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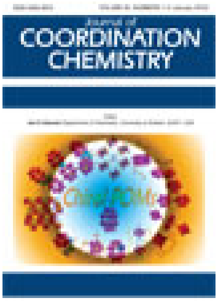

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Published online: 20 Jan 2012.

To cite this article: Xiao-Jun Long , Jing-Wei Dai & Jian-Zhong Wu (2012) Synthesis and supramolecular networks of mono- and dinuclear manganese chloride complexes with 2-(2,2′:6′,2″-terpyridin-4′-yl)phenol, Journal of Coordination Chemistry, 65:2, 316-324, DOI: 10.1080/00958972.2011.652623

To link to this article: http://dx.doi.org/10.1080/00958972.2011.652623

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*Journal of Coordination Chemistry*
Vol. 65, No. 2, 20 January 2012, 316–324

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# Synthesis and supramolecular networks of mono- and dinuclear manganese chloride complexes with 2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenol

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(*Received 30 September 2011; in final form 4 November 2011*)

2-(2,2′ : 6′,2″-Terpyridin-4′-yl)phenol has been prepared with an improved one-pot method. The reaction between the ligand and $MnCl_2$ in ethanol at ambient or hydrothermal conditions afforded dichlorido[2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenol-$\kappa^3 N,N',N''$]manganese(II) and dichloridobis[μ-2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenolate-$\kappa^3 N,N',N''$-$\kappa O$]dimanganese(II), respectively. Face-to-face $\pi$–$\pi$ stacking interactions between the pyridine rings play a crucial role in supramolecular networks of both complexes. Both complexes display weaker photoluminescence than the free ligand and the dinuclear complex luminescence was stronger than the mononuclear one.

*Keywords*: Manganese; Terpyridine; Crystal structure; Luminescence

## 1. Introduction

The coordination and supramolecular chemistry of multi-dentate polypyridine ligands has been an important area of research for decades. The tridentate 2,2′ : 6′,2″-terpyridine and its derivatives are among the most extensively studied polypyridine ligands [1–6]. 2-(2,2′ : 6′,2″-Terpyridin-4′-yl)phenol (HL) has an extra hydroxyl group on the 4′-phenyl ring, which is expected to influence the coordination and supramolecular interactions. However, the compound has not received much attention and there are only four relevant reports [7–10]. Coordination compounds of HL are limited to only two examples, mononuclear $Fe^{II}(HL)_2$ and $Ru^{II}(HL)_2$, in which the hydroxyl group is supposed to be intact and not coordinated without support of crystallographic analysis [10]. Herein, we report the synthesis, crystal structures, and photoluminescence studies of two manganese complexes based on the ligand, dichlorido[2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenol-$\kappa^3 N,N',N''$]manganese(II) (**1**) and dichloridobis[$\mu$-2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenolate-$\kappa^3 N,N',N''$-$\kappa O$]dimanganese(II) (**2**), which were obtained by reaction of the same reactants and solvents but under different temperature and pressure (scheme 1).

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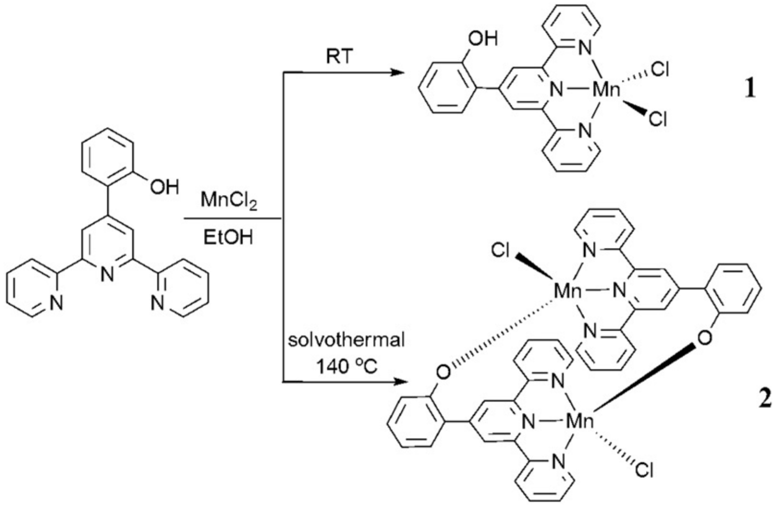
*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.652623



Scheme 1. Schematic representation of the synthesis and structural features of the complexes.

