

含有双膦配体的银(I)配合物的合成、表征和荧光性质

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摘要: 在甲醇与二氯甲烷的混合溶液中分别合成了 2 个新的银(I)配合物, [Ag(XANTphos)]BF₄ (**1**)和[Ag₂Cl₂(DPEphos)₂]·2CH₂Cl₂ (**2**)(XANTphos=4,5-双二苯基膦-9,9-二甲基氧杂蒽; DPEphos=双((2-二苯基膦)苯基)醚), 通过红外光谱、X 射线单晶衍射、核磁共振氢谱和荧光光谱进行分析和表征。**1** 是由 AgBF₄, XANTphos 和 dmp(2,9-二甲基-1,10-菲咯啉)以 1:1:1 的计量比反应得到的单核化合物。中心原子 Ag(I)均通过双膦配体(XANTphos)的螯合作用形成环。而 **2** 是由 AgCl 和 DPEphos 以 1:1 的比例反应得到的双核化合物。在配合物 **2** 的非对称单元中, 每个 DPEphos 配体与一个银离子螯合, 且含有一个游离的二氯甲烷。荧光光谱表明配合物 **1**、**2** 的所有发射峰均源于配体中的 π - π^* 跃迁。

关键词: 4,5-双二苯基膦-9,9-二甲基氧杂蒽; 双((2-二苯基膦)苯基)醚; 银; 荧光

中图分类号: O614.122

文献标识码: A

文章编号: 1001-4861(2018)02-0381-06

DOI: 10.11862/CJIC.2018.034

Syntheses, Characterization and Luminescent Properties of Silver(I) Complexes Based on Diphosphine Ligands

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Abstract: Two novel silver(I) complexes [Ag(XANTphos)]BF₄ (**1**) and [Ag₂Cl₂(DPEphos)₂]·2CH₂Cl₂ (**2**) (XANTphos=9,9-dimethyl-4,5-bis(diphenylphosphanyl)xanthene, DPEphos=bis(2-(diphenylphosphino)phenyl)ether) have been synthesized in mixed solvent CH₃OH and CH₂Cl₂ and characterized by IR, single-crystal X-ray diffraction, ¹H NMR spectroscopy and fluorescence spectra. Complex **1** is of a mononuclear complex, which was generated by the reaction of AgBF₄ and XANTphos with dmp (neocuproine) in 1:1:1 molar ratio. The central ion Ag(I) forms a ring by the chelating bisphosphine ligand (XANTphos). While complex **2** is of a binuclear complex, which was obtained by the reaction of AgCl with DPEphos in 1:1 molar ratio. In the asymmetric unit of complex **2**, each DPEphos ligand chelates one silver(I) cation with a free dichloromethane. The luminescent spectra show that all the emissions of the complexes **1** and **2** are assigned to ligand centered π - π^* transition. CCDC: 1555835, **1**; 1508048, **2**.

Keywords: 9,9-dimethyl-4,5-bis(diphenylphosphanyl)xanthene; bis(2-(diphenylphosphino)phenyl)ether; silver(I); fluorescence

收稿日期: 2017-08-01。收修改稿日期: 2017-11-10。

国家自然科学基金(No.21171119, 81573822)、北京教育委员会基金(No.KM201210028020)、北京市优秀人才项目(No.2010D005016000002)和北京市自然科学基金(No.2172017, 2172012)资助项目。

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0 Introduction

In recent years, the study of silver(I) complexes based on organic phosphine, especially diphosphine ligands, has attracted considerable attention^[1-4]. In coordination chemistry, self-assembled silver(I) complexes usually have structural diversity and potential applications in luminescent material and antimicrobial^[5-8]. According to the hard-soft-acid-base (HSAB) theory, as P-donor ligands, bis(2-(diphenylphosphino)phenyl) ether (DPEphos) and 9,9-dimethyl-4,5-bis(diphenylphosphanyl)xanthene (XANTphos) can both easily coordinate with Ag(I) salts. Since the transition metal chemistry and catalytic function of DPEphos and XANTphos ligands were studied by van Leeuwen and his co-workers^[9] for the first time, various researches about Ag(I) complexes on the two ligands have been published^[10-12].

