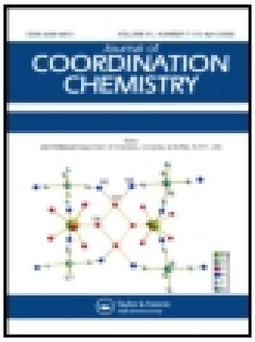

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Synthesis, characterization and luminescent properties of three-coordinate copper(I) halide complexes containing diphenylamino monodentate phosphine ligand

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Three-coordinate copper halide complexes with a bidentate phosphine ligand have received much attention. Here, a series of three-coordinate dinuclear copper halide complexes containing a diphenylamino monodentate phosphine ligand, $[CuX(dpnp)]_2$ (dpnp = N-[2-

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(diphenylphosphino)-4,5-dimethylphenyl]-N-phenylaniline, X = I (**1**), Br (**2**) and Cl (**3**)),were synthesized, and their molecular structures and photophysical properties were investigated. The structural analysis reveals that two copper(I) centers are bridged by two halogen ligands to form a dinuclear structure with a four-membered Cu_2X_2 ring. Crystal structures of **1**-**3** contain 1-D supramolecular arrays constructed by intermolecular C–H···π interactions. These complexes exhibit blue emission in the solid state at room temperature and have peak emission wavelengths at 483-487 nm with microsecond lifetimes (τ = 13.9-38.1 μs) and low emission quantum yields (< 0.01%). The emission of complex **1** mainly originates from intraligand (IL) transition, whereas the emissions of complexes **2** and **3**are from a combination of MLCT, XLCT and IL transitions. The three complexes displayed good thermal stability.

Keywords: Copper complex; Synthesis; Characterization; Luminescent property

1. Introduction

Photoluminescent metal complexes have attracted attention owing to their potential applications as organic light-emitting diodes (OLEDs) [1], solar cells [2], and chemical sensors [3].As an attractive alternative to expensive, less abundant, and more toxic heavy-metal-containing electroluminescent materials, copper(I)-organic compounds have been reported over the past decade [4-16].

Reactions of Cu(I) halides with monodentate aliphatic and aromatic phosphine donors show a remarkable structural diversity, ranging from monomeric and dimeric to polymeric networks [7]. The stereochemistry of copper(I) complexes is dominated by four-coordination, whereas three-coordinate species are less common [8-20].

Recently, a highly efficient, green, three-coordinate Cu(I) halide coordinated by bidentate 1,2-bis(*o*-ditolylphosphino)benzene with an external quantum efficiency (EQE)over 20% was reported [19]. Compared to a large number of cationic Cu(I) compounds, neutral Cu(I) complexes still remain rare. To date, there are only a few reports of devices fabricated by vacuum deposition containing neutral Cu(I) complexes [11, 19, 21-24].

Based on the high luminescent efficiency of the three-coordinate mononuclear [19] and our previously reported four-coordinate dinuclear [25] Cu(I) halide with a bidentate phosphine ligand, it is generally assumed that a rigid/congested structure is important to avoid structural changes in the excited state and to obtain a good emission quantum yield and for this reason bidentate ligands are often employed. Here, a new P, N-bidentate ligand was designed in which the diphenylamino group was initially inserted hypothesizing a P, N bidentate coordination mode to obtain mononuclear Cu(P,N)X complexes, and the steric hindrance of NPh_2 was taken into account to obtain a congested structure. Reported here are a series of three-coordinate dinuclear copper halide complexes $[CuX(dpnp)]_2$ (dpnp = N-[2-(diphenylphosphino)-4,5dimethylphenyl]-N-phenylaniline), X = I (**1**), Br (**2**) and Cl (**3**)). Their molecular structures and photophysical properties were investigated.

2. Experimental

2.1. *General methods*

All reagents and solvents are of commercial reagent grade and used without further purification except where noted. Copper(I) halides and *o*-xylene were purchased from Aladdin Company and used without purification. Tetrahydrofuran (THF) was distilled under nitrogen in the presence of sodium chips by using benzophenone ketyl as an indicator. 1,2-Dibromo-4,5-dimethylbenzene was synthesized according to the literature method [26].

^1H NMR spectra were recorded on a Varian 600 MHz NMR spectrometer using deuterated solvents as the lock and reference. Chemical shifts were reported in ppm relative to $SiMe_4$ for the ^1H. High-resolution mass spectra reported as m/z were obtained on a Bruker Autoflex MALDI-TOF mass spectrometer. C, H and N analyses were determined using a Vario Micro Cube elemental analyzer. The single crystal structures of complexes **1**-**3**were measured at room temperature or low temperature using a Bruker APEX DUO or Bruker D8 Venture diffractometer. UV–vis spectra were recorded on a Unicam Heλios α spectrometer. Photoluminescence spectra were recorded on a FLS920 steady state and time-resolved fluorescence spectrometer. Solid-state Φ_{PL} values were determined using a Hamamatsu system for absolute PL quantum yield measurements equipped with an integrating sphere with Spectralon inner surface coating. The samples were carefully degassed by at least five freeze-pump-thaw cycles. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen.

