

基于 4-二苯基乙酸及 1,3-二(4-吡啶基)丙烷的 两个银配合物的结构和荧光

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摘要: 以同物质的量比例的 4-二苯基乙酸(Hbpa)、1,3-二(4-吡啶基)丙烷(bpp)和 $[\text{Ag}(\text{NH}_3)](\text{OH})$, 在不同反应条件下制备了 2 个基于柔性配体的类三明治配合物 $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2] \cdot 2\text{H}_2\text{O}$ (**1**)和 $[\text{Ag}(\text{bpa})(\text{bpp})] \cdot 2\text{H}_2\text{O}$ (**2**), 对其进行了单晶结构、元素分析、红外光谱、荧光光谱和粉末衍射表征。结构表明 **1** 是由 T 型配位的银离子和 $\text{Ag} \cdots \text{Ag}$ 超分子作用组装而成的二维配合物; 配合物 **2** 则是由四面体构型银离子和 $\pi \cdots \pi$ 堆积作用组装的二维配位超分子。此外, **1** 和 **2** 还可在可见光区的不同位置发射较强荧光。

关键词: 柔性配体; 类三明治; 超分子作用; 荧光

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Structure and Fluorescence of Two Ag(I) Complexes Based on 4-Biphenylacetate and 1,3-Bis(4-pyridyl)propane

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Abstract: Two sandwich-like coordination polymers based on Ag(I) and mixed flexible ligands, $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ag}(\text{bpa})(\text{bpp})] \cdot 2\text{H}_2\text{O}$ (**2**) (bpa⁻=4-biphenylacetate, bpp=1,3-bis(4-pyridyl)propane), have been synthesized by solution reactions of Hbpa, bpp and $[\text{Ag}(\text{NH}_3)](\text{OH})$ with the same ratio under different experimental conditions. They were characterized by single-crystal X-ray diffraction, EA, IR and XRD. Complex **1** is a two-dimensional network based on T-shaped coordination Ag(I) ions and $\text{Ag} \cdots \text{Ag}$ interactions. In **2**, the distorted tetrahedral coordination Ag(I) ions are further organized by $\pi \cdots \pi$ stacking interactions into another two-dimensional network. **1** and **2** exhibit different and intense emissions in the visible region. CCDC: 922168, **1**; 922167, **2**.

Key words: flexible ligand; sandwich-like; supramolecular interaction; luminescence

0 Introduction

The design and construction of coordination polymers is of current interest in the fields of supramolecular chemistry and crystal engineering because of their intriguing variety of structures and

fascinating properties^[1-7]. The construction of coordination polymers is influenced by many factors, such as metal ions, organic ligands, counteranions, experimental temperature, solvent molecules and pH of the reaction mixture, etc^[8-10]. Up to date, many interesting coordination polymers have been constructed by the

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flexible aromatic carboxylate ligands. And flexible polypyridyl ligands are another kinds of interesting linkers with strong coordination ability^[11-14]. We have recently investigated a series of flexible sandwich-like coordination polymers based on mixed flexible ligands of aromatic carboxylate and dipyridyl ligands, such as the Ag/Cu-RCO₂-bpp (R=phenyl or pyridyl, bpp=1,3-bis(4-pyridyl) propane) systems^[15-18]. Sandwich-like coordination polymers could be potential dynamic materials as they sustain the changes caused by external stimuli. In order to study the influence of experimental conditions on the sandwich-like polymers, herein we report two new Ag(I) coordination polymers with mixed flexible ligands {[Ag₂(bpa)₂(bpp)₂]·2H₂O}_n (**1**) and {[Ag(bpa)(bpp)]·2H₂O}_n (**2**) (bpa⁻=4-biphenylacetate), involving different coordination of Ag(I), the conformations of flexible ligands, Ag···Ag or $\pi \cdots \pi$ interactions, solvent molecules, thermal stability, as well as their fluorescence spectrum.