## 2. Experimental

### 2.1. *Materials and physical measurements*

All commercially available chemicals were of analytical pure grade and used without purification. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer as KBr pellets from 400 to 4000 $cm^{-1}$. Electrospray ionization mass spectra (ESI-MS) were obtained on a Thermo LCQ DECA XP MAX mass spectrometer. The melting point was measured with a Beijing Tech X-5 Microscopic Melting Point Detector.

### 2.2. *Synthesis*

**2.2.1. Synthesis of 2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenol (HL).** To a vigorously stirred solution of 2-acetylpyridine (5.23 mL, 0.046 mol) and salicylaldehyde (2.85 mL, 0.027 mol) in ethanol (15 mL) was added a solution of sodium hydroxide (4 g) in water (10 mL) at room temperature. The color of the mixture changed gradually from orange red to dark red. After further stirring for 5 min, the solution was heated to 80°C, aqueous ammonia (25%, 100 mL) was added, and the solution refluxed for 24 h. After removing the condenser, the resulting dark green solution was kept at 50°C to evaporate the excess ammonia and some ethanol and the solution turned brownish yellow. Upon cooling glacial acetic acid was added to yield brownish yellow product, which was collected and washed with water and ethanol. The product was further purified by dissolving in aqueous sodium hydroxide and precipitation with acetic acid. Yield 69%, m.p.: 260–264°C (literature 266–268°C [9], 257–259°C [7]). ESI-MS: $m/z = 326.68$ $[M+H]^+$, 673.06 $[2M+Na]^+$. IR (KBr, $\nu/cm^{-1}$): 3432(s), 3047(s), 1582(vs), 1471(s), 1394(vs), 1298(s), 1258(s), 1159(m), 1125(m), 857(m), 788(s), 764(vs), 630(m), 499(w).

**2.2.2. Synthesis of dichlorido[2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenol-$\kappa^3$*N*,*N*′,*N*″]- manganese(II) ethanol solvate, [Mn(HL)Cl$_2$] · CH$_3$CH$_2$OH (1).** LH (0.016 g, 0.05 mmol) was dissolved in hot ethanol (10 mL) and manganese chloride tetrahydrate (0.010 g, 0.05 mmol) was added and stirred for 15 min. Crystals formed from the bright yellow solution after standing at room temperature for 1 week. IR (KBr, $\nu$/cm$^{-1}$): 3466(s), 1610(m), 1544(w), 1475(w), 1413(m), 1245(w), 1014(w), 792(m), 766(m), 638(w), 563(w).

**2.2.3. Synthesis of dichloridobis[$\mu$-2-(2,2′ : 6′,2″-terpyridin-4′-yl)phenolate-$\kappa^3$*N*,*N*′,*N*″-$\kappa$*O*]-dimanganese(II), [Mn$_2$L$_2$Cl$_2$] (2).** LH (0.016 g, 0.05 mmol) and manganese chloride tetrahydrate (0.010 g, 0.05 mmol) were dissolved in ethanol (10 mL) and sealed in a 15 mL stainless steel bomb with a Teflon liner and heated at 140°C for 48 h. Crystals were obtained after cooling to room temperature. IR (KBr, $\nu$/cm$^{-1}$): 3433(vs), 1595(s), 1474(s), 1409(s), 1316(m), 1248(m), 1156(m), 1012(m), 870(w), 794(m), 747(m), 637(m), 492(w).

