Syntheses, Structures and Properties of Two Cd(II) Complexes Based on the 2-(1*H*-Imidazol-1-yl-methyl)-1*H*-benzimidazole Ligand

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Two new 1-D Cd(II) complexes, $\{[Cd(imb)(\mu_2\text{-}Cl)Cl]\cdot CH_3OH\}_n$ (**1**) and $\{[Cd(imb)(\mu_2\text{-}Cl)Cl]\cdot DMF\}_n$ (**2**), have been synthesized by the reactions of the unsymmetrical ligand 2-(1*H*-imidazol-1-yl-methyl)-1*H*-benzimidazole (imb) with $CdCl_2\cdot 2.5H_2O$ in methanol or methanol/DMF solution at room temperature, and structurally characterized by single-crystal X-ray diffraction. Complex **1** displays a ladder-shaped chain in which $[Cd_2Cl_4]$ units are linked to each other through two bridging imb ligands. Complex **2** features an infinite looped chain structure composed of two kinds of rings, the smaller $[Cd_2Cl_2]$ ring and the larger $[Cd_2imb_2]$ ring, connected alternately *via* their Cd(II) ions. The different architectures of complexes **1** and **2** can be generated by solvent exchange. The IR spectra and fluorescence properties of the complexes have been also investigated.

Key words: Cadmium Complex, 2-(1*H*-Imidazol-1-yl-methyl)-1*H*-benzimidazol, Crystal Structure, Fluorescence

Introduction

Metal-organic frameworks (MOFs) with intriguing structures have received great attention in recent years due to their interesting properties and potential applications for electrical conductivity and magnetism, as sensors, in photocatalysis, and in porous materials [1 – 5]. The choice of the organic ligand is a key step in the construction of specific architectures of the complexes because these are the organic units that serve to coordinate to the metal centers and pass on the structural information expressed in metal coordination preferences throughout the extended structure. In pursuing various structures of complexes, *N*-heterocyclic compounds bearing flexible backbones like alkyl spacers are one of the most widely studied classes of ligands because their flexibility and conformational freedom allow for greater structural diversity [6 – 8]. In virtue of these advantages, a great number of complexes based on flexible *N*-heterocyclic ligands have been synthesized such as $[Cd_2(Hbimt)_2I_4]$, $\{[Cd(Hbimt)(SO_4)(H_2O)_2]\cdot 1.5H_2O\}_n$ (Hbimt = 2-((benzoimidazolyl)methyl)-1*H*-tetrazole), $[Cd(L)_{0.5}(Hbtc)]\cdot 0.2H_2O$, $[Zn_3(L)(btc)_2(H_2O)_2]\cdot 3H_2O$, (L = 1,2,4,5-tetrakis(imidazol-1-yl-methyl)benzene, H_3btc = 1,3,5-benzenetricarboxylic acid), $[Cd_5(N_3)_6(btz)_2]_n$ (H_2btz = 1,5-bis(5-tetrazolo)-3-oxapentane), $[Cu_2(imb)_2Cl_4]\cdot 2CH_3OH$, $\{[Cu(imb)(bdic^{2-})]\cdot 1.5H_2O\cdot DMF\}_n$, and $\{[Cu(imb)(bdic^{2-})]\cdot 2H_2O\}_n$ (imb = 2-(1*H*-imidazol-1-yl-methyl)-1*H*-benzimidazole, H_2bdic = 1,3-benzenedicarboxylic acid) [9 – 12]. Furthermore, the choice of solvents also plays a critical role in the construction of specific metallosupramolecular architectures [13]. On the one hand, the solvent often influences the coordination behavior of the metal ions and then determines the construction of the frameworks [14 – 16]. On the other hand, extra-framework solvent molecules can also influence the structures of the complexes *via* intermolecular interactions with the parent network [17, 18].

In this work, we used a flexible multidentate *N*-heterocyclic compound 2-(1*H*-imidazol-1-yl-methyl)-1*H*-benzimidazole (imb) as ligand to self-assemble with Cd(II) salts in methanol or methanol/DMF, and obtained two new complexes $\{[Cd(imb)(\mu_2\text{-}Cl)Cl]\cdot CH_3OH\}_n$ (**1**) with ladder-shaped chains and

{[Cd(imb)(μ_2-Cl)Cl]·DMF}$_n$ (**2**) with looped chains. Furthermore, the steady state fluorescence properties of the two complexes have been investigated.