1 Experimental

All reagents and solvents employed were commercially available and used as received. FT-IR spectra were recorded from KBr pellets in the range 4 000~400 cm⁻¹ on a Nikolai AVATAR spectrometer. The C, H, and N elemental analyses were carried out with an Elementar Vario-El CHNS analyzer. The solid-state photoexcitation and emission spectra were performed on a PerkinElmer LS55 spectrophotometer at room temperature.

1.1 Synthesis

Complexes **1** and **2** were synthesized by solution reactions of Ag(I), Hbpa and bpp with the same ratio of 1:1:1 under different experimental temperature and solvents.

Synthesis of {[Ag₂(bpa)₂(bpp)₂]·2H₂O}_n (**1**): A mixture of [Ag(NH₃)](OH) (0.5 mmol), Hbpa (106.1 mg, 0.5 mmol), bpp (50.0 mg, 0.5 mmol), methanol (12 mL) and water (4 mL) was vigorously stirred for 30 min at 60 °C. The resulting solution was filtered and allowed to stand in air at room temperature. Block colorless crystals were obtained in 56% yield after three days. Anal. calcd. for C₅₄H₅₄N₄O₆Ag₂ (%): C,

60.57; H, 5.08; N, 5.23. Found(%): C, 60.49; H, 5.14; N, 5.16. IR (KBr, cm⁻¹): 3 303 (m), 3 031 (m), 2 913 (w), 2 366 (w), 1 614 (m), 1 573 (s), 1 509 (s), 1 486 (s), 1 422 (w), 1 382 (vs), 1 168 (w), 1 075 (w), 1 007 (w), 820 (m), 749 (vs), 712 (m), 689 (s), 555 (w).

Synthesis of {[Ag(bpa)(bpp)]·2H₂O}_n (**2**): A mixture of [Ag(NH₃)](OH) (0.5 mmol), Hbpa (106.1 mg, 0.5 mmol), bpp (50.0 mg, 0.5 mmol) and water (16 mL) was vigorously stirred for 30 min under room temperature. Block colorless crystals were obtained in 70% yield after two days. Anal. calcd. for C₂₇H₂₉N₂O₄Ag (%): C, 58.60; H, 5.28; N, 5.06. Found (%): C, 58.67; H, 5.23; N, 5.09. IR data (KBr): 3 297 (s), 3 055 (m), 3 031 (m), 2 925 (m), 2 853 (w), 1 941 (w), 1 604 (vs), 1 573 (s), 1 486 (m), 1 455 (w), 1 420 (s), 1 379 (vs), 1 285 (m), 1 215 (w), 1 155 (m), 1 006 (s), 924 (w), 807 (m), 742 (s), 693 (m), 613 (w), 510 (m).

