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# Computational and spectroscopic studies on luminescence of [Ag(PPh<sub>3</sub>)<sub>2</sub>(NMP)]NO<sub>3</sub>

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#### Abstract

Silver compound [Ag(PPh<sub>3</sub>)<sub>2</sub>(NMP)]NO<sub>3</sub> (1) (NMP=2-(4-Dimethylaminophenyl)imidazo(4,5-f)(1,10)phenanthroline) has been synthesized and characterized by elemental analyses, IR and X-ray diffraction techniques. Two absorption bands (294 and 342 nm) have been observed in UV/vis absorption spectrum of 1. Compound 1 exhibits luminescence in solid state at room temperature and shows broad emission with maximum at 599 nm, which make red shift compared with free ligand NMP ( $\lambda_{max} = 522$  nm). Short lifetime (2.2 ns) indicates that emission of 1 does not come form triplet excited state and the intense spin-orbital coupling of Ag<sup>I</sup> has little effect on the lowest singlet excited state. Excited state of 1 was simulated by using the time-dependent density functional theory, which gave a sound explanation for absorption spectrum and indicated that emission of 1 originates form the metal-perturbed intraligand charge-transfer. © 2005 Elsevier B.V. All rights reserved.

Keywords: Silver; Crystal structure; Luminescence; TDDFT; Molecular orbital; Charge-transfer

# 1. Introduction

The study of luminescent properties of d<sup>10</sup> metal compounds which exhibit intriguing photophysical and photochemical properties has been receiving current attention [1–10]. Among the d<sup>10</sup> metal compounds of Au, Ag and Cu, Ag<sup>I</sup> compounds which exhibit luminescence at room temperature are few [11–16] and most of luminescent Ag<sup>I</sup> compounds exhibit luminescence at low temperature [17–19]. The main reason for this is that singlet excited state of Ag<sup>I</sup> compound is easily changed to triplet excited state by the intense spin-orbital coupling of Ag<sup>I</sup> and the energy gap between triplet excited state and singlet ground state is very small, which causes the luminescent qenching of Ag<sup>I</sup> compound. Interestingly, the silver compound [Ag(PPh<sub>3</sub>)<sub>2</sub>-(NMP)]NO<sub>3</sub> (1) which has been synthesized by us exhibits remarkable luminescence at room temperature.

To further probe and rationalize luminescent property of compound 1, quantum chemical approaches deserve to be considered. The time-dependent density functional theory (TDDFT) approach [20], which is usually recommended for modling excited state, provides satisfactory molecular orbital explanation for the electronic excitation. A number of papers have recently shown that TDDFT approach offers an efficient alternative to high-level ab initio techniques for modling sound excited state [21-30]. In the case of metal compounds of large size, the TDDFT approach is one of the most suitable choices to calculate accurately the excited energy because of its lower computational cost compared with other high-level ab initio techniques and including the effects of electron correlation at some reasonable level. In this paper, we describe the synthesis, crystal structure and luminescence of the silver compound 1. And TDDFT calculation gave a sound explanation for absorption spectrum and luminescence of 1.

# 2. Experimental

2-(4-Dimethylaminophenyl)imidazo(4,5-f)(1,10)phenanthroline (NMP, as shown in scheme 1) [31,32] and Ag(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> [33] were synthesized as literatures.

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Scheme 1. The structure and synthetic route of NMP.

Elemental analyses were performed with a Vario EL III CHNOS Elemental Analyzer. The infrared spectrum of KBr pellet was recorded on a PerkinElmer Spectrum One FT-IR Spectrometer. The UV/vis absorption spectrum was recorded on a PerkinElmer Lambda900 UV/VIS/NIR Spectrometer. The emission spectrum was recorded on a FLS920 fluorescence spectrophotometer.