Experimental Section

All chemicals were purchased of AR grade and used without further purification. The 2-(1*H*-imidazole-1-yl-methyl)-1*H*-benzimidazole (imb) was synthesized according to the literature [19, 20]. The two complexes were characterized by their IR spectra on a Bruker Tensor 27 spectrophotometer with KBr pellets in the range of 400 – 4000 cm^{-1}. Elemental analyses (C, H, and N) were performed on a Flash EA 1112 elemental analyzer. Solid-state luminescence spectra were recorded with a Fluoro Max-P fluorescence spectrophotometer.

*Synthesis of {[Cd(imb)(μ_2-Cl)Cl]·CH$_3$OH}$_n$ (**1**)*

A methanol solution (3 mL) of imb was added dropwise into a methanol solution (2 mL) of $CdCl_2{\cdot}2.5H_2O$ (0.1 mmol) to give a clear solution. Two weeks later colorless crystals suitable for X-ray diffraction were obtained due to the slow evaporation of the solvent at room temperature. Crystals of **1** are stable in the air. Yield: 47 %. – Anal. for $C_{12}H_{14}CdCl_2N_4O$ (413.57): calcd. C 34.82, H 3.39, N 13.54; found C 34.88, H 3.47, N 13.66. – FT-IR (KBr, cm^{-1}): ν = 3429 (s), 3112 (m), 2947 (w), 1599 (m), 1517 (s), 1496 (s), 1453 (s), 1421 (m), 1316 (m), 1280 (s), 1231 (s), 1087 (s), 1007 (s), 842 (m), 745 (s), 658 (m).

*Synthesis of {[Cd(imb)(μ_2-Cl)Cl]·DMF}$_n$ (**2**)*

A methanol solution (3 mL) of imb (0.1 mmol) was added dropwise to a methanol solution containing $CdCl_2{\cdot}2.5H_2O$ (0.1 mmol). Then 1 mL DMF was added to the mixture to give a clear solution. After two weeks at room temperature clear crystals were obtained. Yield: 53 %. - Anal. for $C_{14}H_{17}CdCl_2N_5O$ (454.63): calcd. C 36.99, H 3.77, N 15.40; found C 37.03, H 3.63, N 15.44. – FT-IR (KBr, cm^{-1}): ν = 3007 (m), 2361 (s), 2343 (w), 1686 (w), 1618 (s), 1560 (m), 1438 (m), 1368 (s), 1277 (m), 1108 (m), 1027 (m), 937 (w), 846 (w), 757 (m), 669 (w).

Single-crystal structure determination

The crystals were carefully selected and attached to a thin glass fiber. The data collections were performed on a Rigaku Saturn 724 CCD area detector with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å; 50 kV and 40 mA) at a temperature of 293(2) K in ω scan mode and at a crystal-to-detector distance of 45 mm. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied. The structures were

Table 1. Crystal and structure refinement data of complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{12}H_{14}CdCl_2N_4O$	$C_{14}H_{17}CdCl_2N_5O$
Formula mass M_r	413.57	454.63
Temperature, K	293(2)	293(2)
Crystal size, mm^3	0.21 × 0.18 × 0.15	0.19 × 0.18 × 0.15
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.3263(17)	8.7941(18)
b, Å	10.048(2)	9.871(2)
c, Å	10.073(2)	11.704(2)
α, deg	75.78(3)	71.15(3)
β, deg	87.08(3)	86.38(3)
γ, deg	73.75(3)	68.34(3)
Volume, Å^3	784.1(3)	891.8(3)
Z	2	2
Calculated density, g cm^{-3}	1.75	1.69
Absorption coefficient, mm^{-1}	1.7	1.5
F(000), e	408	452
2θ range for data collection, deg	5.26-55.72	3.68-55.76
hkl range	$\pm10, \pm13, -12 \rightarrow 13$	$\pm11, \pm12, \pm15$
Reflections collected / unique / R_{int}	8558 / 3686 / 0.0205	10902 / 4218 / 0.0279
Data/restraints/parameters	3686 / 0 / 183	4218 / 0 / 208
Final indices$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0262 / 0.0593	0.0324 / 0.0920
Final indices $R1$ / $wR2$ (all data)	0.0292 / 0.0613	0.0356 / 0.1039
Goodness-of-fit on (F^2)	1.035	1.010
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.743 / −0.396	0.731 / −0.758

Table 2. Selected bond lengths (Å) and angles (deg) for complexes**1** and **2**[a].