1.2 Structure determination

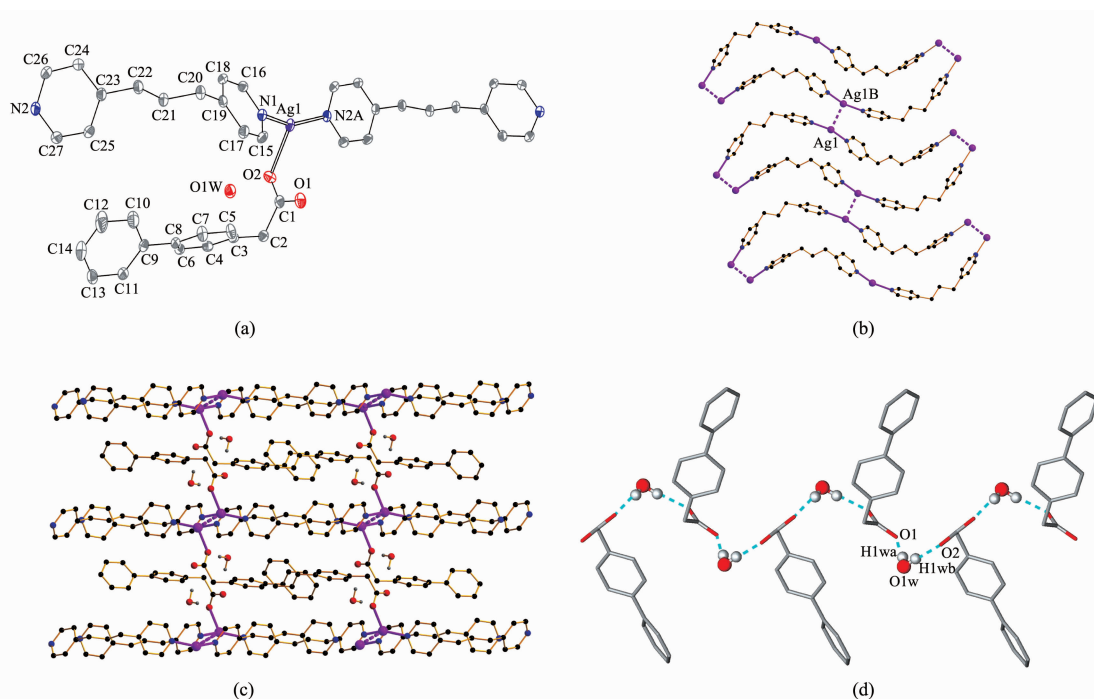
Diffraction collected of **1** with dimensions of 0.20 mm×0.17 mm×0.14 mm and **2** with dimensions of 0.18 mm×0.15 mm×0.10 mm were performed on a Bruker SMART CCD Apex II diffractometer with a graphite-monochromatized Mo K α radiation (λ =0.071 073 nm) using an φ - ω scan mode at 298 K. Multi-scan absorption corrections were applied using SADABS program^[19]. The structures were solved by direct methods and refined anisotropically by full-matrix least-squares methods on F^2 using the SHELXTL program package^[20]. Hydrogen atoms on carbon atoms were placed in calculated positions and refined as riding atoms with isotropic thermal factors; the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors.

CCDC: 922168, **1**; 922167, **2**.

2 Results and discussion

2.1 Crystal structures

X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic $P2_1/n$ space group. Each asymmetric unit contains one Ag(I) cation, one bpa⁻ anion, one bpp and one guest water (Fig.1a). Ag(I) ion displays a T-shaped coordination geometry by coordination with two nitrogen atoms of two bpp



Symmetry codes: A: $-1/2+x, 1/2-y, 1/2+z$; Symmetry codes: B: $-x, 1-y, -z$; Hydrogen atoms on carbon atoms are omitted for clarity in (d)

Fig.1 (a) Coordination environments of Ag(I) atoms with 30% probability displacement ellipsoids in **1**, (b) view of the $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2]_n^{2n+}$ slice, (c) the supramolecule constructed with $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2]_n$ layers by $\text{Ag} \cdots \text{Ag}$ interactions and guest water molecules of **1**, (d) the hydrogen bonds between bpa^- and water molecules along the b axis