Ag(I)-DPEphos/XANTphos complexes are widely studied by us and other researchers^[13-17]. In these complexes, DPEphos/XANTphos is a kind of chelated P-donor ligands, and some bridged co-ligands help to form 1D infinite chains. In some complexes the existence of weak interactions makes the 1D infinite chain structures expanding to 2D networks or 3D architectures. The type of weak interactions appeared in these complexes are hydrogen bond, C-H $\cdots\pi$, $\pi\cdots\pi$, anion $\cdots\pi$ and so on, which can also help to stabilize the supramolecular coordination polymers^[8].

In this paper, two novel Ag-diphosphine complexes, namely [Ag(XANTphos)]BF₄ (**1**) and [Ag₂Cl₂(DPEphos)₂] $\cdot$ 2CH₂Cl₂ (**2**), have been synthesized and characterized by X-ray diffraction, IR, ¹H NMR and fluorescence spectra. The weak interactions and luminescent properties of these complexes are discussed.

1 Experimental

1.1 Materials and measurements

All chemical reagents are commercially available and used without furthermore treatment. FT-IR spectra (KBr pellets) were measured on a Perkin-Elmer Infrared spectrometer. C, H and N elemental analysis were carried out on an Elementar Vario

MICRO CUBE (Germany) elemental analyzer. Room-temperature fluorescence spectra were measured on F-4500 FL Spectrophotometer. ¹H NMR was recorded at room temperature with a Bruker DPX 600 spectrometer.

1.2 Synthesis of [Ag(XANTphos)]BF₄ (**1**)

Complex **1** was prepared by the reaction of AgBF₄ (0.038 4 g, 0.2 mmol), XANTphos (0.115 7 g, 0.2 mmol) and dmp (0.041 7 g, 0.2 mmol, dmp=neocuproine) in the mixed solvents of 5 mL CH₂Cl₂ and 5 mL CH₃OH. The mixture was stirred for 6 h and filtered. Colorless crystals were obtained from the filtrate after standing at room temperature for several days. Yield: 71%. Element analysis Calcd. for C₇₉H₆₈AgBF₄O₃P₄(%): C, 68.51; H, 4.92. Found(%): C, 68.08; H, 4.61. IR data (cm⁻¹, KBr pellets): 3 514w, 3 053w, 2 958w, 1 971w, 1 815w, 1 621m, 1 590m, 1 502m, 1 478vs, 1 434vs, 1 402s, 1 360s, 1 327s, 1 306m, 1 284s, 1 218s, 1 198m, 1 151m, 1 057s, 870m, 857m, 801m, 778s, 746s, 610w, 588w, 548w, 537w, 514s, 498s, 460m. ¹H NMR (600 MHz, CDCl₃, 298 K): δ 7.9~8.4 (m, dissociative dmp-ph), 7.03~7.60 (m, overlap with the solvent peak signal, XANTphos-ph), 2.48 (s, dissociative dmp-CH₃), 1.62 (s, 12H, XANTphos-CH₃).

1.3 Synthesis of [Ag₂Cl₂(DPEphos)₂] $\cdot$ 2CH₂Cl₂ (**2**)

A mixture of AgCl (0.028 7 g, 0.02 mmol) and DPEphos (0.106 8 g, 0.2 mmol) was dissolved in a mixture of 5 mL CH₂Cl₂ and 5 mL CH₃OH, stirred for 6 h and filtered. Colorless crystal **2** was obtained from the filtrate after standing at the room temperature for several days. Yield: 63%. Element analysis Calcd. for C₇₄H₆₀Ag₂Cl₆O₂P₄(%): C, 57.91; H, 3.91. Found(%): C, 57.56; H, 3.60. IR data (cm⁻¹, KBr pellets): 3 422m, 3 051m, 1 624w, 1 586w, 1 564w, 1 479w, 1 461s, 1 434s, 1 259m, 1 222s, 1 159w, 1 095m, 1 027w, 876w, 801w, 745s, 695s, 507m, 422w. ¹H NMR (600 MHz, CDCl₃, 298 K): δ 7.16~6.66 (m, CH_{benzene}), 5.29 (s, CH_{CH₂Cl₂})

1.4 Structure determination

Single crystals of the title complexes were mounted on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Mo K α (λ =0.071 073 nm) radiation at 298 K. Semi-empirical absorption corrections were applied using SABABS

program^[18]. All the structures were solved by direct methods using SHELXS program of the SHELXTL-97 package and refined with SHELXL-97^[19-20]. Metal atom centers were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The

hydrogen atoms were generated geometrically and refined with displacement parameters riding on the concerned atoms.