Complex **1**		Complex **2**	
Cd1–N3	2.2434(18)	Cd1–N3	2.304(3)
Cd1–N1$^{\#1}$	2.343(2)	Cd1–N1$^{\#1}$	2.304(3)
Cd1–Cl2	2.4684(12)	Cd1–Cl2	2.4275(12)
Cd1–Cl1	2.4993(9)	Cd1–Cl1	2.5663(10)
Cd1–Cl1$^{\#2}$	2.7589(10)	Cd1–Cl1$^{\#2}$	2.6467(14)
N3–Cd1–N1$^{\#1}$	89.56(7)	N3–Cd1–N1$^{\#1}$	85.43(10)
N3–Cd1–Cl2	112.26(5)	N3–Cd1–Cl2	112.57(8)
N1$^{\#1}$–Cd1–Cl2	93.01(6)	N1$^{\#1}$–Cd1–Cl2	104.43(9)
N3–Cd1–Cl1	119.56(6)	N3–Cd1–Cl1	136.83(7)
N1$^{\#1}$–Cd1–Cl1	90.83(6)	N1$^{\#1}$–Cd1–Cl1	87.04(8)
Cl2–Cd1–Cl1	128.05(3)	Cl2–Cd1–Cl1	110.48(4)
N3–Cd1–Cl1$^{\#2}$	89.32(5)	N3–Cd1–Cl1$^{\#2}$	85.83(7)
N1$^{\#1}$–Cd1–Cl1$^{\#2}$	175.73(5)	N1$^{\#1}$–Cd1–Cl1$^{\#2}$	153.82(8)
Cl2–Cd1–Cl1$^{\#2}$	91.23(4)	Cl2–Cd1–Cl1$^{\#2}$	101.72(5)
Cl1–Cd1–Cl1$^{\#2}$	86.14(3)	Cl1–Cd1–Cl1$^{\#2}$	82.61(4)
Cd1–Cl1–Cd1$^{\#2}$	93.86(3)	Cd1–Cl1–Cd1$^{\#2}$	97.39(4)

[a] Symmetry transformations used to generate equivalent atoms: **1**: $^{\#1}$ $x+1, y, z$; $^{\#2}$ $-x+1, -y+2, -z+2$; **2**: $^{\#1}$ $-x, -y+2, -z+1$; $^{\#2}$ $-x+1, -y+2, -z+1$.

Table 3. Hydrogen bonds of complexes **1** and **2**[a].

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	(D–H···A) (deg)
		Complex **1**		
N4–H4C ···O1	0.86	1.99	2.821(3)	162.1
O1–H1 ···Cl2$^{\#4}$	0.82	2.37	3.161(2)	162.0
		Complex **2**		
N4–H4C ···O1	0.86	1.96	2.720(4)	146.7

[a] Symmetry transformation used to generate equivalent atoms: **1**: $^{\#4}$ $x, y-1, z$.

solved by Direct Methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2, using the SHELXS/L-97 program package [21]. The hydrogen atoms were assigned common isotropic displacement parameters and included in the final refinement by using geometrical restraints. Crystallographic parameters and structure refinement data are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table 2. Hydrogen bond parameters are listed in Table 3.

CCDC 860559 and 860560 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

*IR spectroscopy of complexes **1** and **2***

In the IR spectra the absorption band at 3429 cm^{-1} for **1** can be attributed to the stretching vibrations of O-H. The absorption bands at 3112 cm^{-1} for **1** and at 3007 cm^{-1} for **2** originate from stretching vibrations of Ar-H. The sharp bands observed at 1517, 1496 and 1453 cm^{-1} for **1**, and at 1618, 1560 and 1438 cm^{-1} for **2**, are due to stretching vibrations of C=C and C=N. In addition, the sharp bands at 1618 cm^{-1} for **2** show the existence of solvate DMF molecules [22]. The bands at 1280 cm^{-1} for **1** and 1277 cm^{-1} for **2** are the results of C-N stretching vibrations. The bands at 745 cm^{-1} for **1** and 757 cm^{-1} for **2** belong to stretching vibrations of the disubstituted phenyl ring. The above analyses are consistent with the results of the X-ray diffraction study.

