phosphorescent manganese(II) complexes with stimuli-responsive photophysical properties (e.g. responsive to solvents) will meet these requirements.

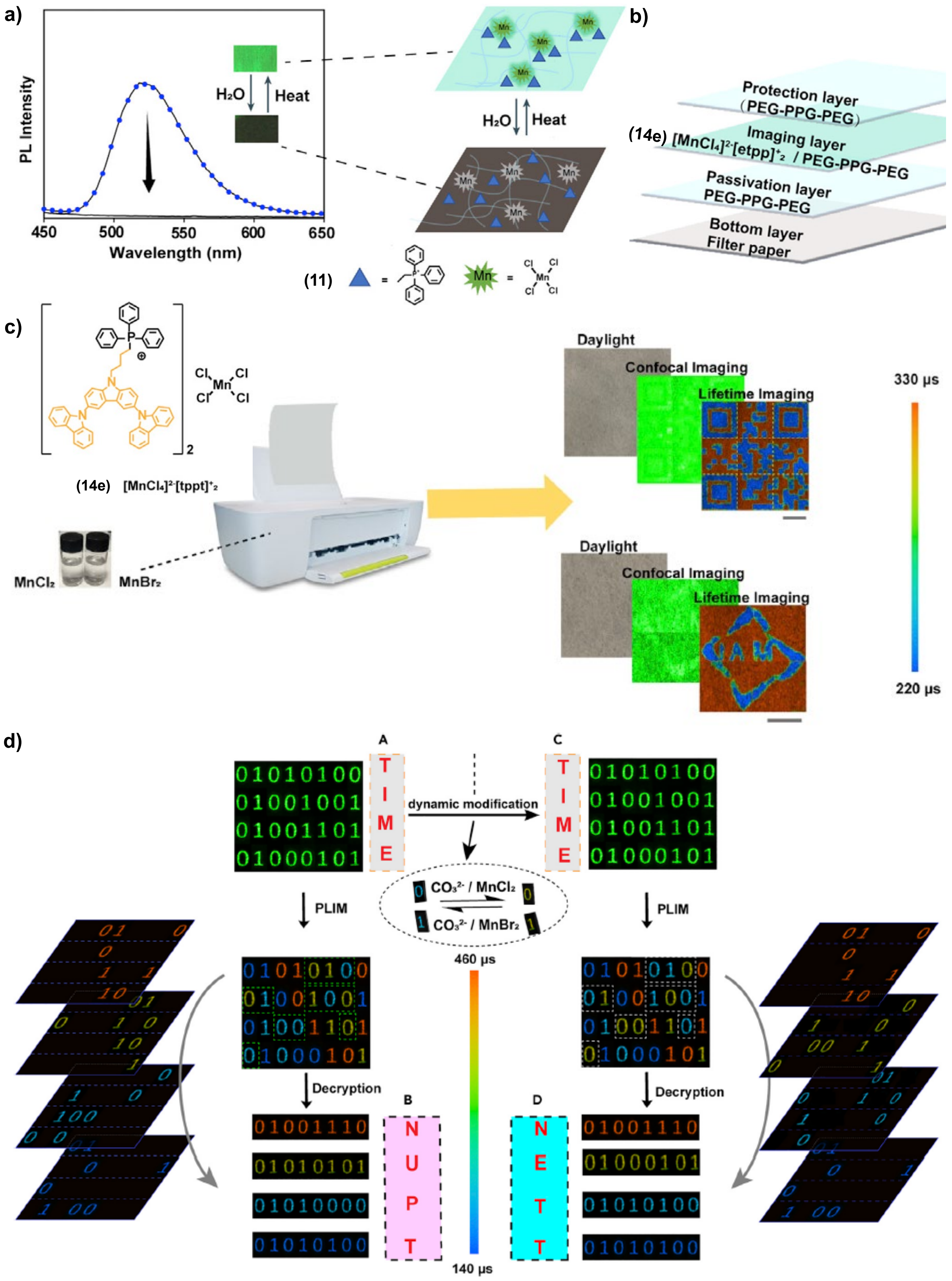

Figure 9. a) The PL spectra of fabricated security paper before and after applying pure water ink; b) schematic illustrations of four-layer structure of water-jet rewritable security paper; c) confocal and lifetime imaging of patterns printed on security paper using an inkjet printer with a cartridge filled with $MnCl_2$ and $MnBr_2$ ethanol solution as inks; d) illustration of multi-level security printing. Reproduced with permission.[24] Copyright 2019, Elsevier Inc.