2.2. *Syntheses*

2.2.1. Synthesis of N-(2-bromo-4,5-dimethylphenyl)-N-phenylaniline. To a solution of 2.64 g (10 mmol) of 1,2-dibromo-4,5-dimethylbenzene in 30 mL of toluene was added 2.05 g (12 mmol) of diphenylamine, 0.77 g (4 mmol) of copper(I) iodide, 0.47 g (4 mmol) of tetramethylethylenediamine and 3.39 g (30 mmol) of potassium *t*-butoxide at ambient temperature. The solution was stirred at 120 °C for 12 h, then allowed to cool to room temperature. The solvents were removed under reduced pressure. After being purified by column chromatography using hexane as the eluent, a white solid was obtained in 45% yield (1.59 g). ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.52 (s, 1H), 7.24 (t, J = 8 Hz, 4H), 7.11 (s, 1H), 6.93 (t, J = 8 Hz, 2H), 6.86 (d, 4H, J = 4 Hz), 2.24 (s, 3H), 2.15 (s, 3H). Anal. Calcd for $C_{20}H_{18}BrN$: C, 68.19; H, 5.15; N, 3.98. Found: C, 68.24; H, 5.13; N, 4.04.

2.2.2. Synthesis of N-[2-(diphenylphosphino)-4,5-dimethylphenyl]-N-phenylaniline(dpnp). To a cooled (-78 °C) solution of 3.51 g (10 mmol) of N-(2-bromo-4,5-dimethylphenyl)-N-phenylaniline in 30 mL of THF was added dropwise 4.2 mL (10 mmol) of a 2.4 M solution of *n*-butyllithium in hexanes under nitrogen. The solution was stirred at -78 °C for 1 h and then 2.43 g (11 mmol) of chlorodiphenylphosphine in THF (15 mL) was added dropwise. The solution was allowed to warm to room temperature, and then dichloromethane was added to the solution. The organic layer was washed with water and saturated sodium chloride and then dried over magnesium sulfate. The solvents were removed under reduced pressure. The crude product was purified by column chromatography using hexane as the eluent. A white solid was obtained in 50% yield (2.29 g). ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.23-7.19 (m, 6H), 7.10 (t, *J* = 6 Hz, 4H), 7.04 (t, *J* = 12 Hz, 4H), 7.00 (d, *J* = 6 Hz, 1H), 6.90 (d, *J* = 6 Hz, 5H), 6.78 (t, *J* = 6 Hz, 2H), 2.19 (s, 3H), 2.15 (s, 3H). ^{31}P NMR (240 M, $CDCl_3$) *δ*:−17.88 (s). Anal. Calcd for $C_{32}H_{28}NP$: C, 84.00; H, 6.17; N, 3.06. Found: C, 84.12; H, 6.20; N, 3.04.

2.2.3. Synthesis of di(μ-iodo)bis{N-[2-(diphenylphosphino)-4,5-dimethylphenyl]-N-phenylaniline copper(I)} (**1**)**.**A suspension of copper(I) iodide (0.040 g, 0.21 mmol) and dpnp (0.096 g, 0.21 mmol) in 30 mL of CH_2Cl_2 was stirred for 5 h at room temperature to form a greenish-yellow precipitate. The precipitate was filtered off, and complex **1** was crystallized from the filtered solution after slow evaporation at room temperature to give greenish-yellow crystals (Yield: 0.112 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.46 (t, *J* = 6 Hz, 8H), 7.29-7.27 (m, 4H), 7.21-7.19 (m, 8H), 6.97 (d, *J* = 6 Hz, 2H), 6.93-6.90 (m, 8H), 6.86-6.85 (m, 8H), 6.80 (d, *J* = 6 Hz, 2H), 6.66 (t, *J* = 12 Hz, 4H), 2.17 (s, 6H), 2.13 (s, 6H). ^{31}P NMR (240 M, $CDCl_3$) *δ*: −15.81 (s). Anal. Calcd for $C_{64}H_{56}I_2Cu_2N_2P_2$: C, 59.31; H, 4.36; N, 2.16. Found: C, 59.40; H, 4.33; N, 2.18. MS (MALDI-TOF): m/z calcd for $[C_{32}H_{28}NP + H]^+$, 458.1993, found: 458.0202.