### 2.3. *Crystal structure determination*

Single-crystal X-ray diffraction data collection was performed on a Bruker Apex II CCD diffractometer using Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Data collection and reduction, and structure solving and refinement were performed using the APEX2 package software [11]. Both structures were solved by direct methods and refined by full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxyl hydrogen atoms were determined from a Fourier difference map, while the other hydrogen atoms were placed in geometrically idealized positions and refined using a riding model. Details of the crystal structure refinements are summarized in table 1.

## 3. Results and discussion

### 3.1. *Synthesis*

The preparation for HL utilized the traditional Michael-type addition reaction [2, 12] between 2-acetyl pyridine and salicylaldehyde. The reaction was conducted in a one-pot manner without separation of the 1,4-dione intermediate. The method is different from the Kröhnke reaction [2] applied by Hanabusa *et al.* [8] wherein the reaction was conducted in methanolic solution in the presence of 1-(2-pyridylcarbonylmethyl)pyridinium iodide and ammonium acetate. The yield for the latter (42%) is lower than the yield reported here (67%). Nagata and Tanaka [7] reported a unique multi-step route through intermediates 4′-((trifluoromethanesulfonyl)oxy)-2,2′ : 6′,2″terpyridine and 4′-(2-methoxyphenyl)-2,2′ : 6′,2″-terpyridine, which is more complicated.

Reaction between MnCl$_2$ and HL in ethanol at room temperature and solvothermal conditions (higher temperature and autogenous pressure) afforded two different Mn(II)

Table 1. Crystallographic data and structure refinement for **1** and **2**.

| Compound reference | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{21}H_{15}Cl_2MnN_3O \cdot C_2H_6O$ | $C_{42}H_{28}Cl_2Mn_2N_6O_2$ |
| Formula weight | 497.27 | 829.48 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 9.0042(13) | 8.1786(17) |
| $b$ | 10.8823(16) | 9.642(2) |
| $c$ | 12.7989(19) | 12.258(3) |
| $\alpha$ | 105.013(2) | 69.136(2) |
| $\beta$ | 107.660(2) | 84.526(2) |
| $\gamma$ | 97.243(2) | 79.798(2) |
| Unit cell volume (Å$^3$), $Z$ | 1125.3(3), 2 | 888.4(3), 1 |
| Absorption coefficient (mm$^{-1}$) | 0.849 | 0.909 |
| No. of reflections measured | 5677 | 4510 |
| No. of independent reflections | 3882 | 3082 |
| Goodness-of-fit on $F^2$ | 1.114 | 1.076 |
| $R_{\text{int}}$ | 0.0483 | 0.0586 |
| Final $R_1$ values [$I > 2\sigma(I)$] | 0.0558 | 0.0404 |
| Final $wR(F^2)$ values [$I > 2\sigma(I)$] | 0.1673 | 0.1110 |
| Final $R_1$ values (all data) | 0.0684 | 0.0467 |
| Final $wR(F^2)$ values (all data) | 0.1743 | 0.1159 |

complexes, which were revealed by X-ray crystal diffraction studies to be mononuclear $[Mn(HL)Cl_2] \cdot CH_3CH_2OH$ and dinuclear $[MnL_2Cl_2]$. The ligand displays different coordination in the two complexes, as will be discussed in detail below.