Crystallographic data and experimental details for structural analysis are summarized in Table 1, and selected bond lengths and angles of complexes **1~2** are summarized in Table 2.

CCDC: 1555835, **1**; 1508048, **2**.

Table 1 Crystallographic data for complexes **1~2**

Complex	1	2
Formula	C ₇₉ H ₆₈ AgBF ₄ O ₃ P ₄	C ₇₄ H ₆₀ Ag ₂ Cl ₆ O ₂ P ₄
Formula weight	1 383.89	1 533.54
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size / mm	0.45×0.40×0.30	0.36×0.328×0.31
<i>a</i> / nm	1.303 20(11)	1.202 80(11)
<i>b</i> / nm	1.320 71(12)	1.258 11(12)
<i>c</i> / nm	2.033 09(16)	1.422 69(13)
α / (°)	95.033 0(10)	114.590(3)
β / (°)	93.985 0(10)	98.963 0(10)
γ / (°)	98.125(2)	107.292(2)
<i>V</i> / nm ³	3.438 8(5)	1.769 7(3)
<i>Z</i>	2	1
<i>F</i> (000)	1 428	776
Goodness-of-fit on F^2	1.027	1.077
R_{int}	0.039 3	0.064 4
R_1 [$I > 2\sigma(I)$] ^a	0.051 2	0.067 8
wR_2 [$I > 2\sigma(I)$] ^b	0.084 1	0.152 2
R_1 (all data) ^a	0.098 6	0.123 9
wR_2 (all data) ^b	0.092 4	0.166 0

^a $R = \sum (|F_o| - |F_c|) / \sum |F_o|$; ^b $wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)]^{1/2}$.

Table 2 Selected bond distances (nm) and bond angles (°) for complexes **1~2**

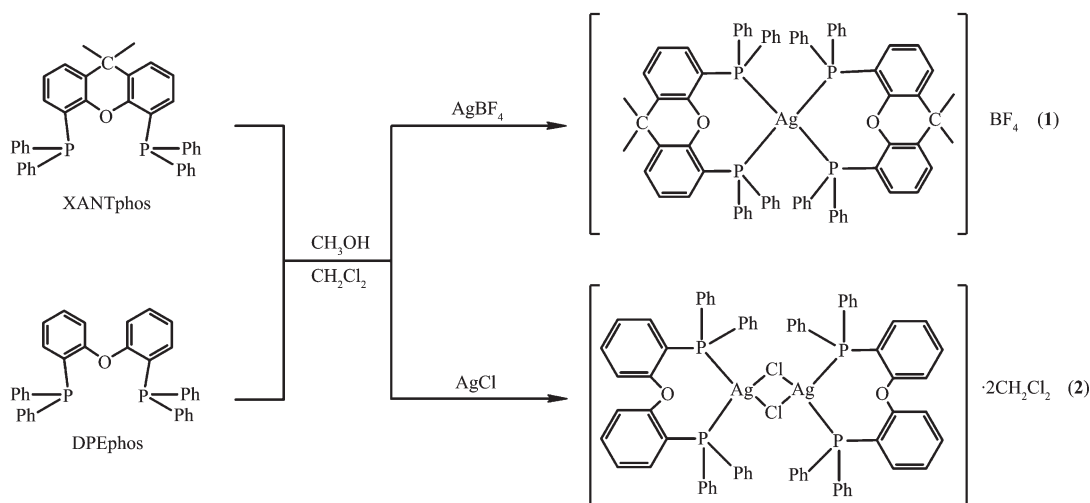
Complex 1					
Ag(1)-P(3)	0.257 9(4)	Ag(1)-P(2)	0.259 1(8)	Ag(1)-P(1)	0.258 5(6)
Ag(1)-P(4)	0.256 0(5)				
P(1)-Ag(1)-P(2)	108.00(7)	P(3)-Ag(1)-P(4)	104.86(9)	P(2)-Ag(1)-P(4)	107.46(9)
P(1)-Ag(1)-P(3)	106.95(8)				
Complex 2					
Ag(1)-P(1)	0.246 4(2)	Ag(1)-Cl(1)	0.262 6(2)	Ag(1)-P(2)	0.249 5(2)
Ag(1)-Cl(1) ⁱ	0.259 3(2)				
P(1)-Ag(1)-P(2)	111.33(7)	P(1)-Ag(1)-Cl(1)	114.67(7)	P(2)-Ag(1)-Cl(1)	105.05(8)
P(1)-Ag(1)-Cl(1) ⁱ	116.76(8)	P(2)-Ag(1)-Cl(1) ⁱ	112.59(7)	Cl(1)-Ag(1)-Cl(1) ⁱ	94.92(6)