2.2.4. Synthesis of di(μ-bromo)bis{N-[2-(diphenylphosphino)-4,5-dimethylphenyl]-N-phenylaniline copper(I)} (**2**)**.** Complex **2**was obtained by a similar method as described for **1**using copper(I) bromide (0.030 g, 0.21 mmol) in place of copper(I) iodide. Greenish-yellow crystals of **2**were obtained (Yield: 0.106 g, 84%).^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.36-7.32 (m, 12H), 7.26-7.20 (m, 10H), 6.99-6.96 (m, 8H), 6.93-6.91 (m, 8H), 6.78 (d, *J* = 12 Hz, 2H), 6.74 (t, *J* = 6 Hz, 4H), 2.19 (s, 6H), 2.14 (s, 6H). ^{31}P NMR (240 M, $CDCl_3$) *δ*:−7.19 (s). Anal. Calcd for $C_{64}H_{56}Br_2Cu_2N_2P_2$: C, 63.95; H, 4.70; N, 2.33. Found: C, 63.89; H, 4.67; N, 2.36. MS (MALDI-TOF): m/z calcd for $[C_{32}H_{28}NP + H]^+$, 458.1993, found: 458.1021.

2.2.5. Synthesis of di(μ-chloro)bis{N-[2-(diphenylphosphino)-4,5-dimethylphenyl]-N-phenylaniline copper(I)} (**3**)**.**Complex **3**was obtained by a similar method as described for **1**using copper(I) chloride (0.021 g, 0.21 mmol) in place of copper(I) iodide. Greenish-yellow crystals of **3**were obtained (Yield: 0.104 g, 89%).^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38-7.36 (m, 4H), 7.29-7.27 (m, 16H), 7.04-7.02 (m, 8H), 6.98 (d, J = 6 Hz, 2H), 6.95-6.94 (m, 8H), 6.85-6.79 (m, 6H), 2.20 (s, 6H), 2.16 (s, 6H). ^{31}P NMR (240 M, $CDCl_3$) δ:−4.12 (s). Anal. Calcd for $C_{64}H_{56}Cl_2Cu_2N_2P_2$: C, 69.06; H, 5.07; N, 2.52. Found: C, 69.10; H, 5.02; N, 2.55. MS (MALDI-TOF): m/z calcd for $[C_{32}H_{28}NP + H]^+$, 458.1993, found 458.1251.

2.3. *X-ray crystallography*

Greenish-yellow crystals of complexes **1-3** suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in dichloromethane at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073Å) on a Bruker AXS APEX II CCD area detector. The collected frames were processed with the software *SAINT*[27], and an absorption correction was applied (*SADABS*) [28] to the collected reflections. The structureswere solved by direct methods (*SHELXTL*) [29] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2. All non-hydrogen atoms were assigned with anisotropic displacement parameters.

The disorder in complex **1** was solved by direct method with the location of I atom. The other atoms were located by the difference Fourier map and refined. The Cu, P and N atoms were disordered, which was caused by similarity of the PPh_2 and NPh_2 fragments. The disorderness is a flip of the P and N atoms, while keeping the five benzene groups positioned, which makes the disorderness of the P-bound copper atom also. Free refinement of the occupancies of the disordered atoms gave rise to a value close to 0.5, which physically sounds right. Therefore, the occupancies of the disordered Cu, P and N were set to be 0.5. With this kind of disorderness, the right configuration of the dinuclear complex is the one with Cu_2I_2nearly in plane.A disorderness for the I atom was not carried out, since the two positions were too close.

2.4. *Theoretical calculations*

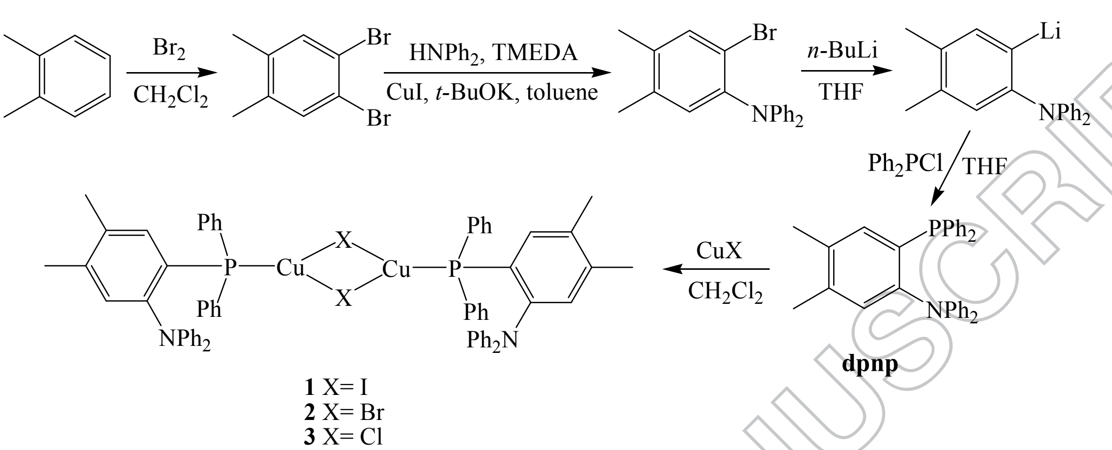
The structural parameters for the three complexes were obtained from the crystal data which are listed in tables 1 and 2. The density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were then performed to compute the HOMO-LUMO energy gap, the natural bond orbital (NBO) analysis as well as the properties of the excited states. X-ray structures were not optimized by DFT prior to orbital and TDDFT calculations. All calculations were manipulated by the Gaussian 09 suite [30] at the B3LYP/DGDZVP level.