# 2.1. Preparation of $[Ag(PPh_3)_2(NMP)]NO_3 \cdot H_2O(1)$

Two mmol Ag(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> reacted with 2 mmol NMP in 20 ml CH<sub>3</sub>CN at room temperature for 1 h. The orange crystals were obtained by natural volatilization. Yield 1.96 g, 93%. Anal. Calcd. For C<sub>57</sub>H<sub>49</sub>Ag<sub>1</sub>N<sub>6</sub>O<sub>4</sub>P<sub>2</sub> (1051.87): C 65.09, H 4.70, N 7.99. found C 65.13, H 4.65, N 8.12. IR (solid KBr pellet/cm<sup>-1</sup>): 3434 s, 1529 m, 1039 w, 816 w (NMP); 1094 m (P–C). UV–vis  $\lambda_{max}$ /nm (CH<sub>3</sub>CN): 294 ( $\epsilon$ /dm<sup>3</sup>mol<sup>-1</sup> cm<sup>-1</sup> 32468), 342 (39243).

#### 2.2. X-ray crystallographic analysis

Suitable single crystal of compound **1** with dimension of  $0.45 \times 0.45 \times 0.10$  was carefully selected and glued to thin glass fiber with epoxy resin. Intensity data for single crystal were collected at 293 K on a Rigaku Mercury CCD diffractometer with graphite-monochromatized Mo Ka radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction was applied using SADABS program [34]. The structure was solved by direct method and refined on  $F^2$  by full-matrix least-squares technique using the SHELX97 program package [35,36]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The crystallographic data are listed in Table 1.

CCDC-247808 contains the supplementary crystallographic data for the compound **1**. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.)+44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk].

#### 2.3. Calculational details

TDDFT calculation on excited state of  $[Ag(PPh_3)_2(NMP)]^+$  was performed with the GAUSSIAN 03 suite of programs [37]. The contour plots of MOs were obtained with the GaussianView program. The model of

 $[Ag(PPh_3)_2(NMP)]^+$  was obtained directly from the crystal structure of compound **1**.

## 3. Results and discussion

#### 3.1. Synthesis and molecular structure

The title compound **1** was easily obtained by reaction of ligand NMP with  $Ag(PPh_3)_2NO_3$  at room temperature. Fig. 1 shows perspective view of the cation in compound **1**. NMP chelates to Ag(I) by using N1 and N2 in phenanthroline derivative, which make Ag(I) four-coordinated. The angle of P1–Ag–P2 (122.13(4)°) is quite larger than that of N1–Ag–N2 (70.44(11)°), indicating a distorted tetrahedral geometry around the silver atom. Nearly planar structure of NMP favors charge-transfer along the long-conjugated ligand.

Table 1	
Crystallographic data for	: 1

Formula	$C_{57}H_{49}Ag_1N_6O_4P_2$	
Formula weight	1051.87	
Crystal size (mm <sup>3</sup> )	$0.45 \times 0.45 \times 0.10$	
Crystal color	Orange	
Crystal system	Triclinic	
Space group	ΡĪ	
a (Å)	10.971(4)	
$b(\mathbf{A})$	14.472(5)	
c (Å)	20.053(6)	
α (°)	96.475(3)	
$\beta$ (°)	97.895(2)	
$\gamma$ (°)	111.252(5)	
$V(Å^3)$	2893.5(16)	
Z	2	
$D_{\text{caled.}} (\text{g cm}^{-3})$	1.204	
F(000)	1078	
$\mu (\mathrm{mm}^{-1})$	1.150	
$\theta$ for data collection (°)	2.08-27.48	
Reflections collected	21894	
Unique reflections	12802	
(R(int))	[R(int)=0.0219]	
Parameters	631	
GOF	1.014	
R1, wR2 $[I > 2\sigma(I)]$	0.0726, 0.1991	
R1, wR2 (all data)	0.0854, 0.2150	

 $R1 = \sum (|F_{o}| - |F_{c}|) / \sum |F_{o}|, \quad wR2 = \left[ \sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2} \right]^{0.5}.$ 



Fig. 1. ORTEP drawing of the cation of **1** with 30% probability ellipsoids. Selected bond distances (Å) and angles (°): Ag–N1 2.347(3), Ag–N2 2.414(3), Ag–P1 2.4488(12), Ag–P2 2.4608(12), N1–Ag–N2 70.44(11), P1–Ag–P2 122.13(4), N1–Ag–P1 114.27(9), N1–Ag–P2 119.43(9), N2–Ag–P1 116.55(9), N2–Ag–P2 100.58(9).

