

Phosphinine-Based Ligands for the Design of Novel Luminescent d¹⁰ Transition Metal Complexes

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Summary

In modern coordination chemistry, the search for novel ligands is one of the aims of principal importance. Pyridyl-functionalized phosphinines can be an example of new potentially applicable ligand class. In this contribution, we examined the reactivity of chelating phosphinine towards copper(I) and zinc(II). Four novel phosphinine-containing copper(I) complexes were synthesized and characterized. These compounds exhibit intriguing photophysical properties. Low-temperature solid-state emission spectra reveal the thermally activated delayed fluorescent nature of the emission state. It has also been found that phosphinine-containing zinc(II) complex is unstable.

1. Introduction

Luminescent Cu(I) complexes have been extensively studied during the last decades. The reasons for that is both affordable price of copper comparing to noble metals and intriguing photophysical properties, such as thermally activated delayed fluorescence (TADF) [1]. The latter is characteristic, among others, for phosphine-diimine Cu(I) complexes and can lead to substantial improvement in electroluminescent devices efficiency [2]. Thus, systems of this type can be successfully utilized in OLEDs and LEECs [3], in photocatalysis [4] and sensing [5]. However, the popularity of the topic resulted in the close exhaustion of the currently known pool of classical ligands. Consequently, the search for novel classes of ligands for the design of luminescent Cu(I) complexes is one of the main aims for scientists in this field. Pyridyl-functionalized phosphinines [6], isostructural to 2,2'-bipyridines, are the example of such new potentially applicable ligands.

Phosphinines are a class of organophosphorus compounds exhibiting unusual donor-acceptor properties. [7] Polydentate phosphinines possess a range of coordination modes and are therefore particularly versatile for the construction of novel transition metal complexes. Recent attempts to stabilize transition metal centers in medium to high oxidation states by chelating phosphinines [8] have led to the development of a new range of complexes with potential applicability in single-molecule-based materials. Although phosphinines appear as very promising ligands due to their rich and flexible electronic and steric properties, these phosphorus heterocycles have not been widely used for the design of emissive molecules and materials. For now this field is limited by only a few fragmentary examples.

The first phosphinine-based coordination compounds of Cu(I) have already been prepared [9]. In present study we report the synthesis and complete characterization of novel phosphinine-based Cu(I) complexes as well as synthesis of Zn(II) phosphinine-based complex. The photophysical properties of novel compounds are investigated and described.

Keywords: phosphinine, Cu(I) complexes, Zn(II) complexes, luminescence, TADF

2. Methods

General remarks

Precursors 2-(2-Pyridyl)-4,6-diphenyl- λ^3 -phosphinine (PN ligand), $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$, $[\text{Cu}(\text{MeCN})_2\text{Xantphos}]\text{PF}_6$, $[\text{Cu}(\text{MeCN})_2(\text{PPh}_3)_2]\text{PF}_6$ and $[\text{Cu}(\text{MeCN})_2\text{BINAP}]\text{PF}_6$ were synthesized according to the literature methods. All other reagents were purchased from Aldrich and ABCR and used without further purification. Dry solvents were used from an MBraun solvent purification system. Diethyl ether was distilled under argon over sodium/benzophenone. All Cu(I) and Zn(II) complexes obtained were synthesized under inert atmosphere using standard Schlenk techniques. Their characterization included NMR spectroscopy, mass-spectrometry and elemental analysis. ^1H , ^{31}P and ^1H - ^1H COSY spectra were recorded on a JEOL EXZ400 (400 MHz) and Bruker Avance 400 (400 MHz). Mass spectra were recorded on an Agilent 6210 ESI-TOF instrument (Agilent Technologies) in the ESI⁺ mode. Microanalyses were carried out using vario MICRO cube CHNS-analyzer (Elementar). The crystal structure of $[\text{Cu}(\text{PN})\text{Xantphos}]\text{PF}_6$ was determined by the means of single crystal XRD analysis using Rigaku Oxford Diffraction XtaLAB HyPix-3000 diffractometer for the data collection at a temperature of 100K. Diffraction data were processed in *CrysAlisPro* program. The structures were solved by dual-space algorithm and refined using the *SHELX* programs [10,11] incorporated in the *OLEX2* program package. [12] The UV/vis absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer in a 1 cm quartz cuvette (dichloromethane, 10^{-5} M). The excitation and emission spectra for solid samples at room temperature and at 77 K were measured on a Fluorolog 3 (JY Horiba Inc.) spectrofluorimeter.

Synthesis of Cu(I) and Zn(II) complexes

All **heteroleptic Cu(I) complexes** were synthesized according to the general two-step procedure.