3. Results and discussion

3.1. *Description of syntheses and structures*

The synthetic routes for the Cu(I) complexes are outlined in scheme 1. First, Br_2 was used to brominate the 1,2-position of *o*-xylene in high yield to furnish 1,2-dibromo-4,5-dimethylbenzene. After amination of 1,2-dibromo-4,5-dimethylbenzene with diphenylamine, copper(I) iodide as catalyst in the mixture of tetramethylethylenediamine (TMEDA) and potassium *t*-butoxide, N-(2-bromo-4,5-dimethylphenyl)-N-phenylaniline was obtained in moderate yield. Then the synthesis of N-(4,5-dimethylphenyl) lithium-N-phenylaniline was carried out in a mixture with the mole ratio of 1:1 for N-(2-bromo-4,5-dimethylphenyl)-N-phenylaniline and *n*-butyllithium. By the addition of chlorodiphenylphosphine to 2-(diphenylamino)-4,5-dimethylphenyl lithium in THF at -78 °C under nitrogen, dpnp was synthesized in 50% yield. Complexes **1**-**3** were prepared in 82-89% yield by mixing a suspension of CuX (X = I for **1**, Br for **2**, Cl for **3**) in dichloromethane with 1 equiv of dpnp. All the new Cu(I) complexes were obtained as air stable solids in high purity and found to be generally soluble in CH_2Cl_2. They all gave satisfactory analytical data and were characterized by NMR spectroscopy, MALDI-TOF spectrometry and single crystal X-ray diffraction. The structures of

Cu(I) complexes **1**-**3** are not our expected Cu(P,N)X complexes in which P, N bidentate coordinated with Cu(I). We speculate that low electron density of N atom and large steric hindrance of NPh_2 are the main reasons which result in the non-coordination with Cu(I).



Scheme 1. Synthetic pathways to ligand dpnp and their dinuclear copper(I) complexes.

3.2. *X-ray crystallographic study*

Perspective views of complexes **1**-**3** are shown in figure 1. The structure of complex **1** has two solvent CH_2Cl_2molecules. Crystallographic data and selected bond lengths and angles are given in tables 1 and 2, respectively. X-ray crystallographic studies on **1**-**3**reveal that two copper(I) centers are bridged by two halogen ligands to form a dinuclear structure with a four-membered Cu_2X_2 ring. Complexes **2** and**3** have planar Cu_2X_2 geometries, analogous to halogen-bridged copper complexes which typically have a planar Cu_2X_2 geometry [31-34]. The Cu_2X_2 rings of complex **1**are significantly deformed by bending along the X···X axis [35], the dihedral angles between two CuX_2 triangles in Cu_2X_2 is 158.8° (Cu1-Cu1'), 171.6° (Cu1-Cu1) and 147.6° (Cu1'-Cu1'), similar with those observed in dinuclear Cu(I) halide with 1,2-bis(diphenylphosphino)-4,5-dimethylbenzene(152.31–160. 92°)[25]. As listed in table 1, the Cu–X distances of complexes **1**, **2**and**3**elongate with an increase in the van der Waals radius of X. The Cu···Cu distances are 2.690, 2.859 and 2.462 Å for complex **1** and2.920 and 2.862 Å for complexes **2**and **3**, respectively, indicating a weak interaction between two copper atoms, as compared with the sum of van der Waals radius of copper (2.8Å), resembling dinuclear, four-coordinate Cu(I) halides with a bidentate ligand [31-33].

The coordination geometry of the copper centers in **1**-**3**is closely trigonal-planar; the sum of the angles around the Cu(I) center are 355.69, 358.99 and 359.08°, respectively, similar to the reported mononuclear three-coordinate Cu(I) halide with a bidentate ligand (359.66°) [19]. In complex **1**, the distance from the halogen to the closest H atom, H···I is 3.156 Å, displaying a potential hydrogen bond. Intermolecular hydrogen bonds can be observed in **2**and **3**, with the closest Br-to-H and Cl-to-H distances of 2.911 and 2.806 Å, respectively. In the solid state, **1**and**3**show intermolecular C–H···π interactions between the phenyl ring attached to phosphorus and phenyl ring attached to nitrogen with the closest H-to-H and C-to-H distances of 3.040 and 2.786 Å for **1**, 3.306 and 2.861 Å for **3**, and dihedral angles of 82.24° for **1** and 89.80° for **3** are observed. Similar intermolecular C–H···π interactions can be observed in **2** between phenyl rings attached to nitrogen with the closest H-to-H and C-to-H distances of 2.689 and 2.987 Å and dihedral angle of 61.66°. Overall, all these intermolecular interactions are incorporated into 1-D tape-like arrays along the *a*-axis for **1**-**3** (Supporting Information figures S7-S9).