#### 3.2. Luminescence

Fig. 2 shows emission spectra of **1** and ligand NMP in solid state at room temperature. Compound **1** exhibits broad emission with maximum at 599 nm, which make red shift compared with free ligand NMP ( $\lambda_{max}$ =522 nm). Short lifetime (2.2 ns) indicates that emission of **1** does not come from triplet excited state and the intense spin-orbital coupling of Ag<sup>I</sup> has little effect on the lowest singlet excited state.

Although NMP has strong electronic donor dimethylamino, the lowest excited state of **1** with character of LMCT is impossible. Because compound **1** has electron rich metal Ag(I) (d(10)) and low-lying  $p_{\pi}$ -acceptor orbitals of phenanthroline derivative in the ligand NMP. If the lowest excited state was MLCT in nature, the intense spin-orbital



Fig. 2. Emission spectra of 1 and NMP in solid state at room temperature.

coupling of  $Ag^{I}$  would make effect, which causes luminescent qenching. TDDFT calculation indicated that the emission of **1** is neither MLCT nor LMCT in nature and can probably be assigned to the metal-perturbed intraligand fluorescent emission which make red shift compared with free ligand NMP.

# 3.3. TDDFT calculation

We simulated 30 singlet excited states of  $[Ag(PPh_3)_2(NMP)]^+$  by using TDDFT approach with an objective to evaluate the electronic structure of excited states and understand the origin of UV/vis absorption and luminescence of **1**. The method three-parameter hybrid functional according to Becke with additional correlations due to Lee et al. (B3LYP) [38,39] was adopted all along calculation process.

Two calculational schemes were adopted. One was that excited state of  $[Ag(PPh_3)_2(NMP)]^+$  was directly calculated with basis set LanL2DZ upon unoptimized geommetry. In order to obtain more reliable result, the second

able 2		
The main optimize	d geometry parameter	rs of [Ag(PPh <sub>3</sub> ) <sub>2</sub> (NMP)]

Parameter	Calculational	Experimental	
Bond length (Å)			
Ag–N1	2.400	2.347(3)	
Ag–N2	2.430	2.414(3)	
Ag–P1	2.514	2.4488(12)	
Ag–P2	2.509	2.4608(12)	
Bond angle (°)			
N1–Ag–N2	69.8	70.44(11)	
P1-Ag-P2	120.7	122.13(4)	



Fig. 3. Simulated UV/vis absorption spectrum of  $[Ag(PPh_3)_2(NMP)]^+$  from the LanL2DZ (a) and mixed basis sets (b) results. Each absorption peak has been convoluted by using a Gaussian function of which the width at halve maximum amounts to 30 nm.

scheme was that structure was optimized with the mixed basis sets (Ag CEP-121G; C H 3-21G; N P 3-21G(D)) and upon the optimized geometry excited state was calculated with the same mixed basis sets. The main geometry parameters optimized with the mixed basis sets are listed in Table 2.

For excitation energy studies on small molecules, the basis sets with diffuse functions need to be used to describe the outer molecular region. However, for the system of such large size under study, the main effects are related to ordinary bound orbitals, which are well described with the used basis sets. As shown in Fig. 3, two absorption peaks also exist in the simulated UV/vis absorption spectrum of  $[Ag(PPh_3)_2(NMP)]^+$ , which is close to the experimental absorption spectrum (294 nm and 342 nm). As listed in Table 3 and 4, the two calculational schemes gave similar results for excited states, especially for the four lowest excited states and the contour plots of frontier molecular orbitals relative to those excited states are also similar.

