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# Synthesis, structure, terahertz spectroscopy and luminescent properties of copper (I) complexes with bis(diphenylphosphino) methane and N-donor ligands

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ABSTRACT

The reactions of copper(I) salts CuX [X = Cl, OTf (OTf = $CF_3SO_3$) and $ClO_4$] and bis(diphenylphosphino) methane (dppm) with 4,4-bipyridine (4,4-bipy), 2,2-bipyridine (2,2-bipy), isoquinoline (i-$C_9H_7N$) and 1,10-phenanthroline (phen) lead to five new copper(I) complexes: $[CuCl(dppm)(i\text{-}C_9H_7N)]_2$ (**1**), $\{[CuCl(dppm)(phen)]_2{\bullet}5H_2O\}_n$ (**2**), $[Cu_2Cl_2(dppm)_2(4,4\text{-}bipy)]{\bullet}4CH_3CN$ (**3**), $[Cu(dppm)(2,2\text{-}bipy)]_2(OTf)_2$ (**4**), $\{[Cu_2Cl(dppm)_2(4,4\text{-}bipy)](ClO_4)\}_n$ (**5**). Complexes **1**, **3** and **4** are of dinuclear structure with eight-membered $Cu_2P_4C_2$ rings. The structure of compound **2** can be simplified as three-dimensional topology. Complex **5** is of infinite chain structure linked by 4,4-bipy. All these complexes are characterized by IR, elemental analyses, single-crystal X-ray diffraction analysis, luminescence, NMR and terahertz time-domain spectroscopy.



## 1. Introduction

Cu(I) complexes prepared from phosphines ($PPh_3$) and nitrogen ligands such as 2,2-bipyridine (bipy) or 1,10-phenanthroline (phen) were first investigated in detail more than 30 years ago, because of their various applications ranging from biological sensors and interesting physical properties to catalysis, optics and luminescent materials [1–5]. Besides that, copper(I) complexes are widely studied, based on their relative abundance, low cost and susceptibility to structural changes in the excited state [6,7]. As is well known, organic ligands play crucial roles in the construction of novel coordination complexes, and subtle changes in the disposition of the coordinating atoms and the flexibility of the ligands can lead to remarkable structural differences [8]. But $PPh_3$ is a bulky ligand with strong sterically congested system that may lead to exciplex quenching. Thus we need to find a phosphine ligand that can form a rigid environment around the Cu(I) center, and effectively suppresses the nonradiative processes. McMillin and his coworkers reported mixed-ligand Cu(I) complexes prepared from 1,10-phenathroline derivatives and bis[2-(diphenylphosphino) phenyl]ether (POP) in two papers[9–10]. All these compounds exhibit unusually efficient, long lived photoluminescence signals even in a coordinating solvent [9,10]. Afterwards this investigation was extended to heteroleptic Cu(I) complexes based on bisphosphine and aromatic diimine ligands [11–17].

In our previous works, a number of mixed-ligand coordination compounds of copper(I) salts with heterocyclic nitrogen ligand and diphosphane were prepared and structurally characterized. For example, some 1D nitrogen-heterocyclic copper(I)-diphosphine polymers were reported in Refs. [18,19]. In this paper, we successfully synthesized a series of new Cu(I) complexes $\{[CuCl(dppm)(i\text{-}C_9H_7N)]_2$ (1), $[CuCl(dppm)(phen)]_2{\bullet}5H_2O$ (2), $[Cu_2Cl_2(dppm)_2(4,4\text{-}bipy)]{\bullet}4CH_3CN$ (3), $[Cu(dppm)(2,2\text{-}bipy)]_2(OTf)_2$ (4), $\{[Cu_2Cl(dppm)_2(4,4\text{-}bipy)](ClO_4)\}_n$ (5). All complexes are characterized by IR, elemental analyses, X-ray diffraction, fluorescence, $^1H$ NMR and $^{31}P$ NMR spectroscopy and terahertz time-domain spectroscopy (THz-TDS).

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## 2. Experimental

### 2.1. Materials and measurements

All chemical reagents are commercially available and used without further purification. $[Cu(CH_3CN)_4][SO_3CF_3]$ and $[Cu(CH_3CN)_4][ClO_4]$ were prepared by reported procedures [20]. Elemental analyses (C, H, N) were determined on a Vario EL elemental analyzer. Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet in the range of 400–4000 $cm^{-1}$. Excitation and emission spectra of the solid samples were recorded on an F-4500 fluorescence spectrophotometer at room temperature. $^1H$ NMR was recorded at room temperature with a Bruker DPX 600 MHz spectrometer and $^{31}P$ NMR was recorded at room temperature with a Bruker DPX 400 MHz spectrometer. The THz absorption spectra were recorded on the THz timedomain device of Capital Normal University of China, based on photoconductive switches for generation and electro-optical crystal detection of the far-infrared light. The preparation of the samples is by pressing the pure crystals into pellet. The detection of THz absorption spectra is carried out at $N_2$ atmosphere to avoid the influence of water vapor. The THz absorption spectra of the samples are obtained by the THz time-domain device and the effective spectrum range is 0.2–3.0 THz.

### 2.2. Synthesis of complex **1**

A mixture of CuCl (29.7 mg, 0.3 mmol) and dppm (115.3 mg, 0.3 mmol) with an excess of isoquinoline (5 mL) were dissolved in $CH_2Cl_2$ (5 mL) and $CH_3OH$ (5 mL) solution, stirred at room temperature for 6 h. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature to yield yellow crystalline products. Yield: 75%. Anal. Calc. For $C_{68}H_{58}Cl_2Cu_2N_2P_4$: C, 66.67, H, 4.77, N, 2.29. Found: C, 66.62, H, 4.75, N, 2.32. IR (KBr disc, $cm^{-1}$): 3325m, 3049m, 2918s, 2853m, 1628s, 1587m, 1483s, 1433vs, 1383s, 1278w, 1098s, 1036s, 832s, 787vs, 740vs, 717s, 693vs, 638s, 519s, 481s.