3.3. *Photophysical properties*

The absorption spectra of complexes **1**-**3** and dpnp in CH_2Cl_2 at room temperature are shown in figure 2. The absorption spectrum of dpnp exhibits a broad, intense band at 295 nm ($\varepsilon = 8.97 \times 10^4\ M^{-1}\ cm^{-1}$), which is characteristic of an aryl phosphine and amine compound. As compared to the absorption band at 282 nm of 1,2-bis(diphenylphosphino)-4,5-dimethylbenzene [25], the absorption of dpnpis red-shifted by about 13 nm, due to the more intense electron-donating conjugation effect of N than P. This band is assigned to a mixed transition of n→π* and π→π*,analogous to those in related three-coordinate mononuclear Cu(I) complexes [19]. Complexes **1**-**3** have an intense absorption band with a maximum at 271 nm [$\varepsilon = (5.29\text{-}7.93) \times 10^4\ M^{-1}\ cm^{-1}$] and a broad shoulder at 304 nm and a weaker band tail at 340-380 nm. The weaker band tail may be attributed to the electronic transition affected by the copper ions, the halide ligands, or both,or ligand-to-ligand charge transfer character. As shown in figure 3, DFT calculations carried out for complexes **1-3** reveal that the electrons in the highest occupied molecular orbital (HOMO) are mainly distributed over the copper, halogen, ligand for **2** and **3**, and ligand for **1**, while those in the lowest unoccupied molecular orbital (LUMO) are localized on ligand. We can thus conclude that the lowest energy excited states of **2**and**3**consist of a metal-to-ligand charge transfer (MLCT), a halogen-to-ligand charge transfer (XLCT), and an intraligand transfer, analogous to those in related tetrahedral complexes [19, 36]. The lowest energy excited states of **1**mainlyconsist of an intraligand transition. MLCT and XLCT are very weak for complex **1**.

The emission spectra of complexes **1**-**3** in the solid state measured at 298 and 77 K are shown in figure 4. Summarized in table 3 are the emission maxima, lifetimes and quantum yields of the complexes at 298 and 77 K, and TDDFT calculation data based on the structures obtained by X-ray structural analysis. Complexes **1**-**3** show blue emission between 483 and 487 nm with $\Phi_{PL}< 0.01\%$ at room temperature.

At 77 K, the emission maxima of complexes **1-3** are located at 502, 507 and 507 nm, respectively. The emission bands are red-shifted upon cooling because the thermal population of a lower excited state (T_1) dominates at low temperature.Observed long emission decay times between 13.9 and 38.1 μs and blue-shifted band at 298 K, an occurrence of a TADF (thermally activated delayed fluorescence),is indicated [37-42]. Natural bond orbital (NBO) calculations and analysis indicate that the hole/electron pairs can be used to describe these transitions. The hole is approximately in the HOMO and the electron is approximately in the LUMO. The energy level of singlet and triplet state and $\Delta E(S_1-T_1)$ of complexes **1**-**3** are summarized in table 3. The energy gaps between S_1 and T_1 level of complexes **1**-**3** are small (0.076-0.105 eV), which provide further evidence to prove that complexes**1**-**3** exhibit TADF [19].

According to the calculated frontier orbitals shown in figure 3, for complexes **1**-**3**, the contribution from the Cu, halogen and ligand to the hole distribution is 5, 35, 33; 5, 23, 14; 90, 42 and 53%, respectively. The electron distribution is confined to the phenyl rings of diphenylphosphine and dimethylphenyl rings in dpnp. These indicate that the luminescence arises from the MLCT, XLCT and intraligand transitions. Compared with complexes **2** and **3**, MLCT and XLCT transitions for complex **1** are much weaker, intraligand charge transfer dominates emissive state for complex **1**. We speculated that halogens and structures of complexes including intermolecular interactions are the reasons for this difference. We found that the lifetimes of luminescence in the solid state at 298 K for **1**-**3** (13.9-38.1 μs) are 2 orders of magnitude shorter than those at 77 K (3954-7457 μs), which is also consistent with TADF.

3.4. *Thermal properties*

Since good thermal stabilities of the complexes are important for OLED applications, the onset decomposition temperatures (T_{dec}) of complexes **1**-**3** were determined by thermogravimetric analysis (TGA) under a stream of nitrogen. From the onset of the TGA curves (figure 5), all complexes show good thermal stabilities with their T_{dec} values ranging from 372 to 395 °C. A sharp one-step weight loss for all the complexes of *ca.* 71~82% was observed between 395 and 645 °C, which can be ascribed to the removal of dpnp ligand. These data render the materials suitable for the fabrication of OLEDs by using the vacuum thermal deposition method.