### 3.2. *Structural descriptions*

The asymmetric unit of $[Mn(HL)Cl_2] \cdot CH_3CH_2OH$ is shown in figure 1. Mn(II) is five-coordinate by two $Cl^-$ and one tridentate HL molecule. The coordination geometry can be best described as distorted square pyramidal, since its trigonality index $\tau = 0.111$ ($\tau = (\beta - \alpha)/60°$, where $\beta$ and $\alpha$ are the largest two angles in the coordination sphere; $\tau = 0$ for a perfect square pyramid and 1 for a perfect trigonal bipyramid [13]). The equatorial plane is composed of three nitrogen atoms from terpyridine of HL and one of the two chlorides, Cl(2). Another chloride, Cl(1), occupies the axial position. The three pyridine rings are in the same plane, as the dihedral angles between the middle pyridine ring and either edge pyridine is very small, 0.86(11)° for the N1 containing ring and 1.48(11)° for the N3 containing pyridine ring. The phenyl ring and its 2-OH group are in another plane. These two planes are inclined by a large angle of 39.4(1)°, ascribable to the steric hindrance caused by the 2-OH group. The hydroxyl group of the lattice ethanol is a hydrogen donor or acceptor to form two classic hydrogen bonds with Cl(1) and the phenolic hydroxyl, respectively (table 2). This results in the formation of a supramolecular hydrogen-bonded centrosymmetric dimer, as shown in figure 2. Each dimer is further connected to four neighboring dimers through interaction of the planar terpyridine moieties, since the interplane distance is 3.583(4) Å and there exist two kinds of off-set face-to-face $\pi$–$\pi$ stacking interactions between pyridine rings with the centroids of the pyridine rings being separated by 3.7812(3) Å ($C_g$(N2, C6–C10)$\cdots C_g$(N1, C1–C5)$^{\text{i}}$, symmetry code $^{\text{i}} = 2-x, 2-y, 2-z$) or 3.7898(4) Å ($C_g$(N3, C11–C15)$\cdots C_g$(N3, C11–C15)$^{\text{ii}}$, $^{\text{ii}} = 2-x,\ 2-y,\ 1-z$). Such $\pi$–$\pi$ stacking interactions lead to the formation of a 2-D layer, as depicted in figure 3.

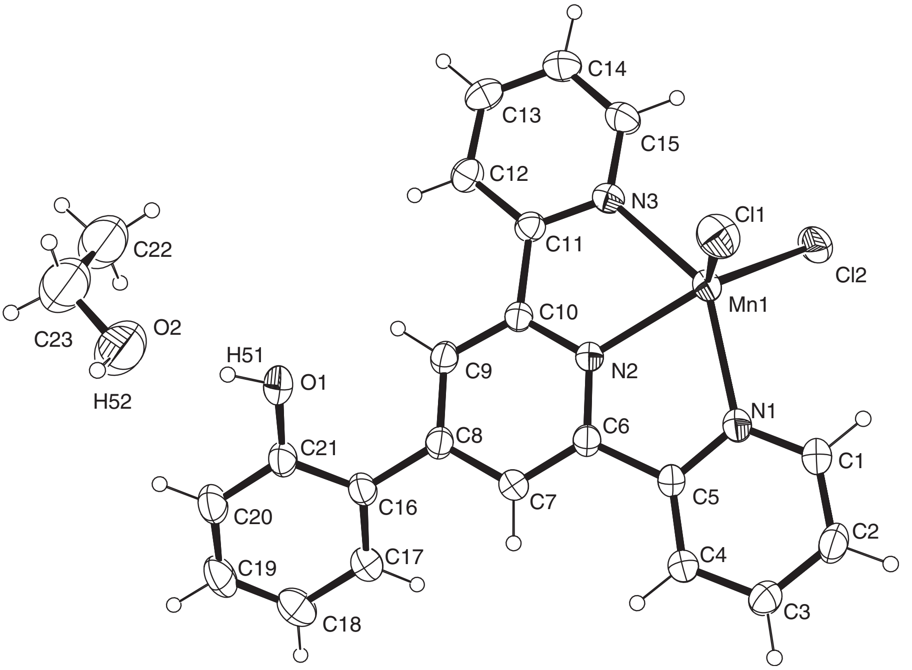


Figure 1. ORTEP drawing of **1** with the atom-numbering scheme. The atoms are represented by 30% probability thermal ellipsoids.

Table 2. Hydrogen bond data (Å and °) for **1**.

| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| O(1)–H(51)···O(2) | 0.82 | 1.86 | 2.660(5) | 165 |
| O(2)–H(52)···Cl(1)$^{i}$ | 0.82 | 2.58 | 3.162(6) | 129 |

Symmetry code: $^{i}$ $1-x$, $2-y$, $1-z$.