1) $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ and corresponding P[^]P ligand were dissolved in dry DCM and stirred in inert atmosphere for 3 hours, then passed through celites. The resulting solution was directly used in the next step.

2) DCM solution of the PN or NN ligand was added dropwise to the solution of $[\text{Cu}(\text{MeCN})_2(\text{P}^{\wedge}\text{P})]\text{PF}_6$, and the reaction mixture was stirred for 1 hour at room temperature under Ar. Then it was evaporated to minimal volume, and diethyl ether was added to yield crude product as yellow solid. The obtained powder was recrystallized using dichloromethane/diethyl ether mixture, washed with diethyl ether and dried.

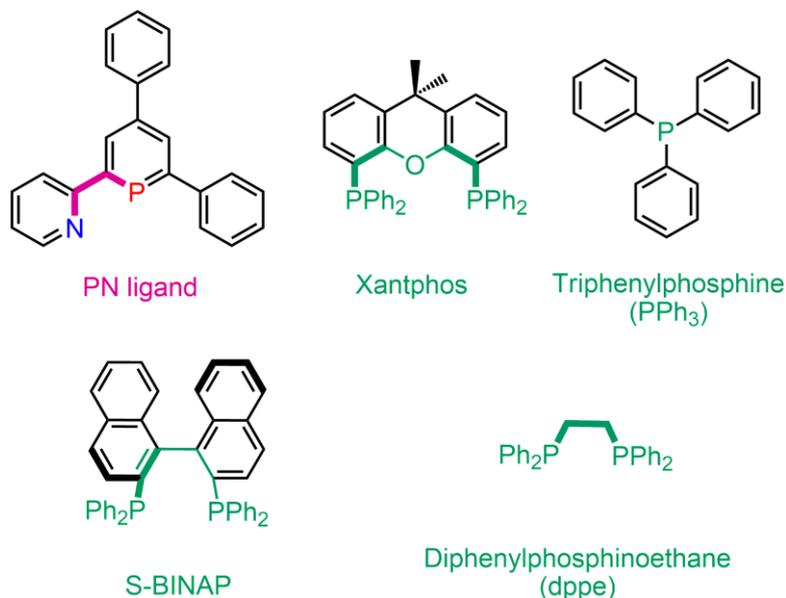
Homoleptic Cu(I) complexes were synthesized *via* one-step route. $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ and 2 equivalents of PN or NN ligand were dissolved in dry DCM and stirred for 1 hour at room temperature under Ar. Then it was evaporated to minimal volume, and diethyl ether was added to yield crude product as red (PN) or dark-red (NN) solid.

Zn(II) complexes. ZnCl_2 and corresponding PN or NN ligand were dissolved in $\text{Et}_2\text{O}/\text{DCM}$ mixture under Ar and stirred for 2 hours. The solvents were evaporated, and the crude products were washed with Et_2O and dried *in vacuo*.