4. Conclusion

A series of three-coordinate dinuclear copper halide complexes **1**-**3**were synthesized. These complexes exhibit blue emission in the solid state at room temperature and have peak emission wavelengths at 483-487 nm. Small S_1–T_1 energy gaps in the solid state indicate that the emission occurred from a thermally activated excited singlet state at ambient temperature. The low emission quantum yields (< 0.01%) are attributed to the poor rigid environment around the copper center, which results in radiationless deactivations. The introduction of more rigid ligands to the Cu(I) complexes is in progress.

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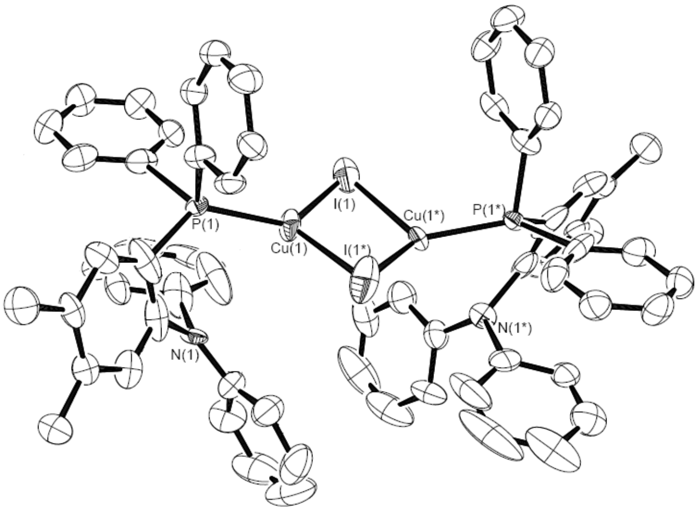

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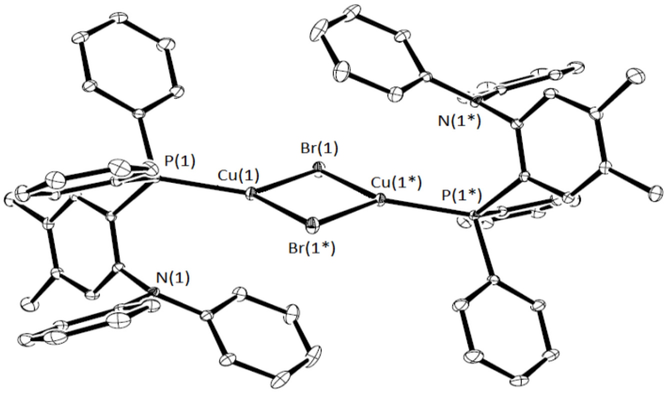

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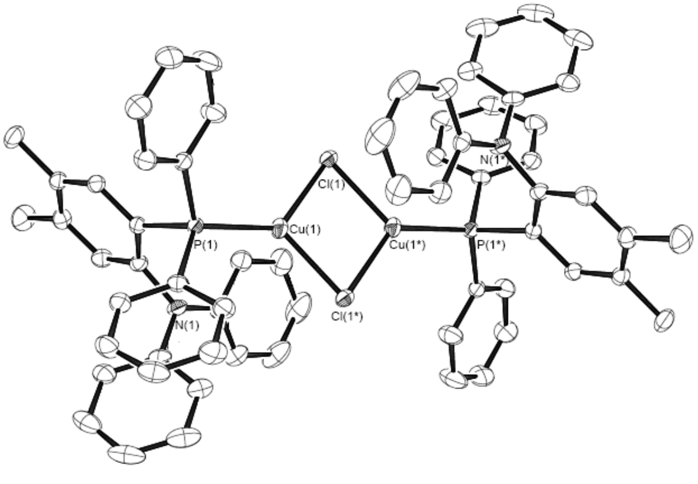

3

Figure 1. ORTEP diagrams of complexes **1**-**3**.

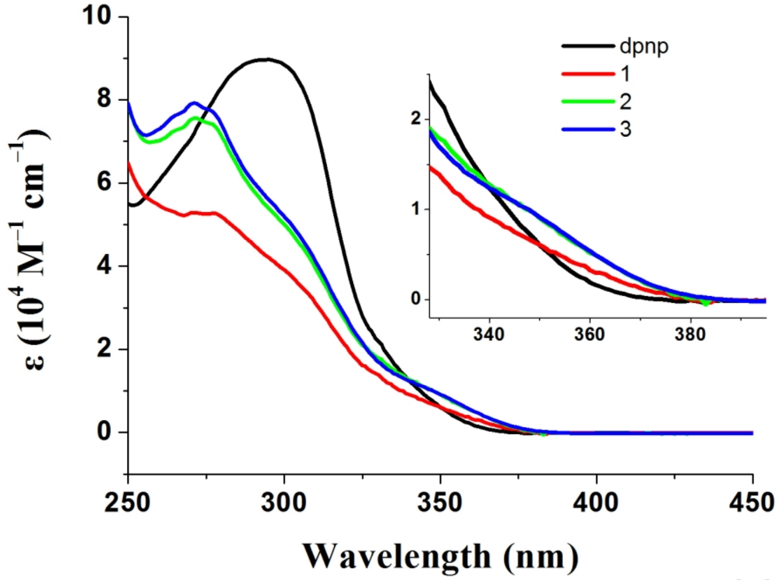

Figure 2. Absorption spectra of complexes **1-3** and dpnp in CH_2Cl_2 at 298K. The inset shows a magnified view of the absorption edges.