For an ionic manganese(II) complex, firstly, the energy migration from the ligand (sensitizer) to manganese(II) center (emitter) can be manipulated precisely by ionic interactions,[101] thereby resulting in the switch of emission intensity. Secondly, the manganese(II) complex exhibits the long-lived emission owing to the phosphorescent nature of the $^4T_1$-$^6A_1$ transition of the manganese(II) ion in a d^5 configuration, making it possible for lifetime-based multiplexing assays. Taking the above advantages of an ionic manganese(II) complex, very recently, as shown in **Figure 9**, the emission intensity and lifetime switching was realized by controlling the dynamic ionic coordination of manganese(II) complex **14** to demonstrate the multi-level confidential information encryption and decryption with various inkjet-printed patterns using time-resolved luminescence imaging techniques.[24] As depicted in **Figure 9a** and **9b**, we coated the polymer film containing ionic manganese(II) complexes on a filter paper where confidential information can be repeatedly printed using pure water as the ink, which can destroy ionic coordination for the complexes. The printed information and images can be erased conveniently by heating the paper to restore the ionic coordination between the sensitizer and the emitter. Furthermore, as discussed in the above section, the emission lifetimes of ionic manganese(II) complexes can be finely tuned over a wide range by changing the halide ions around the metal center. **Figure 9c** shows that the printed images are invisible to the naked eye under ambient light or UV excitation because of similar emission color of complexes **14c** and **14d**. However, when the photoluminescence lifetime imaging microscopy (PLIM) is used, the concealed images can be clearly revealed owing to the distinct luminescence lifetimes of the background and images, resulting in higher security level printing. Besides, multi-level security printing was also demonstrated based on the dynamic control of emission lifetimes (**Figure 9d**). This application study successfully suggests that by manipulating the reversible ionic interactions between the ligand and the manganese(II) center to control the photophysical properties of the manganese(II) complex is a promising method to achieve security printing on a paper substrate.

4.3. Temperature Sensors

The temperature-dependent emissive property of phosphorescent manganese(II) complexes can make them excellent candidates for temperature sensing. In 2018, Fu and coworkers reported the simulated application of optoelectronic multifunctional molecular switch based on the ionic complex **23** (**Figure 10d**).[41] As discussed in the previous section, the ionic complex **23** undergoes a process of phase transition during the heating or cooling process (**Figure 10a**). This phase transition is also accompanied by the observation of the red phosphorescence (**Figure 10b**, **10c**, and **10d**). One function of this optoelectronic multifunctional molecular switch is to monitor the temperature variations by monitoring the intensity changes of red phosphorescence with high signal-to-noise ratio. This work can provide us a practical example on the application of phosphorescent manganese(II) complex in temperature sensing.