3. Results and Discussion

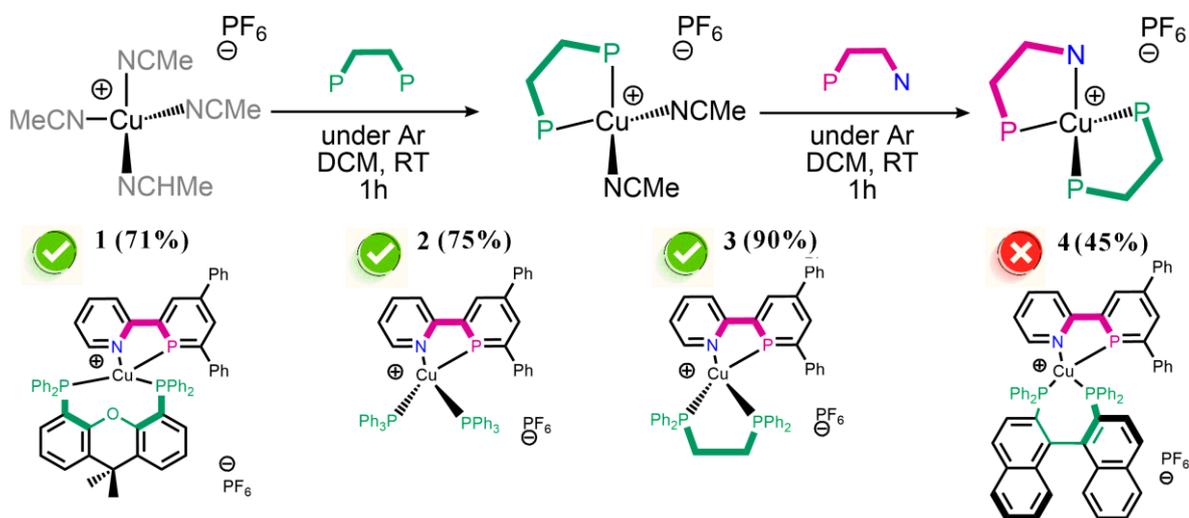
1) Copper(I) complexes

PN ligand, being isostructural to regular 2,2'-bipyridines (Scheme 1), easily reacts with $[\text{Cu}(\text{MeCN})_2(\text{P}^{\wedge}\text{P})]\text{PF}_6$, forming heteroleptic Cu(I) complexes of general formula $[\text{Cu}(\text{PN})(\text{P}^{\wedge}\text{P})]\text{PF}_6$. (Scheme 2).



Scheme 1. Schemes of ligands used in present study.

We isolated four target heteroleptic complexes with different phosphine ligands in good yields (45–90%). The detailed synthetic pathway is described in the **Methods**. Crude complexes 1-4 are yellow powders, stable to air and moisture and well soluble in ordinary organic solvents (acetone, DCM). However, these compounds are unstable in solution under UV light or direct sunlight. We were able to recrystallize and purify all complexes, except of $[\text{Cu}(\text{PN})(\text{S-BINAP})]\text{PF}_6$. The structure and the purity of recrystallized compounds were confirmed by ^1H and ^{31}P NMR spectroscopy (DCM- d_2 , RT, 400 MHz). All NMR signals correspond to proposed structure. ESI+ mass-spectroscopy and elemental analysis are also in a good agreement with calculated results.



Scheme 2. The synthetic route and schemes of $[\text{Cu}(\text{PN})(\text{P}^{\wedge}\text{P})]\text{PF}_6$ complexes 1-4.

We also managed to obtain crystals of complex **1**, suitable for X-Ray diffraction measurements (Figure 1). In this structure, copper(I) has typical distorted tetrahedral coordination environment formed by two chelating ligands. The Cu-P bond length is slightly bigger than Cu-N bond length, which corresponds to the literature data (tungsten-phosphinine complexes [8]). The PN ligand adopts slightly twisted conformation, whereas the Xantphos moiety forms “bowl” similar to phosphine-diimine complexes reported in literature [13]. Crystal structure in the solid state completely matches the NMR data for **1**.

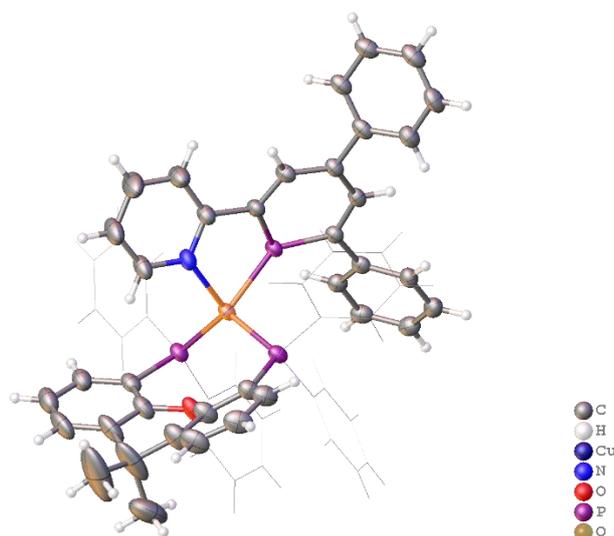
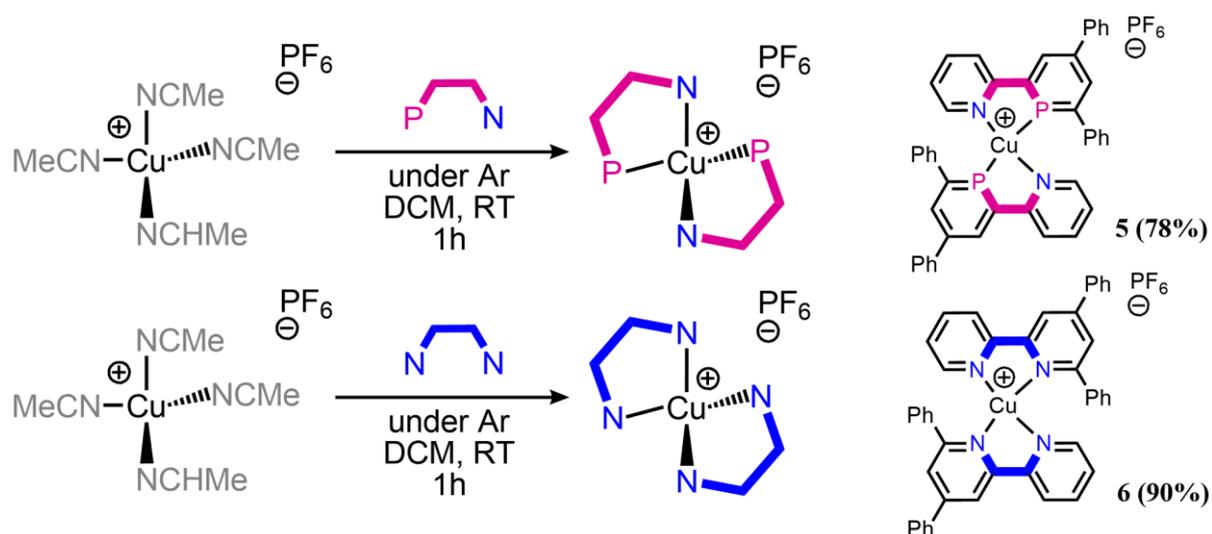