HOMO E=–5.024656 eV

LUMO E= –0.943568 eV

1

HOMO E=–4.940608 eV

LUMO E= –0.828512 eV

2

HOMO E=–4.976784 eV

LUMO E= –0.892432 eV

3

Figure 3. Molecular orbitals of complexes **1-3** as calculated by DFT.

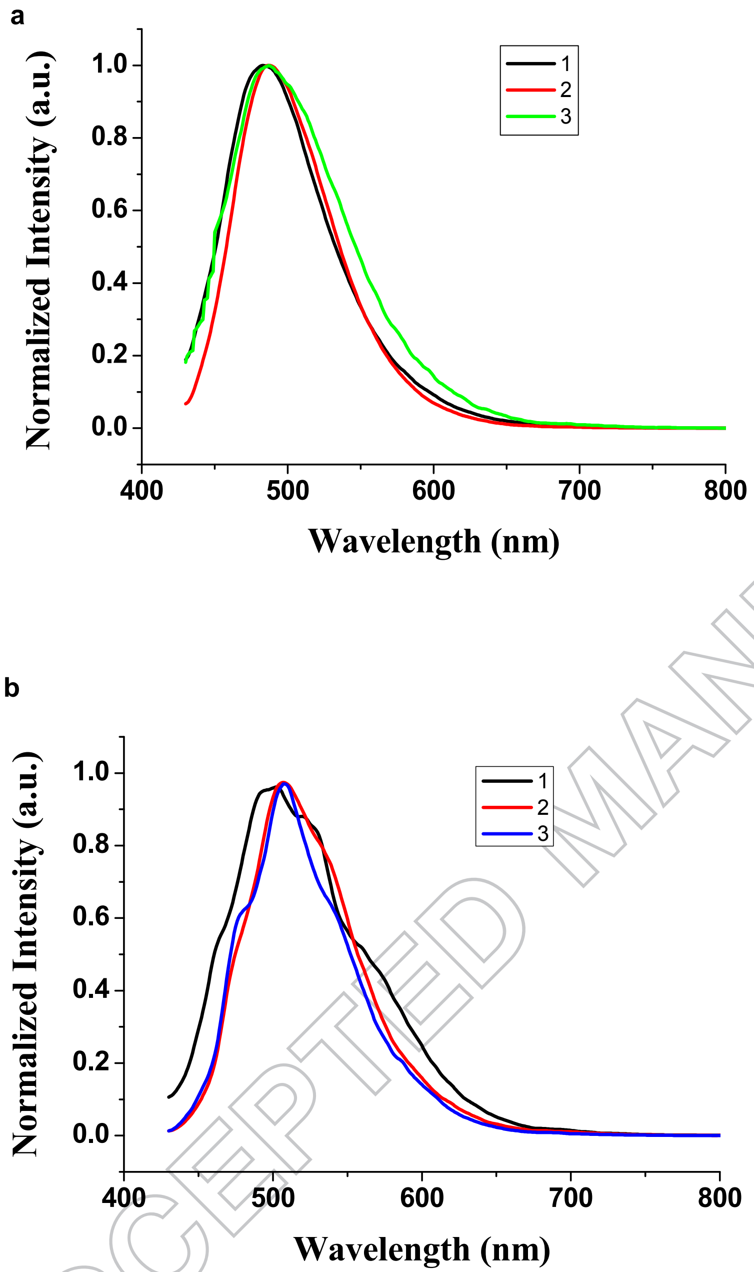

Figure 4. Normalized emission spectra of complexes **1**-**3** in the solid state at (a) 298 K and (b) 77 K. λ_{exc} = 417 nm.