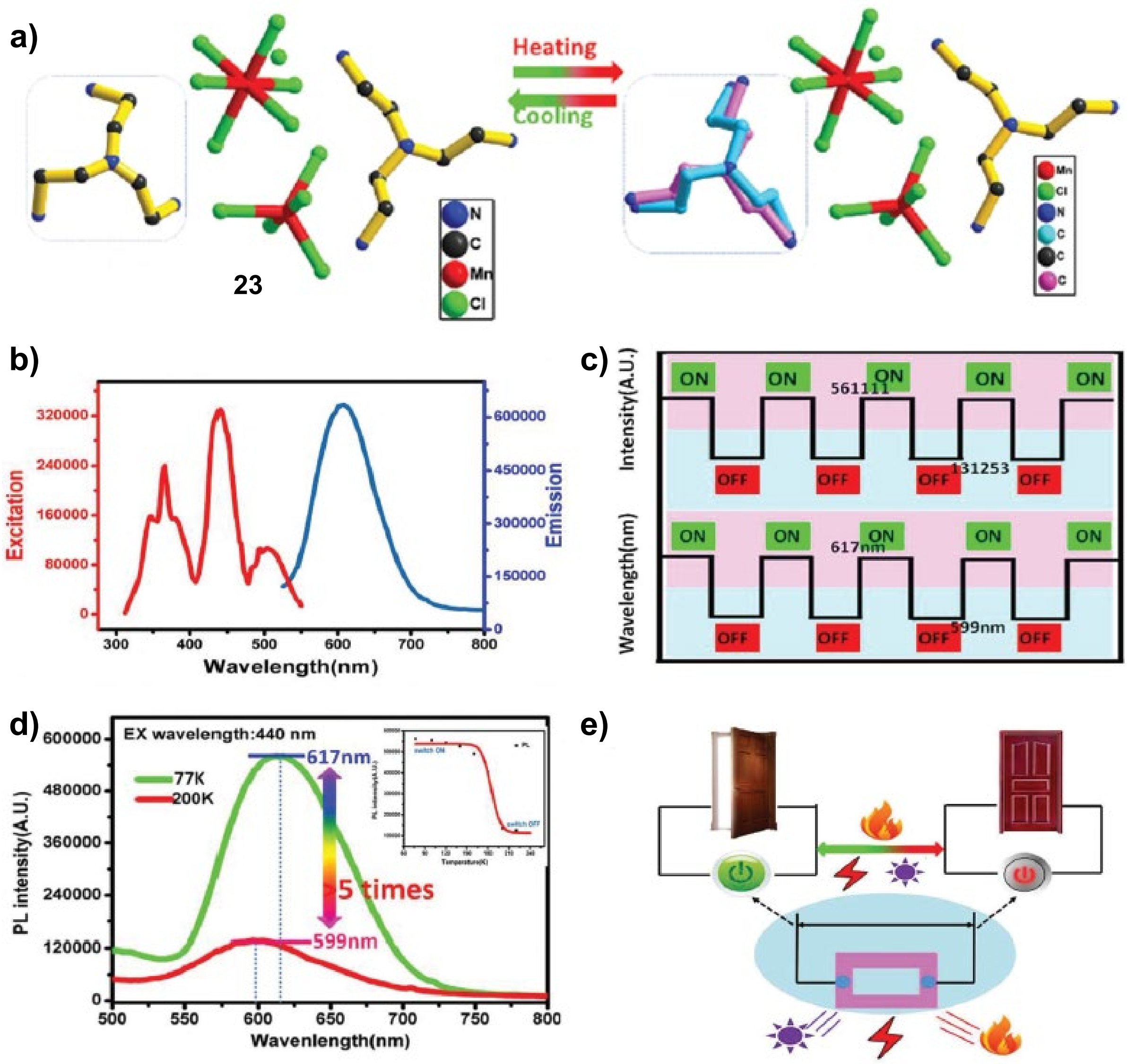

Figure 10. a) The phase transitions of complex **23** between 103 and 293 K; b) excitation and emission spectra of **23** at room temperature; c) the switching cycles of photoluminescent intensity and emission wavelength; d) emission spectra of **23** at 100 and 200 K for an excitation wavelength of 440 nm; e) the simulated application of the red-light optoelectronic multifunctional molecular switch. Reproduced with permission.[41] Copyright 2018, The Royal Society of Chemistry.

5. Conclusion and Outlook

In summary, this progress report presents a comprehensive review on the molecular design of phosphorescent manganese(II) complexes, mechanism of their phosphorescence, tuning of their photophysical properties and the emerging applications in organic light-emitting diodes, information recording and security protection, and temperature sensors. In the current research stage of phosphorescent manganese(II) complexes, the emission colors and efficiency can be effectively tuned by ligands, counterions, coordination atoms and coordination number. The resulting phosphorescent manganese(II) complexes show efficient phosphorescence covering the spectral region from green to far-red. This feasible and versatile structural design method opens a new material system and provides the possibility of developing other potential applications. The highly efficient phosphorescent manganese(II) complexes enable the fabrication of low-cost green OLEDs with maximum CE of 35.47 cd/A, PE of 34.35 lm/W, and EQE of 10.49% by the vacuum deposition method. The stimuli-responsive properties also make them good candidates for applications in information recording and security protection. Moreover, the temperature-dependent emission properties of phosphorescent manganese(II) complexes show a good promise in temperature sensing.

However, compared with the noble metal-based phosphors (such as iridium(III) and platinum(II) complexes), the exploration of phosphorescent manganese(II) complexes is just in its early stage, although there is a rapid research pace in this direction. The current research is mainly focused on the molecular design, structure-property relationships and the potential applications of this class of metal complexes. In terms of future research directions, several significant areas and key challenges should be addressed as follows: 1) The diversity of organic ligands or counterions with suitable triplet energy level for phosphorescent manganese(II) complexes need to be enriched; 2) for electroluminescence applications, more attention should be paid on the organic ligands or counterions with excellent bipolar charge transport ability to improve the device performance; 3) investigation on the ionic phosphorescent manganese(II) complex-based light-emitting quantum dots for electroluminescence would be intriguing; 4) it would be desirable to give phosphorescent manganese(II) complex new features (such as circularly polarized phosphorescence, *etc.*) by a rational molecular design of the organic ligands or counterions; 5) the relationships between chemical structure and triboluminescent property is not clear, this structure-property relationships need to be further established; 6) stress and crack sensor may be one of the promising application areas of phosphorescent and triboluminescent manganese(II) complexes. Because there are growing demands for low-cost and environmental-friendly phosphorescent light-emitting materials, we believe that this article will not only provide deep insights into the recent advances of low-cost transition-metal phosphorescent materials but also stimulate the interest of both scientists and engineers toward the further development of this type of relatively unexplored PTMCs.

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Conflict of Interest

The authors declare no conflict of interest.

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Compared with the noble metals, manganese has abundant reserves, is environmentally friendly, and inexpensive. Phosphorescent manganese(II) complexes are emerging as new generation of phosphorescent materials with great potential in many application areas. An overview of the molecular design, synthesis, photophysics, and recent research progress on phosphorescent manganese(II) complexes and their emerging applications is provided.

Keyword: energy transfer, manganese(II) complexes, phosphorescence, structure-property relationships, triboluminescence

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