Figure 1. The crystal structure of compound **1**.

We have also synthesized three phosphine-diimine Cu(I) complexes, isostructural to compounds **1-3**. That was not the main aim of the project, but in future it should be promising to compare the photophysical properties of isostructural complexes and see, how changing P atom to N atom affects absorption and luminescence.

Two isostructural homoleptic Cu(I) complexes with PN and NN ligands were synthesized via one-pot route described in **Methods** (Scheme 3). They form amorphous red (PN) and dark-red (NN) solids soluble in ordinary solvents (DCM, acetone) and stable to air and moisture.



Scheme 3. The synthetic route and schemes of homoleptic Cu(I) complexes **5,6**.

Complexes **5** and **6** were characterized by ^1H and ^{31}P NMR spectroscopy and mass-spectrometry. The number and integral intensities of NMR signals correspond to proposed

structure. ESI+ mass-spectra contain signals of molecular ions whose position and isotopic pattern also match predicted molecular ions formulae.

2) Optical and photophysical properties of complexes **1-3**, **5** and **6**

The UV-vis absorption spectra of compounds **1-3** demonstrate typical features of phosphine-containing heteroleptic Cu(I) complexes [14]. The high-energy band might be assigned to spin-allowed $\pi\pi^*$ intraligand (1IL) transitions localized on the aromatic system of both PN and P[^]P ligands. However, compared to phosphine-diimine complexes reported in the literature [15], the high-energy band has bathochromic shift of ca. 20 nm. This phenomenon can be explained by different nature of PN and diimine ligands. Bands with lower energy (ca. 350-450 nm) might emerge due to metal-to-ligand charge transfer (MLCT) from $d\pi$ -orbitals of copper(I) to π^* -orbitals of the ligands.

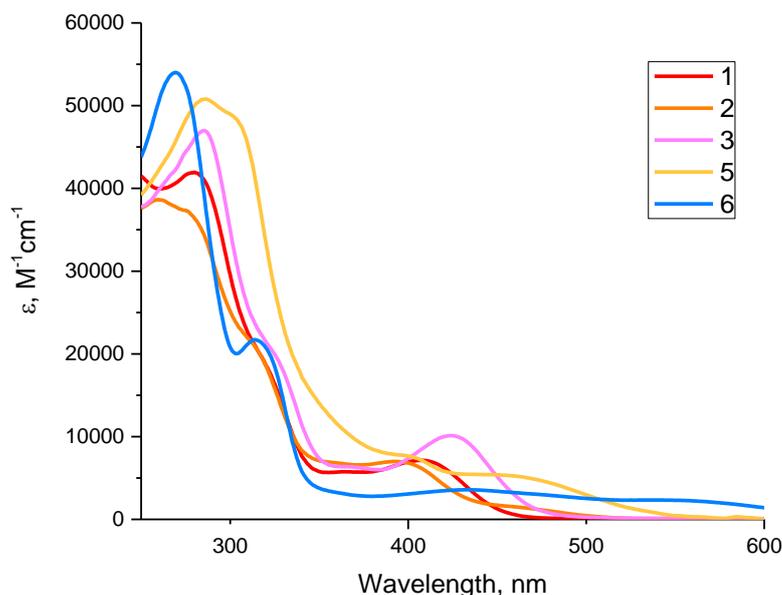


Figure 2. Absorption spectra of **1-3**, **5** and **6** in 1,2-dichloroethane solution at r.t.