Symmetry codes: ⁱ 1-*x*, 1-*y*, 1-*z*

2 Results and discussion

2.1 Syntheses of the complexes

Two functional Ag(I) complexes **1**~**2** have been synthesized by one-pot reaction of different silver(I) salts with DPEphos and XANTphos ligands (Scheme 1). The influence of the anions on the coordination



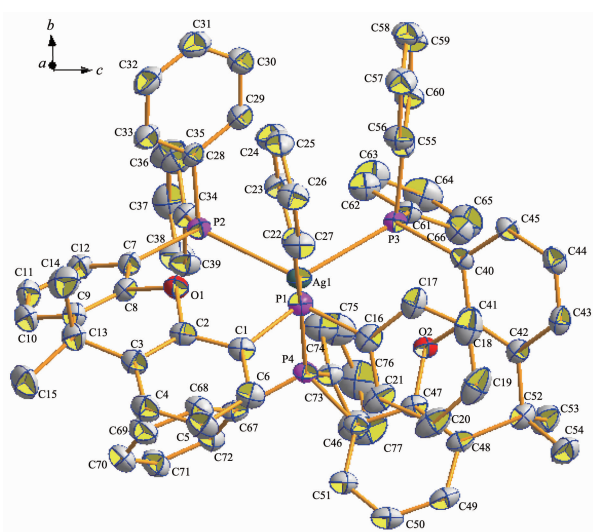
Scheme 1 Routine of synthesis for complexes **1** and **2**

2.2 Description of crystal structures

Complex **1** crystallizes in the triclinic crystal system and contains a crystallographic center of symmetry (Fig.1). In complex **1**, the central ion Ag(I) forms a ring by the chelating bisphosphine ligand (XANTphos), and each Ag(I) is coordinated with a P

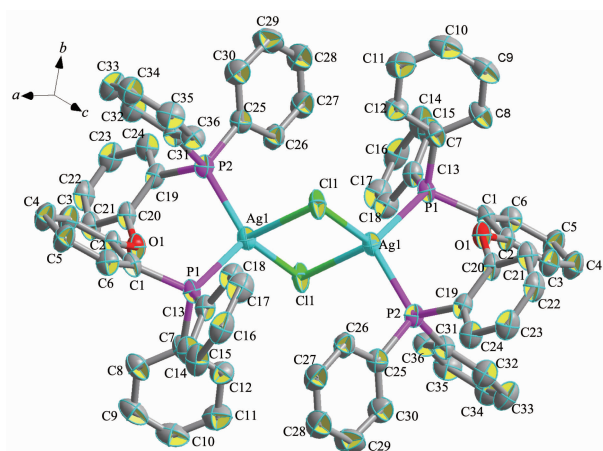
atom from a different XANTphos molecule to form a distorted tetrahedron. Compared to the similar Ag-XANTphos complex, the Ag-P (0.258 5 and 0.259 1 nm) distance in complex **1** is longer than that in [AgBr(XANTphos)(py2SH)]·C₂H₅OH (Ag-P 0.248 4 and 0.250 0 nm)^[16], and the P-Ag-P angle (108.00°) is smaller than that in the complex above.

