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Mononuclear Copper(I) Complexes Based on Phenanthroline derivatives P^N^NP Tetradentate Ligands: Syntheses, Crystal Structure, Photochemical Properties

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The novel heteroleptic Cu(I) complexes with the tetradentate phenanthroline-based P^N^NP-type ligands have been prepared and studied.



Mononuclear Copper(I) Complexes Based on Phenanthroline derivatives P^N^NP Tetradentate Ligands: Syntheses, Crystal Structure, Photochemical Properties

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Abstract: Two novel heteroleptic Cu(I) complexes with the single tetradentate ligands have been designed and synthesized from phenanthroline. The complexes having one copper structure were fully characterized by NMR, ESI-MS and the single-crystal X-ray structures. Their photoelectric chemical properties were investigated by using cyclic voltammetry, UV/vis and fluorescence spectroscopy. Compared with the classic Cu(P^P)(N^N) complexes, this distorted tetrahedral coordination structure of Cu(P^N^NP) complexes showed a wider excitation wavelength and a red-shifted about 100 nm emission peak, due to the link function between phenanthroline and phosphorus ligands. Moreover, the copper complex **B** having the naphthyl link groups displayed high red-emissive photoluminescence quantum efficiency (PLQY), which was up to 3.8%.

Keywords: heteroleptic Cu(I) complexes, tetradentate ligand, phenanthroline.

Introduction

The metal complexes consisted of diverse ligands have various performance requirements, such as Ru¹, Ir^{2, 3}, Ni⁴, Cu^{5, 6}, which are considered as active components in organic light emitting diodes (OLEDs)^{7, 8}, as photosensitizers^{9, 10} in solar-energy conversion system, as photocatalysts¹¹ and photoinitiators¹² in the photocatalytic reactions, etc. The first row transition metal compounds are noticeable because of the price and abundance in the world. In addition, they are less toxic and more easily available than the currently used second and third row noble metal complexes which are expensive, toxic and difficult to obtain. Above all, Cu(I) complexes exhibit an electron arrangement with a d¹⁰ structure and a relatively large number of coordination mode.¹³⁻¹⁶ Considering the characteristic combination of chemical stabilities, redox properties, luminescence emission and excited state lifetime, most of the work on Cu(I) complexes with phenanthroline and P-donor ligands have attracted considerable attention scaffold.¹⁷⁻¹⁹ As an important ligand, 1, 10-phenanthroline, its structural unit is rigid, and could offer two aromatic nitrogens whose unshared electron pairs were perfectly placed to act cooperatively in chelating transition metal cations. Interestingly, phosphorus ligands could effectively stabilize Cu(I)-d¹⁰ metal centers owing to the soft nature of the P-donor atoms.²⁰ These heteroleptic Cu(I) complexes showed excellent photophysical properties and high photocalalytic activities in solar-energy conversion system.

Recently, scientists have committed to design and synthesize complicated N^P mono- or multi-nuclear Cu(I) complexes with a specific function. In 2018, Ishitani's group reported a dinuclear Cu(I) complexes based on phenanthroline ligands²¹ (Scheme 1) and Mn-catalysts in photocatalytic systems for CO₂ reduction. And just this year, Sauvage's group also reported a series of heteroleptic copper(I) complexes constructed from macrocyclic with different ring sizes and bis-phosphines²² (Scheme 1). Compared to analogous [Cu^I(P^P)(N^N)]⁺ built from acyclic NN ligands, a high stability and PLQY have been demonstrated for the systems incorporating macrocyclic phenanthrolines through photophysical properties.

Our interest in designing new P^N^NP-type ligands and studying the photo- and electro-chemistry behavior of mononuclear Cu(I) complexes based on the single tetradentate phenanthroline ligands has produced from the previous studies (Scheme 2). In this context, two novel Cu(I) complexes **A** and **B** with the tetradentate phenanthroline ligands successfully prepared by a six-step reaction. Their structures were determined by X-ray diffraction analysis. Next, the photophysical and electrochemical properties as well as the density functional theory (DFT) study of these Cu(I) complexes were also probed.