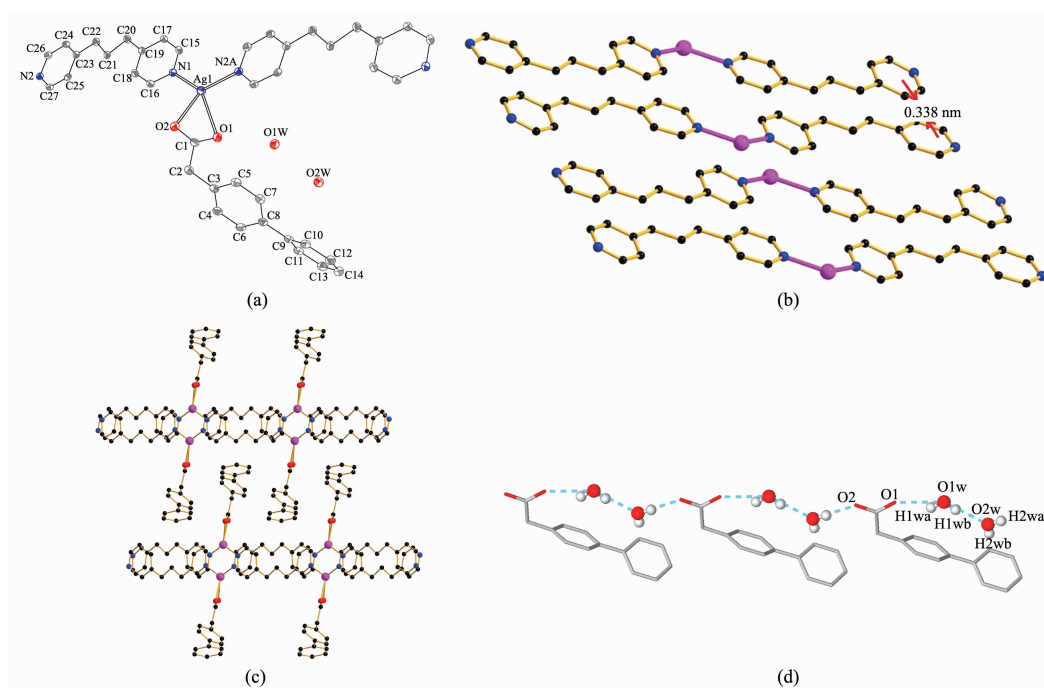
ligands and one O atom of the bpa^- ligand. The Ag1-O distance is 0.242 6(2) nm. The Ag1-N distances are at 0.216 8(2)~0.218 6(2) nm. The adjacent Ag(I) atoms are ligated into 1D $[\text{Ag}(\text{bpp})]_n$ chains by bpp ligands. The adjacent $[\text{Ag}(\text{bpp})]_n$ chains are further linked into 2D $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2]_n$ layer by $\text{Ag} \cdots \text{Ag}$ interactions with the distance of 0.308 8(1) nm (Fig.1b), shorter than Van der Waals radii of two Ag(I) ions^[21]. The coordinated bpa^- ligands stand alternatively on sides of $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2]_n$ layer (Fig.1c). The adjacent water molecules and bpa^- are connected by hydrogen bonds along the b axis (Fig.1d). The O1w \cdots O2 and O1w \cdots O1 distances are 0.277 4 and 0.302 7 nm. The bpp ligands possess the TT conformation (T=trans) with the N \cdots N distance of 0.958 1 nm^[14]. The overall sandwich-like supramolecule consists of mutually interdigitated $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2]_n$ layers and guest water molecules.

2 crystallizes in $P\bar{1}$ space group with lower symmetry. Each asymmetric unit contains one Ag(I) cation, one bpa^- anion, one bpp and two guest water molecules (Fig.2a). The Ag(I) atom displays a distorted tetrahedral geometry connected by two bpp

and one bidentate bpa^- ligands. The Ag1-O distances are 0.241 0(2)~0.251 9(2) nm. Furthermore, all the atoms of bpp ligand in **2** are coplanar with the N \cdots N distance of 1.000 3 nm, indicating different conformation from bpp molecule in **1**. The parallel $[\text{Ag}(\text{bpa})(\text{bpp})]_n$ chains were held together into $[\text{Ag}_2(\text{bpa})_2(\text{bpp})_2]_n$ layers by $\pi \cdots \pi$ stacking interactions of planer bpp with the distance of 0.338 nm (Fig.2b, 2c). The adjacent water molecules and bpa^- are connected by hydrogen bonds along the b axis. The O1 \cdots O1w, O1w \cdots O2w and O2w \cdots O2 distances are 0.281 0, 0.283 6 and 0.265 6 nm (Fig.2d).