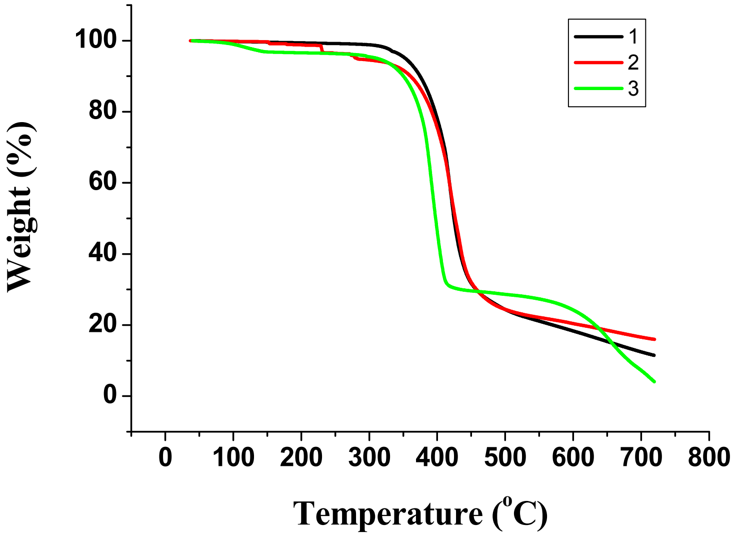

Figure 5. TGA traces of complexes **1-3**.

Table 1. Crystallographic data and details for **1-3**.

	1 • 2CH$_2$Cl$_2$	**2**	**3**
Empirical formula	$C_{64}H_{56}I_2Cu_2N_2P_2$•2CH$_2Cl_2$	$C_{64}H_{56}Br_2Cu_2N_2P_2$	$C_{64}H_{56}Cl_2Cu_2N_2P_2$
Formula weight	1465.80	1201.94	1113.09
Temperature (K)	173(2)	301(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/*n*	P2(1)/*n*
a (Å)	23.441(3)	16.513(2)	16.357(7)
b (Å)	14.0826(17)	9.3929(11)	9.267(4)
c (Å)	19.019(2)	19.211(3)	19.041(9)
V (Å^3)	6223.7(14)	2806.9(6)	2711(2)
Z	4	2	2
ρ (g cm^{-3})	1.564	1.422	1.364
μ (mm^{-1})	1.940	2.279	0.985
F (0 0 0)	2928	1224	1152
θ range for data collection (°)	1.691 to 24.736	2.823 to 27.569	2.278 to 27.529
Index ranges	$-21 \le h \le 27$	$-21 \le h \le 21$	$-18 \le h \le 21$
	$-16 \le k \le 16$	$-9 \le k \le 12$	$-12 \le k \le 12$
	$-22 \le l \le 22$	$-24 \le l \le 24$	$-24 \le l \le 24$
Independent reflections	5302 [*R*(int)=0.0890]	6453 [*R*(int)=0.0371]	6213 [*R*(int)=0.0217]
Completeness to θ = 25.242°	99.6%	99.7%	99.7%
Max. and min. transmission	0.7451 and 0.5863	0.796 and 0.727	0.7456 and 0.6238
Gof	1.039	1.018	1.022
Final *R* indices [$I > 2\sigma(I)$]	R_1= 0.0740	R_1= 0.0414	R_1= 0.0309
	wR_2= 0.1569	wR_2= 0.1059	wR_2= 0.0818
R (all data)	R_1= 0.1515	R_1= 0.0679	R_1= 0.0387
	wR_2= 0.1817	wR_2= 0.1196	wR_2= 0.0864
Max/min (e Å^3)	0.824 and −1.535	0.607 and −0.933	0.721 and −0.376

Table 2. Selected bond lengths (Å) and angles (°) for complexes **1-3**.

Complex	**1**• $2CH_2Cl_2$	**2**	**3**
Cu–X	2.454(7), 2.455(6) 2.628(7), 2.690(7)	2.3909(5), 2.4168(6)	2.2907(11), 2.3068(9)
Cu–P	2.176(7), 2.232(8)	2.1919(8)	2.1739(10)
Cu···Cu	2.859(11), 2.690(7), 2.462(11)	2.9200(8)	2.8615(13)
X–Cu–X	112.2(2), 114.4(2)	105.203(19)	103.02(3)
Cu–X–Cu	67.3(2), 57.8(2)	74.796(19)	76.98(3)
P–Cu–X	128.8(3), 115.7(3) 118.7(3), 125.1(3)	126.16(3), 127.63(3)	126.77(3), 129.29(3)

Table 3. Photophysical data of complexes **1-3** in the solid state.

	λ_{max} (nm)[a]		τ (μs)[b]		Φ [c]	S_1 (eV)[d]	T_1 (eV)[d]	Δ E(S_1-T_1) (eV)[d]
	298 K	77 K	298 K	77 K	298 K			
1	483	502	13.9	3954	< 0.01	2.567	2.470	0.097
2	487	507	29.0	7457	< 0.01	2.551	2.446	0.105
3	487	507	38.1	6733	< 0.01	2.546	2.470	0.076

[a] Emission peak wavelength.[b] Emission lifetime. Experimental errors are ± 5%.[c] Absolute emission quantum in the solid state. Experimental errors are ± 5%.[d] Determined results (S_1 and T_1 energy levels, and energy gap between $S_1$and T_1) obtained from the emission spectra at 77 K and 298 K.

Graphical abstract