Scheme 1 The chemical structures of the Cu(I) complexes.



Scheme 2 The structural design of the Cu(I) complexes.

Results and discussion

Syntheses

The detailed syntheses routes of the complexes **A** and **B** were presented in Fig.1. As shown in Fig. 1, the two new complexes **A** and **B** composed of a unique ligand structure unit were designed and obtained under the six typical reactions:(1) palladium-catalyzed synthesis of phenylboronate²³; (2) NBS-bromination²⁴; (3) P-nucleophilic substitution reaction²⁵; (4) Suzuki-reaction²⁶; (5) and (6) reduction reaction²⁷ and in situ reaction. In the third-step reaction, the original P-reagent we used was diphenylphosphine. Later, we replaced it with diphenylphosphine oxide because of the oxidation properties of the P atom in the air, which could make manipulations easier. In the end, phosphine oxides had to be reduction and then coordinated with Cu(I) ion using in situ method.



Fig. 1 Illustration for the syntheses of the Cu(I) complexes **A** (solid) and **B** (dash). Reagents and conditions: (1) PdCl₂(dppf), KOAc, dioxane, reflux (2) NBS, AIBN, CH₃CN, reflux (3) diphenylphosphine oxide, NaH, THF, rt (4) 2,9- dibromo - 4,7-diphenyl-1,10-phenanthroline, Pd(PPh₃)₄, K₂CO₃, C₆H₅CH₃, CH₃CH₂OH, H₂O, reflux (5) Ti(OⁱPr)₄, HSi(OC₂H₅)₃, C₆H₅CH₃, reflux (6) Cu(CH₃CN)₄PF₆, DCM, rt.

Structural characterization

The mononuclear Cu(I) complexes **A** and **B** were elucidated in the solid state by the single-crystal X-ray diffraction analysis (Fig. 2 and Table S1[†]). Their crystal structures revealed a big distorted tetrahedral geometry around the copper center (plane angle: 74.3 for **A** and 75.3 for **B**), which was consistent with previous research of complex **C** ([Cu^I(xantphos)(bcp)]⁺ (bcp = bathocuproine))²⁸. The distortion developed mainly from the considerable differences in the bite-angles of the P-Cu-P (for complex **A** in Table 1: P(1)-Cu(1)-P(2) 130.23(7)°) compared to that of xantphos in complex **C** (P(1)-Cu(1)-P(2) 119.48(4)°) and also from intramolecular ligand interactions. Owing to the limitations of the single phenanthroline-based P^N^NP ligand, the two compounds exhibited similar Cu-N, Cu-P bond lengths, the values of the bite-angles of N-Cu-N and P-Cu-P. All results implied a reactively small effect of phenyl or nathphyl substituents in complexes **A** and **B** onto photophysical properties that were also in agreement with the electronic characteristics (see below).

11 0		
	Complex A	Complex B
Bond lengths, Å		
Cu(1)-N(1)	2.044(6)	2.052(5)
Cu(1)-N(2)	2.062(6)	2.085(5)
Cu(1)-P(1)	2.2225(17)	2.248(2)
Cu(1)-P(2)	2.218(2)	2.239(2)
Bond angles,°		
N(1)-Cu(1)-N(2)	81.5(2)	80.1(2)
N(1)-Cu(1)-P(1)	97.90(14)	100.52(15)
N(1)-Cu(1)-P(2)	120.35(16)	111.70(16)
N(2)-Cu(1)-P(2)	100.26(15)	97.20(15)
N(2)-Cu(1)-P(1)	116.94(15)	124.78(16)

Table 1 Selected crystallographic bond lengths and angles of complexes A and B. For more detailed information see the supporting information.

	Journal Pre-pr		
$P(1)_{-}Cu(1)_{-}P(2)$	130 23(7)	130.05(8)	
I(1)-Cu(1)-I(2)	150.25(7)	150.95(8)	
plane angle	74.3 ^[a]	75.3 ^[a]	

[a] Calculated angle between the NN ligands and PP ligands.