*Crystal structure of {[Cd(imb)(μ$_2$-Cl)Cl]·CH$_3$OH}$_n$ (**1**)*

Single-crystal X-ray diffraction analysis has revealed that complex **1** crystallizes in the triclinic space group. As depicted in Fig. 1a, the Cd(II) ion is in a distorted trigonal-bipyramidal coordination environment with two nitrogen atoms from the benzimidazole and imidazole rings of two imb ligands, two bridging chlo-

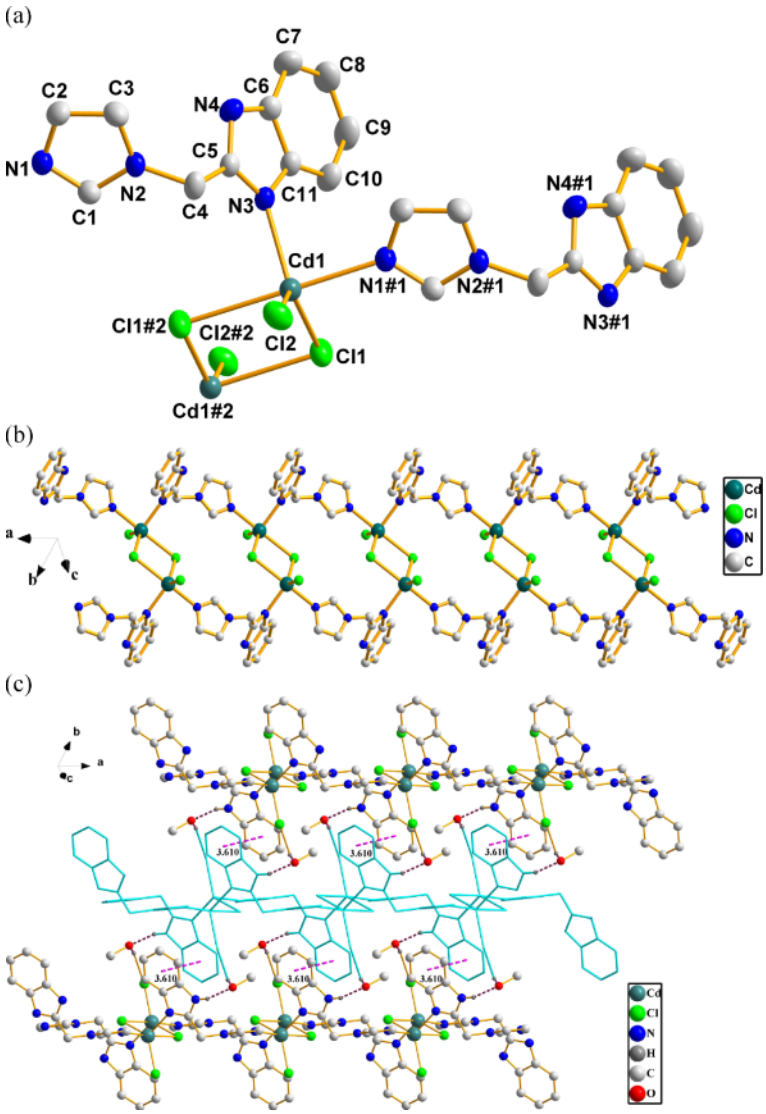

Fig. 1 (color online). (a) Coordination environment of Cd(II) in **1** with ellipsoids drawn at the 30% probability level (hydrogen atoms and free methanol molecules were omitted for clarity); (b) ladder chain of complex **1** parallel to the crystallographic *a* direction (hydrogen atoms and methanol molecules are omitted for clarity); (c) 2-D structure of complex **1** constructed by hydrogen bonds and $\pi\cdots\pi$ stacking interactions.