The molecular structure of dinuclear **2** is shown in figure 4. The phenol of HL is deprotonated in **2**. The phenolate ring is twisted from the attached middle pyridine ring by 29.5(1)°, smaller than that in **1**. The two edge pyridines are inclined to the middle one by 2.86(8)° and 3.24(7)°. The terpyridine chelates to Mn(II) and the phenolate binds to another Mn(II), leading to the formation of a covalently bonded and center related dinuclear molecule. Each Mn(II) is in a slightly distorted square-pyramidal $MnN_3OCl$ geometry as $\tau = 0.032$ [13], with the phenolate at the apical position. The length of the phenolate C–O bond (C(17)–O(1), 1.317(3) Å) in **2** is remarkably shorter than that of the corresponding phenol C–O bond (C(21)–O(1), 1.361(5) Å) in **1**, reflecting the strengthening of the phenolic C–O bond after the O–H bond is broken. Without hydroxyl groups, there are no classic hydrogen bonds in **2**. But similar to **1**, one dinuclear molecule is further linked to four neighboring molecules through interaction of the planar terpyridines. The interplane distance is 3.442(7) Å and the two inter-pyridine face-to-face $\pi$–$\pi$ stacking interactions are characterized by the inter-centroid distances 3.7907(6)

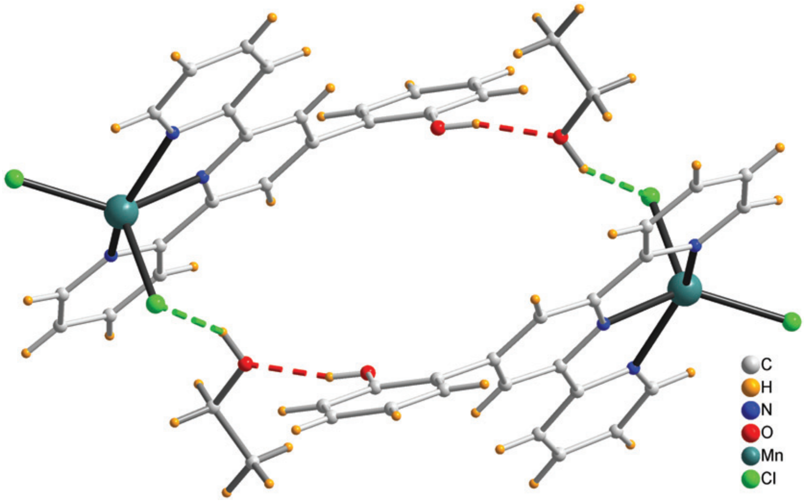


Figure 2. Hydrogen-bonded dimer of **1**. The hydrogen bonds are shown in dashed lines.