Fig. 2 Solid-state molecular structures (ORTEP) of complexes **A** (left) and **B** (right) with thermal ellipsoids set at a probability level of 50%. Hydrogen atoms, counter anions and solvent molecules have been omitted for clarity. Photophysical and electrochemical properties

The photophysical investigation was measured in THF and the data were given in Table 2. As can be seen from the Fig. 3, the absorption and fluorescence spectra of A and B were essentially identical, which were determined by the structure of the complexes. The as-synthesized tetradentate Cu(I) complexes presented very strong absorption at about 300 nm, which was clearly ascribed to the ligand-centered π - π * intraligand charge transfer (ILCT) located on phenanthroline^{29, 30} (L-A-4 and L-B-4). In particular, the absorption peaks at around 350nm were observed in the spectra of complex B and the L-B-4 because of the connections between the naphthyl link groups and phenanthroline (ILCT). Furthermore, the slight broad shoulder absorption at 425 nm of the complexes A and B were observed, corresponded to metal-to-ligand charge-transfer (MLCT) transition which was feature absorption peak³¹. The fluorescence spectra of L-A-4 and L-B-4 were at 430nm, while the fluorescence spectra of A and B showed clearly red shift because of MLCT in Fig 3. Furthermore, compared with the classic Cu(P^P)(N^N) complexes $(\lambda_{em} = 520-570 \text{ nm})^{28}$, they also showed a red-shifted about 100 nm emission peak. This might be explained by a more distorted structure in A and B with π - π -interaction between one phenyl or one nathphyl ring and phenanthroline ring of ligands. The excited state lifetime (τ) (Fig. S1 and S2) and the quantum yield (PLQY) of the complexes were also calculated in Table 2. The copper complex **B** having the naphthyl link groups displayed higher quantum efficiency than the complex A having the phenyl link groups and complex C $(3.1 \%)^{32}$ because of a more strong interactions in **B**. More importantly, the photostability tests of these complexes were also measured. The results manifested that the photostability of the complexes A and B were better than complex C in THF solution (Fig. S3). Later, upon cyclic voltammetry, the two complexes presented a comparable electrochemical behavior with the two reversible reduction waves (Complex A at -2.04 V vs. Fc/Fc^+ and -1.65 V vs. Fc/Fc^+ ; Complex B at -2.01 V vs. Fc/Fc^+ and -1.65 V vs. Fc/Fc^+) and three irreversible oxidation processes in acetonitrile solution (Fig. 4), which was resemble to this type of compounds³³. The reversible reduction waves of \mathbf{A} and \mathbf{B} were at around -2.00 V and -1.65 V, ascribed to the one-electron reduction of the diimine ligand and the

		Absorption ^[a]		Emission ^[a]				
Entry	Complex	λmax	8	λmax	$E_{ox}^{[b]}$	$E_{red}^{[b]}$	PLQY ^[c]	τ
		(nm)	$(M^{-1}cm^{-1})$	(nm)	(V)	(V)	(%)	(ns)
1	Α	425	2857	637	+1.17	-2.04	<mark>2.9</mark>	88.6
					+1.39			
					+1.64			
2	В	428	3142	627	+1.19	-2.01	<mark>3.8</mark>	86.9
					+1.40			
					+1.57			

cationic copper, whereas the oxidation of both complexes occurred about 1.17-1.64 V. **Table 2** Photophysical and electrochemical properties of Cu(I) complexes.

[a] Absorption and emission spectra were measured in THF solution at room temperature. [b] Eletrochemical measurement was performed at oxygen free condition in acetonitrile vs. Fc/Fc^+ and the redox events were not reversible. [c] Measured with respect to quinine sulfate (1 N, H₂SO₄) as standard (PLQY= 0.546).



Fig. 3 UV-visible absorption and photoluminescence spectra of L-A-4, L-B-4, A and B in THF at room temperature.



Fig. 4 Cyclic voltammograms of A, B in CH₃CN solution, containing 0.1M Bu_4NPF_6 as a supporting electrolyte under a scam rate of 100 mV \cdot s⁻¹.