ride anions and one terminal chloride anion. The equatorial plane is occupied by N3, Cl1, Cl2, and Cd(II) atoms with the mean deviations of 0.0185 Å, while the $Cl1^{\#2}$ and $N1^{\#1}$ atoms occupy the axial positions with an $N1^{\#1}$–Cd1–$Cl^{\#2}$ angle of 175.73(5)°. Cd1 and $Cd1^{\#2}$ are bridged by two chloride atoms to give a dinuclear unit $[Cd_2Cl_4]$ with a Cd1···$Cd1^{\#2}$ distance of 3.846(1) Å. Each $[Cd_2Cl_4]$ unit is connected with two identical units through two bridging imb ligands, leading to the formation of a ladder-shaped chain parallel to the *a* direction, as shown in Fig. 1b. The dihedral angle between benzoimidazole and imidazole rings in the imb ligand is 68.01(9)°. The intrachain Cd···Cd distance is 8.3263 Å. In complex **1**, there are O–H···Cl and N–H···O hydrogen bonds between uncoordinated methanol molecules and terminal chlorine atoms (O···Cl: 3.161(2) Å), and between the benzoimidazole rings and uncoordinated methanol molecules (N···O: 2.821(3) Å). The ladder-shaped chains are further connected into a 2-D structure through hydrogen bonds and $\pi\cdots\pi$ stacking interactions between benzoimidazole rings of adjacent chains (the centroid-to-centroid distance is 3.6096(11) Å), as shown in Fig. 1c.

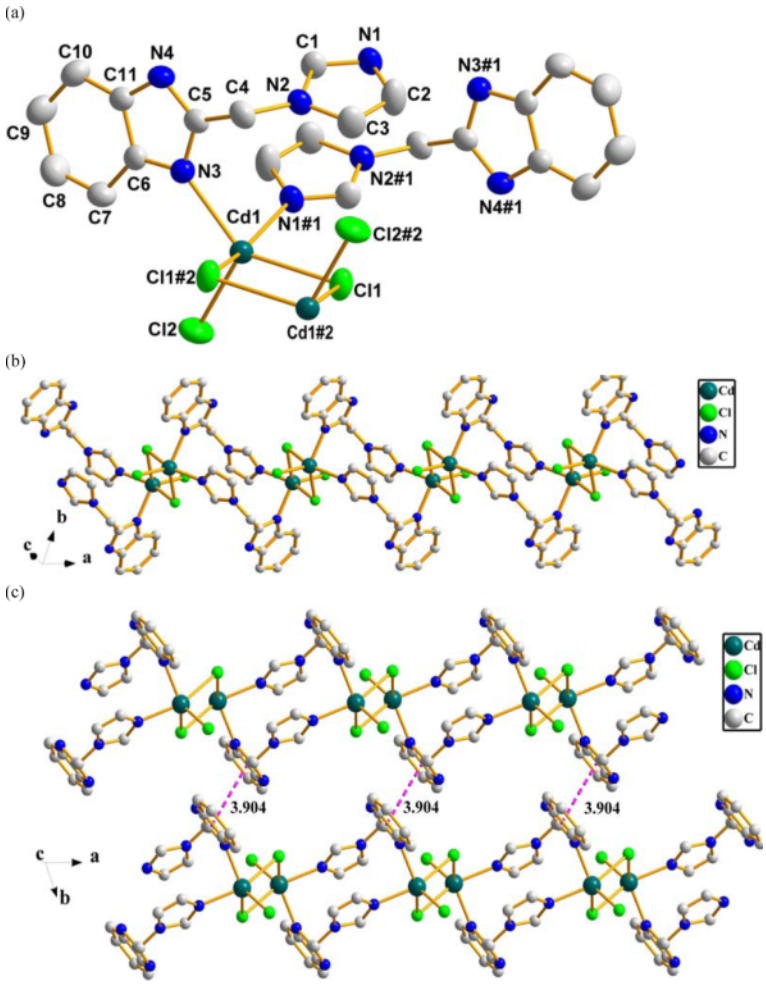

Fig. 2 (color online). (a) Coordination environment of Cd(II) in **2** with ellipsoids drawn at the 30% probability level (hydrogen atoms and free DMF molecules were omitted for clarity); (b) looped chain structure of complex **2** composed of two kinds of rings parallel to the crystallographic *a* direction; (c) view of the $\pi\cdots\pi$ stacking interactions between benzoimidazole rings in complex **2**.