Complex **2** consists of inversion symmetric dimers with a diamond-shaped Ag₂Cl₂ group at the center. In the asymmetric unit of complex **2**, each DPEphos ligand chelates one silver(I) cation with a free dichloromethane in it. Two silver cations are connected by two Cl⁻ anions in the formation of a binuclear structure (Fig.2). The sum of the internal angles of the four-member ring [-Ag-Cl-Ag-Cl-] in the Ag₂Cl₂ core are 360°, demonstrating that the ring is a parallelogram. The geometry around each silver center is distorted tetrahedral, which is evident from the angles around the Ag ion in the range of 94.92°~116.76°. The distance of Ag···Ag is 0.352 9 nm, which exceeds the sum of two van der Waals radius of silver atoms (0.344 0 nm)^[25], so the metal-metal interaction can be



All hydrogen atoms are omitted for clarity; Thermal ellipsoids: 30% probability level

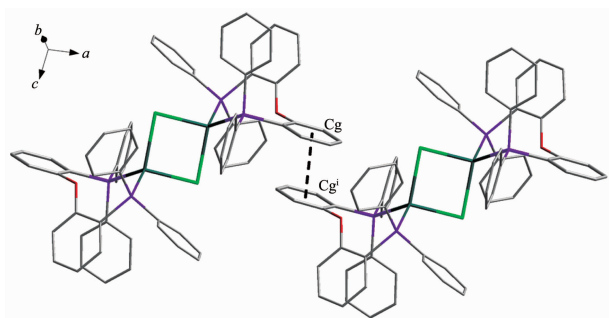
Fig.1 Molecular structure of complex **1**



All hydrogen atoms are omitted for clarity; Thermal ellipsoids: 30% probability level; Symmetry codes: $i: 1-x, 1-y, 1-z$

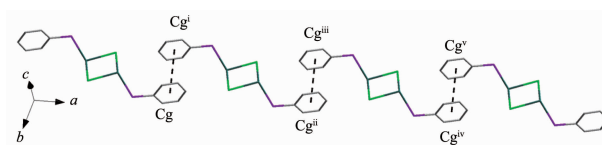
Fig.2 Molecular structure of complex **2**

neglected in complex **2**. The bite angle of the DPEphos ligand is 111° , which is 9° larger than its natural bite angle (β_n)^[9]. In both of two complexes in this paper, the ether O atoms of the DPEphos ligands are always at a nonbonding distance from the metal centers. The lattice structure is stabilized by an intermolecular $\pi \cdots \pi$ stacking interactions (Fig.3) between the C19-C24 rings of DPEphos ligand, with the interplanar distance of 0.381 3 nm. The center-of-mass coordinate of the ring is $(-0.014\ 48, 0.389\ 77, 0.561\ 57)$ and the dihedral angle is 0° . The adjacent molecules in complex **2** are connected by the $\pi \cdots \pi$ weak interactions to form a 1D infinite chain (Fig.4). The distance of $\text{Cl} \cdots \pi$ weak interaction (0.383 0 nm) found in complex **2** is shorter than that in the literature^[8]. Those weaker interactions stabilize the supra-molecular frameworks.



All hydrogen atoms are omitted for clarity; Symmetry codes: $i: 1-x, 1-y, 1-z$

Fig.3 Neighboring molecular entities of the cations in complex **2** displaying the offset $\pi \cdots \pi$ interaction



Symmetry codes: $i: 1-x, 1-y, 1-z$; $ii: 1+x, y, z$; $iii: 1-x, 1-y, 1-z$; $iv: -2+x, y, z$; $v: -2-x, 1-y, 1-z$

Fig.4 One dimensional structure bridging by $\pi \cdots \pi$ interaction of complex **2**

2.3 Infrared and ^1H NMR spectroscopy

The infrared spectra of **1~2** show C-C stretch vibration of the phenyl rings whose absorptions are found in $1\ 434\ \text{cm}^{-1}$. The middle absorptions around $3\ 051\ \text{cm}^{-1}$ are caused by C-H vibration of the phenyl rings. The absorption in $1\ 057\ \text{cm}^{-1}$ is derived from tetrafluoroborate (BF_4^-) in complex **1**.

The singlet near $\delta\ 1.62$ in ^1H NMR spectrum of **1** is assigned to the protons of methylene groups in the aromatic rings from XANTphos ligand. The ^1H NMR spectrum of complexes **2** exhibit signals (multiple peaks) between 7.1 and 6.6, which can be attributed to protons from the benzene rings of the bis-(2-(diphenylphosphino)phenyl)ether (DPEphos) ligand. In complex **2**, the signals of protons from the dichloromethane solvent molecule are shown at 5.29.