Turning to homoleptic Cu(I) complexes **5** and **6**, we can see some significant changes in the UV-vis absorption spectra compared with heteroleptic species **1-3**. The shape and wavelength maximum of the high-energy band of **5** is similar to those in [Cu(PN)(P[^]P)]PF₆ complexes. On the contrary, the low-energy band has significant red shift (ca. 50 nm) and a complex shape. The UV-vis absorption spectrum of **6** is sufficiently close to the spectra of bis-diimine complexes reported in the literature, though its low-energy band is more wide comparing to literature data [16]. It is worth noting that the shape of low-energy absorption band allows us to assume the distorted geometry of complex **6** in the solution. [17] All above mentioned suggestions are based on a literature data of heteroleptic phosphine-diimine and homoleptic bis-diimine Cu(I) complexes and will be proved later by quantum chemical calculations.

Complexes **1-3** and **5** are unstable in solution under UV irradiation. However, heteroleptic compounds **1-3** are emissive in the solid state, showing no signs of decomposition. Solid-state excitation and emission spectra for these samples were measured both at room temperature and at 77 K. Low-temperature measurements were performed to determine the presence of thermally activated delayed fluorescence (TADF), which is characteristic for most of heteroleptic phosphine-diimine Cu(I) complexes.

The solid-state emission spectra of complexes **1-3** at room temperature exhibit broad structureless emission bands with emission wavelength maxima in the range of 570-661 nm

(Figure 3). This is substantially red-shifted emission in comparison with phosphine-diimine Cu(I) complexes. [1]

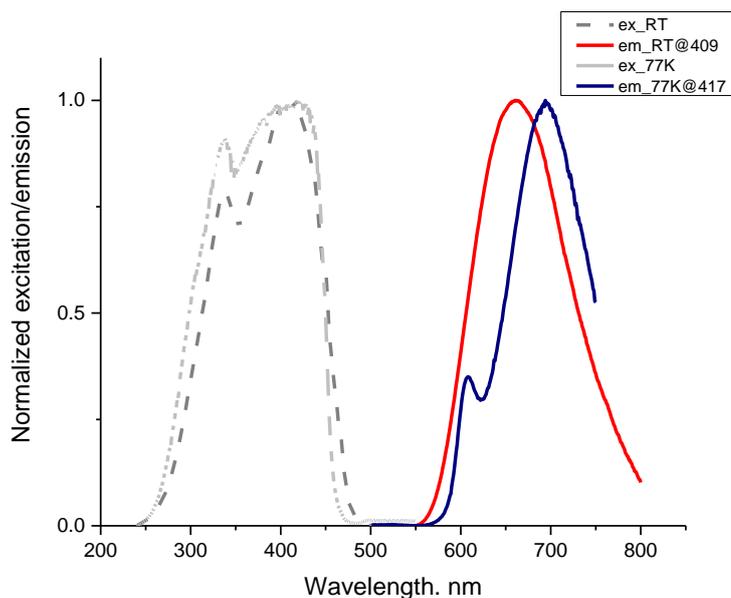


Figure 3. Solid-state excitation and emission spectra of compound **1**.

Emission spectra of all compounds **1-3** in the solid state are dependent on the temperature. (Table 1) The emission maximum wavelength demonstrates clear red shift, and some additional bands appear. More thorough investigation of this emission behaviour will be done later, as well as quantum chemical calculations for the nature of the emission.

Table 1. Photophysical properties of **1-3** in solid state at room temperature and 77K.

Compound	$\lambda_{em}(RT)$, nm	$\lambda_{em}(77K)$, nm	Shift, nm
Cu(PN)Xantphos	661	696	35
Cu(PN)(PPh ₃) ₂	628	663	35
Cu(PN)dppe	570	632	62

3) Zn(II) complexes

Zn(II) complexes with PN and NN ligand were synthesized according to the synthetic procedure described in **Methods**. Zn(PN)Cl₂ complex was found to be unstable, and all the attempts to purify it finished in decomposition of the target compound. Zn(NN)Cl₂ was obtained in a good yield, its ¹H NMR spectrum and mass-spectrum correspond to the proposed structure. This compound will be reported elsewhere.

4. Conclusion

Herein we report the synthesis and characterization of four novel phosphinine-containing Cu(I) complexes, exhibiting peculiar photophysical properties. The solid-state emission spectra of obtained compounds at room temperature and 77K indicate the presence of thermally activated delayed fluorescence. The more detailed photophysical properties are a subject of further investigation. The emission properties will also be compared with those of isostructural Cu(I) complexes with diimine ligands, also synthesized during this project. All experimental results will be proved by quantum-chemical calculations.

Zn(II) complex with phosphinine ligand was found to be unstable.

5. References

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