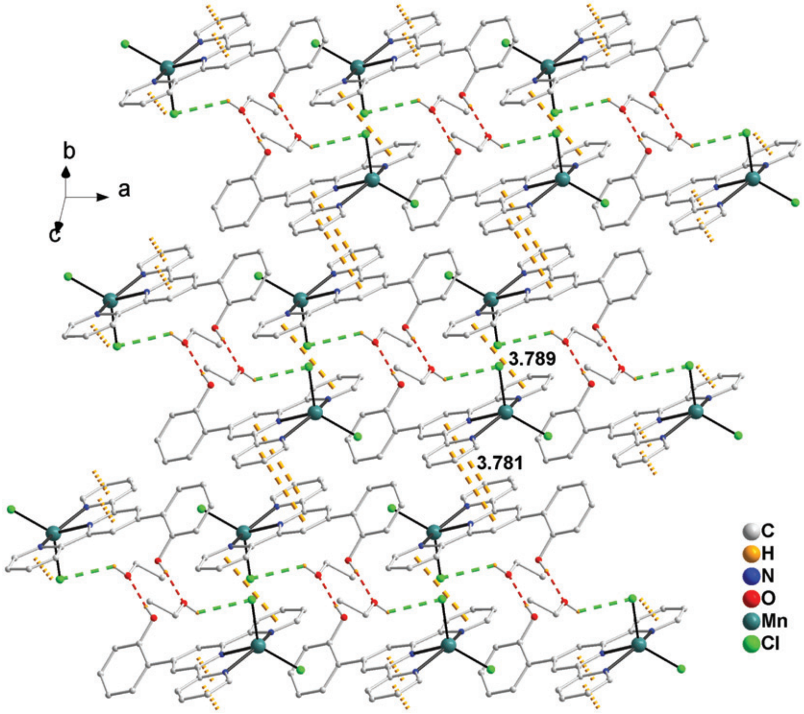


Figure 3. Face-to-face inter-pyridine $\pi$–$\pi$ stacking interactions connect the hydrogen-bonded dimers to a 2-D network in **1**. Hydrogen atoms other than those of hydroxyl groups are omitted for clarity.

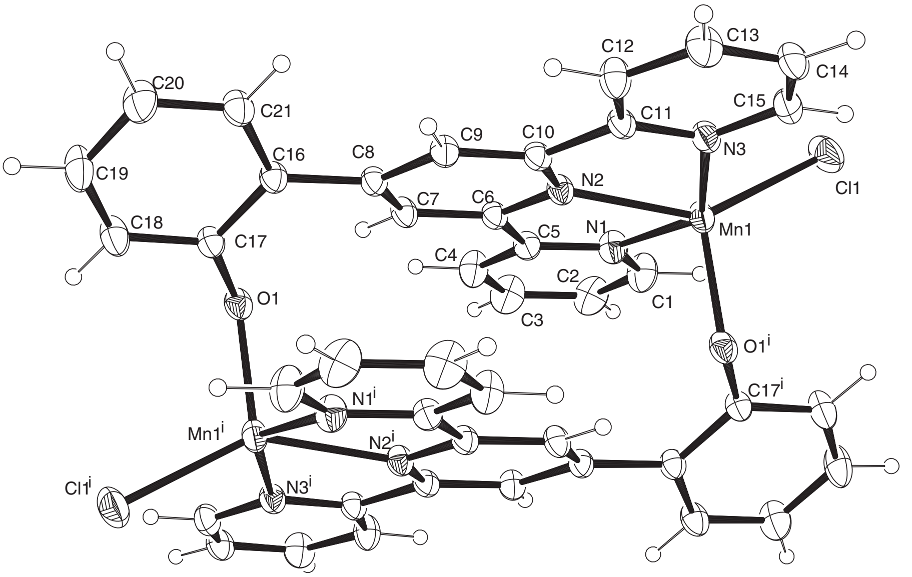


Figure 4. ORTEP drawing of **2** with the atom-numbering scheme. The atoms are represented by 30% probability thermal ellipsoids. Symmetry code: $^{i}$, $2-x$, $1-y$, $1-z$.