Energy and composition of MOs are a good tool to get a first insight into the nature of excited states. As shown in Fig. 4, electronic cloud of HOMO is distributed to dimethylaminophenyl imidazole derivative in the ligand

Table 3 Excitation energy ( $\lambda$ , nm), the corresponding oscillator strength (*f*) and composition for the lowest excited states calculated with basis set LANL2DZ

State	$\lambda/f$	Composition	Assignment
1 <sup>1</sup> A	578.6/0.0157	$0.70 (HOMO \rightarrow LUMO)$	Metal-per- turbed ILCT
$2^{1}A$	479.7/0.0952	$0.69 (HOMO \rightarrow LUMO + 1)$	ILCT
3 <sup>1</sup> A	386.6/0.1506	0.68 (HOMO-1 $\rightarrow$ LUMO) -0.12 (HOMO $\rightarrow$ LUMO+2)	MLCT
4 <sup>1</sup> A	369.8/0.6438	0.12 (HOMO-1 $\rightarrow$ LUMO) +0.66 (HOMO $\rightarrow$ LUMO+2)	$\pi \rightarrow \pi^*$

Table 4

Excitation energy ( $\lambda$ , nm), the corresponding oscillator strength (*f*) and composition for the lowest excited states calculated with mixed basis sets

State	$\lambda/f$	Composition	Assignment
1 <sup>1</sup> A	567.0/0.0555	0.70 (HOMO→LUMO)	Metal-per- turbed ILCT
$2^{1}A$	440.9/0.1760	$0.68 (HOMO \rightarrow LUMO + 1)$	ILCT
3 <sup>1</sup> A	361.3/0.2259	$0.68 (HOMO-1 \rightarrow LUMO)$	MLCT
4 <sup>1</sup> A	349.6/0.6834	$-0.17$ (HOMO $\rightarrow$ LUMO $+2$ ) $-0.18$ (HOMO-1 $\rightarrow$ LUMO) $+0.64$ (HOMO $\rightarrow$ LUMO $+2$ )	$\pi \! \rightarrow \! \pi^*$

NMP. HOMO-1 is mainly metal-localized with some contribution of PPh<sub>3</sub> group. LUMO and LUMO+1 are mainly localized on the phenanthroline derivative in the ligand NMP. But orbital analyses showed that orbital composition of LUMO differs from that of LUMO+1. Silver uses d orbital to take part in formation of LUMO and imidazole ring has no contribution for LUMO, while LUMO+1 is partly localized on  $p_{\pi}$  orbital of imidazole ring. LUMO+2 is  $\pi^*$  orbital of NMP.

Low-energy absorption band is composed of excitation from the ground state to optical allowed 3<sup>1</sup>A and 4<sup>1</sup>A state. 3<sup>1</sup>A has a predominant metal to ligand charge-transfer (MLCT) character, with a minor  $\pi \rightarrow \pi^*$  contribution. 4<sup>1</sup>A exhibits contrary multitransition character compared with 3<sup>1</sup>A. Oscillator strength of 4<sup>1</sup>A is higher than that of 3<sup>1</sup>A, which indicates that the low-energy absorption band mainly derives from  $\pi \rightarrow \pi^*$  transfer and the information of MLCT excited state is obscured. High-energy excited states relative to high-energy absorption exhibit complicated multitransition character, which brings difficulty for assignment of charge-transfer.

The lowest singlet excited state  $1^{1}A$  denotes to HOMO  $\rightarrow$  LUMO transition and is assigned to metalperturbed intraligand transition excited state. Excited state  $2^{1}A$  denotes to HOMO  $\rightarrow$  LUMO + 1 transition and is assigned to intraligand charge-transfer (ILCT) excited state. The two lowest excited states have low oscillator strength and thus cannot be embodied in absorption spectrum. The calculated energy of  $1^{1}A$  is close to emission energy. The emission of 1 originate from metal-perturbed intraligand transition. If one considers that luminescence commonly originates from the lowest excited state because of vibrational relaxation and internal conversion between excited states, the fact that ILCT excited state also cannot be embodied in the emission spectrum is perfectly understandable.

As shown in the plots of HOMO and LOMO involving in charge-transfer of the lowest excited state  $1^{1}$ A, silver only make disturbed effect on charge-transfer of  $1^{1}$ A. The intense spin-orbital coupling of Ag<sup>1</sup> have little effect on  $1^{1}$ A and the lowest singlet excited state is not easily changed into triplet excited state. So the title compound exhibit character of fluorescence at room temperature.



Fig. 4. Frontier molecular orbital diagrams related to the lowest excitations obtained with the second calculational scheme.

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