2.4 Fluorescence spectra

At room temperature, the solid-state excitation and emission spectra of complexes **1~2** and the DPEphos and XANTphos ligands were measured.

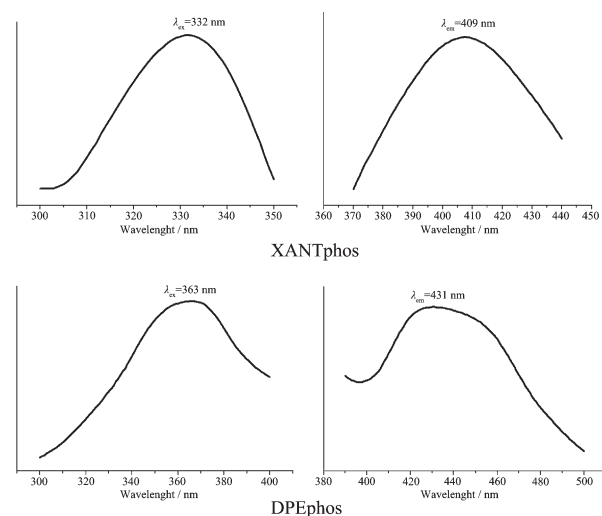


Fig.5 Luminescent spectra of XANTphos and DPEphos ligands in the solid state at room temperature

When being excited at 332 nm, the XANTphos ligand displays a fluorescence emission peak at 409 nm, and the emission peak of the DPEphos ligand is found at 431 nm with excitation at 363 nm (Fig.5). It was found that the emission peak is centered at 487 nm with $\lambda_{\text{ex}}=370$ nm for complex **1**, and it is centered at 438 nm with $\lambda_{\text{ex}}=361$ nm for complex **2** (Fig.6). Compared to the free ligand, the emission peak of **1** is red-shifted by about 78 nm, however, the emission peak of **2** is red-shifted by about 7 nm. The difference of luminescent properties is attributed to their different structures. These shifts of emission peak are derived from ligand-centered $\pi-\pi^*$ transition.

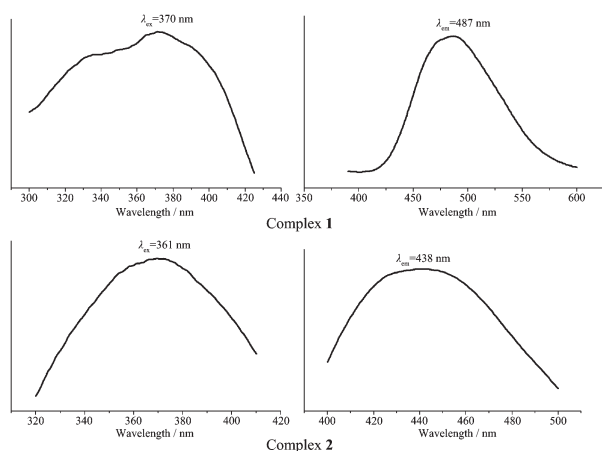


Fig.6 Luminescent spectra of **1-2** in the solid state at 298 K

3 Conclusions

Two novel Ag-biphosphine complexes, namely $[\text{Ag}(\text{XANTphos})]\text{BF}_4$ and $[\text{Ag}_2\text{Cl}_2(\text{DPEphos})_2] \cdot 2\text{CH}_2\text{Cl}_2$, have been synthesized and characterized by X-ray diffraction, IR, ^1H NMR and fluorescence spectra. Single-crystal X-ray diffraction analysis reveals that the complex **1** crystallizes with triclinic system, $P\bar{1}$ space group. Complex **2** consists of inversion symmetric dimers with a diamond-shaped Ag_2Cl_2 group at the center. The adjacent molecules in complex **2** are connected by $\pi \cdots \pi$ weak interactions to form a 1D infinite chain. In the emission spectra, shifts of emission peak are derived from ligand-centered $\pi-\pi^*$ transition. We hope our results could offer a new strategy for the design of supramolecular complexes.

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