*Crystal structure of {[Cd(imb)(μ_2-Cl)Cl]·DMF}$_n$ (**2**)*

The introduction of DMF into the reaction system influences the final structure of the product and gives rise to a new complex **2** with a different structure as compared to **1**. In complex **2**, the imb ligands coordinate to Cd(II) ions with the dihedral angle of the benzoimidazole and imidazole rings being 72.658(15)°. Thus complex **2** displays an infinite looped chain structure composed of two kinds of rings (Fig. 2b). The smaller ring is formed by two chloride anions bridging two Cd(II) cations with a Cd···Cd distance of 3.917(1) Å. The larger ring is defined by two imb molecules bridging two Cd(II) ions, where the Cd···Cd distance is 7.081(2) Å. The two kinds of rings are connected alternately *via* Cd(II) ions yielding an infinite chain. There are N–H···O hydrogen bonds between benzimidazole rings and uncoordinated DMF molecules (N···O: 2.720(4) Å), and $\pi\cdots\pi$ stacking interactions between the benzimidazole rings of adjacent chains with a centroid-to-centroid distances of 3.904(20) Å (Fig. 2c). The coordination geometry of the Cd(II) ion is similar to that of complex **1**, as shown in Fig. 2a. Each Cd(II) cation is five-coordinated by two nitrogen atoms from the benzimidazole and imidazole rings of two imb ligands, two bridging chloride anions and one terminal chloride anion in a distorted trigonal-bipyramidal coordination environment. The equatorial plane is completed by N3, Cl1, Cl2, and Cd(II) with a mean deviation of 0.0176 Å, while $Cl1^{\#2}$ and $N1^{\#1}$ occupy the axial positions with an $N1^{\#1}$–Cd1–$Cl1^{\#2}$ angle of 153.82(8)°.

Fluorescence spectra

A number of Zn(II) and Cd(II) complexes have been investigated regarding their fluorescence properties because of their potential applications in chemical sensors, photochemistry, and light-emitting diodes (LEDs) [10, 23, 24]. The solid-state luminescence properties of complexes **1** and **2** were investigated at room temperature. As shown in Fig. 3, the main emission peaks of the complexes are observed at 318 nm for **1** when excited at 293 nm, and at 317 nm for **2** when excited at 285 nm. The photoluminescence spectrum of the free ligand imb was also measured in the solid state. It displays an intense emission band at 305 nm (λ_{ex} = 285 nm) attributable to $\pi \rightarrow \pi^*$ transitions. The emission spectra of complexes **1** and **2** are also tentatively assigned to the intra-ligand charge transfer which is slightly red-shifted owing to the coordination of organic ligands to the metal ions [10].

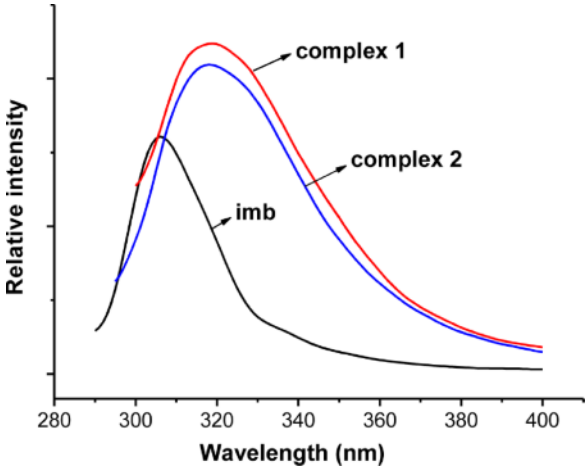

Fig. 3 (color online). Solid-state emission spectra of the imb ligand and the complexes **1** and **2** at room temperature.

Conclusion

In this work, we have prepared and characterized two new chain frameworks with different structures based on imb ligands from $CdCl_2 \cdot 2.5H_2O$ in different solvent systems. The results indicate that the rational change of solvent can influence significant details of the architectures of the complexes.

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