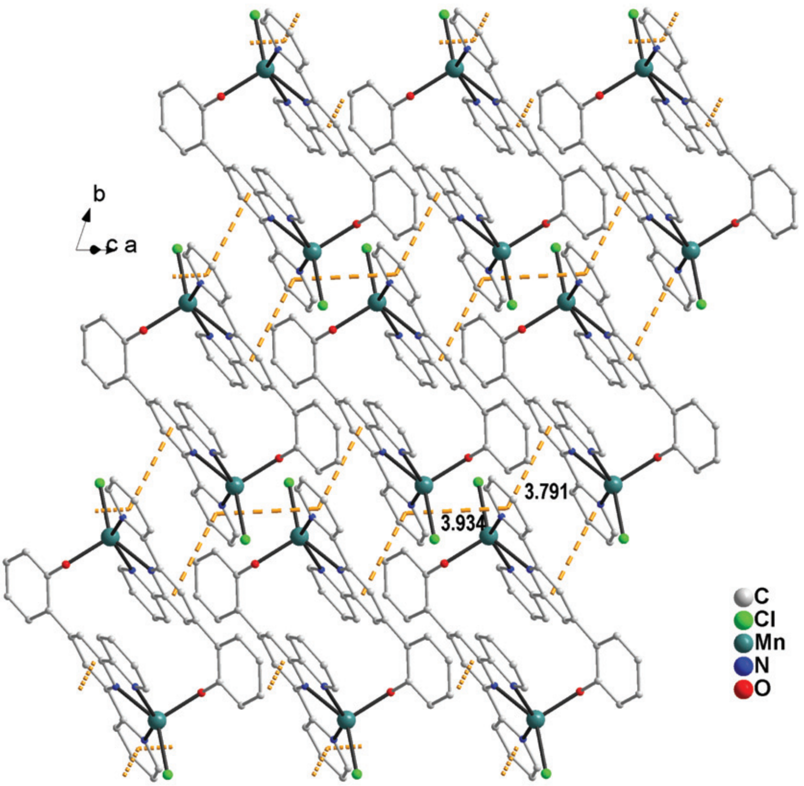


Figure 5. The dinuclear molecules of **2** are connected through $\pi$–$\pi$ stacking interactions to form a 2-D network. Hydrogen atoms are omitted for clarity.

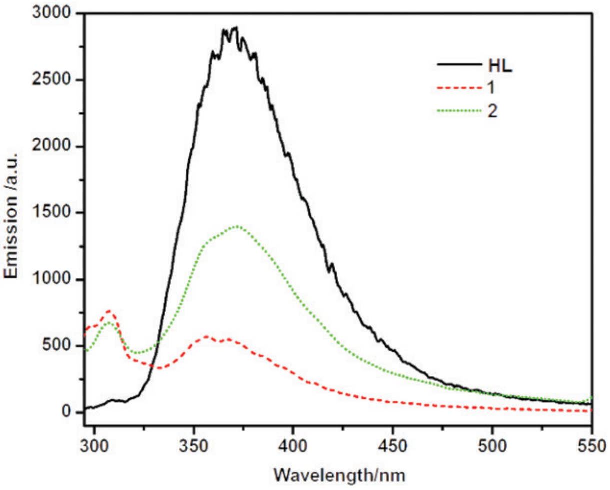


Figure 6. Fluorescence spectra of the free ligand and its coordination compounds at room temperature excited at 280 nm.

Å ($C_g$(N2, C6–C10) $\cdots$ $C_g$(N3, C11–C15)$^{i}$, $i = 2 - x, -y, 1 - z$) and 3.9338(7) Å ($C_g$(N3, C11–C15) $\cdots$ $C_g$(N3, C11–C15)$^{ii}$, $ii = 3 - x, -y, 1 - z$). A 2-D layer is formed as a consequence, as presented in figure 5.

### 3.3. *Fluorescent properties*

Like many other terpyridine compounds, free HL displays remarkable photoluminescence. As shown in figure 6, when excited by 280 nm light, HL exhibits emission around 370 nm. Coordination to a metal cation may have two opposite effects on the luminescence of a ligand. Restriction of the vibration and enhancement of planarity of the ligand upon ligation could increase luminescence while the Lewis acidic metal cation may function like an electron-withdrawing group decreasing luminescence intensity. The experimental results presented in figure 6 show that the emission intensity around 370 nm for **1** and **2** is significantly weaker than that of the free ligand, implying that the latter effect is more pronounced here. The reduced luminescence may be also due to the presence of unpaired electrons on Mn(II). Comparing the two complexes, dinuclear **2** emits stronger than mononuclear **1**, owing to more rigidity of **2**, as proven by the X-ray structural analysis. A new emission peak appears around 310 nm for both complexes, which might be caused by the metal-to-ligand charge transfer.

## 4. Conclusions

2-(2,2′ : 6′,2″-Terpyridin-4′-yl)phenol has been prepared with a convenient one-pot Michael reaction approach. The reaction with $MnCl_2$ in ethanol at ambient or solvothermal conditions yields mononuclear or dinuclear coordination compounds, respectively. The two complexes display different structural features and photoluminescence properties.

## Supplementary material

Crystallographic information of **1** and **2** has been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 841846 and 841847. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

## Acknowledgments

This study was supported by South China Normal University and Guangdong Natural Science Foundation.

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