### 2.3. Synthesis of complex **2**

A mixture of CuCl (29.7 mg, 0.3 mmol) and dppm (115.3 mg, 0.3 mmol) were dissolved in 10 mL $CH_3CN$ solution. Worth to mention, there is a small amount of water in $CH_3CN$. After stirring for 4 h, the 1,10-phen was added to the resulting yellow solution to afford the yellow precipitate, which was then filtered off. The filtrate gave yellow crystals after a few days. Yield: 69%. Anal. Calc. For $C_{74}H_{70}Cl_2Cu_2N_4O_5P_4$: C, 62.71, H, 4.98, N, 3.95. Found: C, 62.70, H, 4.95, N, 3.87. IR (KBr disc, $cm^{-1}$): 3393s, 3049w, 2025s, 1624s, 1584w, 1510s, 1481s, 1433s, 1422s, 1371w, 1144w, 1069s, 840s, 774vs, 745vs, 727vs, 695vs, 514s, 482vs.

### 2.4. Synthesis of complex **3**

A mixture of CuCl (29.7 mg, 0.3 mmol), dppm (115.3 mg, 0.3 mmol) and 4,4-bipyridyl (46.9 mg, 0.3 mmol) were dissolved in 10 mL $CH_3CN$ solution, stirred for 6 h. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature for a week to yield yellow crystalline products. Yield: 70%. Anal. Calc. For $C_{68}H_{64}Cl_2Cu_2N_6P_4$: C, 63.45, H, 5.01, N, 6.53. Found: C, 63.41, H, 4.97, N, 6.45. IR (KBr disc, $cm^{-1)}$: 3413m, 3049s, 1594s, 1483vs, 1434vs, 1406w, 1368w, 1216w, 1188w, 1095v, 1066w, 1026w, 998w, 808vs, 780w, 737vs, 692vs, 617m, 514s, 477s.

### 2.5. Synthesis of complex **4**

A mixture of $[Cu(CH_3CN)_4][CF_3SO_3]$ (113.0 mg, 0.3 mmol) and dppm (115.3 mg, 0.3 mmol) with an excess of 2,2-bipyridyl (46.9 mg, 0.3 mmol) were dissolved in $CH_2Cl_2$ (5 mL) and $CH_3OH$ (5 mL) solution, stirred at room temperature for 6 h. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature to yield yellow crystalline products. Yield: 79%. Anal. Calc. For $C_{72}H_{60}Cu_2F_6N_4O_6P_4S_2$: C, 57.41, H, 4.01, N, 3.72. Found: C, 57.36, H, 4.00, N, 3.54. IR (KBr disc, $cm^{-1}$): 3479w, 3414w, 3235w, 1638w, 1618s, 1599w, 1437s, 1384s, 1262s, 1222m, 1154s, 1097w, 1031s, 790m, 738s, 694s, 637vs, 516vs, 481vs.

### 2.6. Synthesis of complex **5**

A mixture of $[Cu(CH_3CN)_4][ClO_4]$ (98.3 mg, 0.3 mmol) and dppm (115.3 mg, 0.3 mmol) were dissolved in $CH_2Cl_2$ (6 mL). After stirring for 4 h at room temperature, the $CH_2Cl_2$ solution was concentrated to half its original volume and dry diethyl ether (5 ml) was added. Then a white precipitate was obtained. After that, the mixture of the above-mentioned white precipate and 4,4-bipyridyl (59.4 mg, 0.3 mmol) were dissolved in $CH_3CN$(7 mL) and $CH_2Cl_2$(3 mL) solution, stirred for another 6 h. The yellow powder of the mixed-ligand complex $\{[Cu_2Cl(dppm)_2(4,4\text{-bipy})](ClO_4)\}_n$ was given. Yield: 50%. Anal. Calc. For $C_{60}H_{52}Cl_2Cu_2N_2O_4P_4$: C, 60.72, H, 4.42, N, 2.36. Found: C, 60.69, H, 4.45, N,2.32. IR (KBr disc, $cm^{-1}$): 3551w, 3477w, 3414w,3235w, 2427w, 1638m, 1618m,1483w, 1436m, 1385s, 1095s, 999w, 782w, 739s, 718w, 694m, 623m, 512m, 477w.

### 2.7. Single crystal X-ray crystallography

Single-crystal X-ray diffraction studies of complexes **1**–**5** were performed on a Brucker SMART diffractometer equipped with CCD area detector with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo κα radiation ($\lambda = 0.71073$ Å) by ω scan mode. All data were corrected by semi-empirical method using SADABS program. The program SAINT was used for integration of the diffraction profiles. All structures were solved by direct methods using SHELXL program of the SHELEX-97 package and refined with SHELXL-97 [21]. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier synthesis. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on $F^2$. All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. A summary of the crystallographic data and details of the structural refinements are listed in Table 1. Selected bond distances and bond angles are listed in Table S1.

## 3. Results and discussion

### 3.1. General aspects

Copper(I) complexes **1**–**5** (with the general formula $[\{Cu_2(\mu\text{-}X)_2(dppm)_2\}(L)_n]$) were first prepared by combination of CuX with dppm and N-heteroaromatic ligand (isoquinoline, phen, 4,4-bipy and 2,2-bipy) in the mixture of $CH_2Cl_2$ and $CH_3OH$ or in $CH_3CN$ solution (Scheme 1). **1**–**5** are insoluble in diethyl ether but soluble in methanol, ethanol, acetonitrile, chloroform, N,N-dimethylformamide and dimethylsulfoxide. When the N-