2.2 Photoluminescence properties

The photoluminescence of **1**, **2**, Hbpa and bpp in the solid state were investigated at room temperature (Fig.3). The free Hbpa and bpp ligands in the solid-state display emissions at 342 nm ($\lambda_{\text{ex}}=257$ nm) and 402 nm ($\lambda_{\text{ex}}=332$ nm), while **1** exhibits an intense broad emission at 445 nm upon excitation at 238 nm. **2** presents an intense broad emission at 431 nm ($\lambda_{\text{ex}}=338$ nm). Compared with the emission spectra of the Hbpa and bpp ligands, the broad red shifts may be



Symmetry codes: A: $1+x, 1+y, z$; Hydrogen atoms on carbon atoms are omitted for clarity in (d)

Fig.2 (a) Asymmetric unit and coordination environment of Ag(I) with 30% probability displacement ellipsoids in **2**, (b) the $\pi \cdots \pi$ stacking interactions between 1D $[\text{Ag}(\text{bpp})]_n^{n+}$ chains, (c) the sandwich-like supramolecule of **2**, (d) the hydrogen bonds between bpa^- and water molecules along the b axis

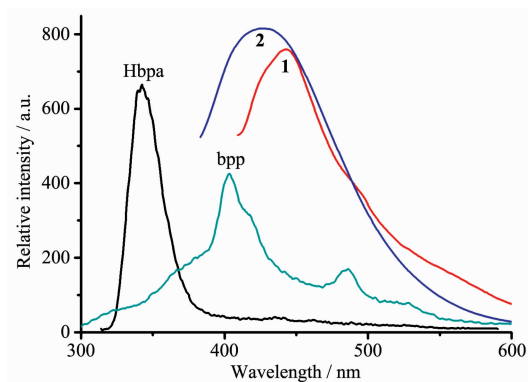


Fig.3 Solid-state photoluminescent spectrum

attributed to the ligand-to-metal charge transfer (LMCT)^[22-23]. Phase purity of the bulk materials of **1** and **2** was confirmed by comparison of their powder diffraction (XRD) patterns with those calculated from single crystal X-ray diffraction studies (Fig.4).

3 Conclusions

In summary, two Ag (I) complexes were constructed from the same ratio of Ag(I), Hbpa and bpp under different experimental temperature and solvents, involving different coordination of Ag(I), the

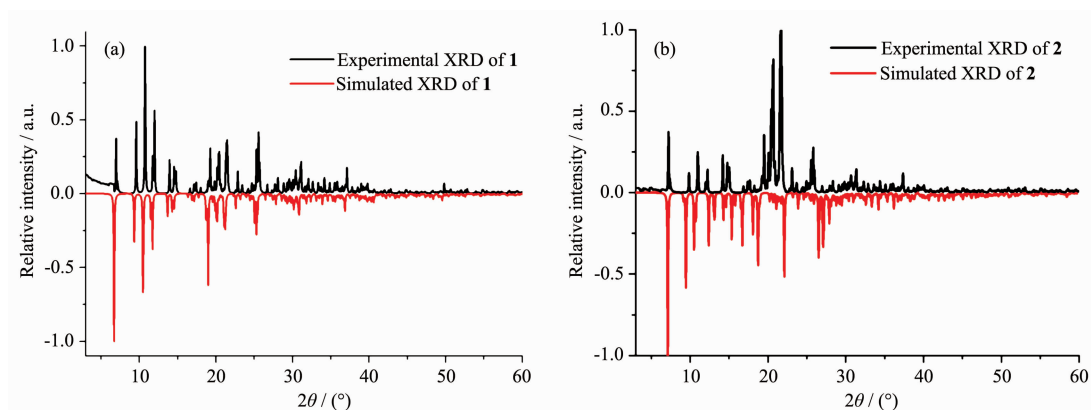


Fig.4 Experimental and simulated powder XRD patterns of **1** (a) and **2** (b)

conformations of flexible ligands, $\text{Ag} \cdots \text{Ag}$ or $\pi \cdots \pi$ interactions, solvent molecules, thermal stability, as well as their fluorescence spectrum. Complex **1** presents T-shaped coordination $\text{Ag}(\text{I})$ ions extended by $\text{Ag} \cdots \text{Ag}$ interactions and less solvents, whereas **2** has distorted tetrahedral coordination $\text{Ag}(\text{I})$ ions organized by $\pi \cdots \pi$ stacking interactions and more solvents. **1** and **2** exhibit different and intense emissions in the visible region. The flexible combinations of carboxylates and dipyrindine linkers may provide a feasible strategy to study the effect of experimental conditions on flexible coordination polymers.

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