Theoretical calculation

Theory (DFT) and Time-Dependent DFT (TD-DFT) calculations of complexes **A** and **B** (simplified P-ligands to decrease complexity) were undertaken (Table S2 and S3). Through the DFT/TD-DFT calculations, the above spectral viewpoints were supported. Molecular orbitals

involving the distribution of HOMO and LUMO in the MLCT transition were calculated. The spatial plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for complexes **A** and **B** were represented in Fig. 6 and they were in consonance with previous reports on bidentate NP Cu(I) complexes⁶. The HOMO and LUMO were apparently parted, suggesting intramolecular charge separation interactions between the separated fragments in the complexes. For complexes **A** and **B**, the electron density of the HOMO was found to be mainly distributed to the copper moiety (A-58%, B-62%) and the LUMO had main contributions from the phenanthroline moiety (A-96%, B-92%). In terms of the MLCT transition, it was reported that the tetrahedral spatial configuration of the Cu^I complex was distorted upon transition because Cu^I was oxidized to Cu^{II}, which favored square planar geometry. Normally, such molecular distortion going along with the electronic transition on levels triggered the non-radiative deactivation pathway to lower the PLQY and curtail the PL lifetime.



Fig. 5 Molecular orbital contour diagrams of complexes A and B.

Conclusion

In this work, both heteroleptic Cu(I) complexes **A** and **B** containing a tetradentate phenanthroline-based P^N^NP-type ligands were firstly synthesized. The structures of the new complexes were confirmed by the single-crystal X-ray diffraction. Also, their photophysical and electrochemical properties were investigated. Compared with the typical Cu(P^P)(N^N) complexes, the results showed that they had the broad metal-to-ligand charge-transfer (MLCT) transition and a red-shifted about emission peak. Moreover, the copper complex B having the naphthyl link groups displayed higher quantum efficiency than the complex A having the phenyl link groups, which was up to 3.8%. These not only provided new ideas for the design of copper complexes, but also contributed to discover potentially application in the electro-optic field.

Experimental section

Syntheses

All reactions and operations involving air or moisture sensitive compounds were carried out under dry nitrogen. All commercially available chemicals were purchased and used without further purification from Energy Chem. Anhydrous THF, toluene were freshly distilled through Na and benzophenone. Anhydrous DMF was freshly distilled over calcium hydride. Reactions were monitored by thin layer chromatography (TLC) and column chromatography purifications were carried out using silica gel (200-300 mesh).

4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (A-1)

1-bromo-2-methylbenzene (1.71 g, 10 mmol), bis(pinacolato)diboron (5.08 g, 20 mmol), KOAc (5.89 g, 60 mmol) and PdCl₂(dppf) (366 mg, 0.5 mmol) were dissolved in DMF (100 mL) under argon atmosphere. The reaction mixture was stirred at 85 °C for 48 hours and cooled to room temperature. Then, water (500 mL) was added and extracted with ethyl acetate (3×100 mL). The organic layer was washed with brine, dried with anhydrous sodium sulfate and evaporated under reduced pressure to yield a crude reaction product which was purified through column chromatography (petroleum ether) to provide **A-1** (1.2 g, 55%). ¹H NMR (500 MHz, CDCl₃) δ 7.77 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.29 (m, 1H), 7.14 (m, 2H), 2.54 (s, 3H), 1.32 (s, 12H). The NMR spectra were consistent with literature values.³⁴

2-(2-(Bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (A-2)

The **A-1** (2.18 g, 10 mmol),N-bromosuccinimide (1.96 g, 11 mmol), azobisisobutylonitrile (16 mg, 1 mol %), and acetonitrile (50 mL) were refluxed at 90°C for 2 h under nitrogen and then allowed to cool to room temperature. The mixture was condensed under reduced pressure until a solid began to form. The solid was filtered, and the filtrate was condensed further. The crude product was then purified using flash chromatography on silica gel (with petroleum ether as eluent) to yield compound **A-2** as a white solid (2.73 g, 92 %). ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.79 (m, 1H), 7.43 – 7.36 (m, 2H), 7.28 (m, 1H), 4.92 (s, 2H), 1.37 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 144.24, 136.39, 131.29, 130.05, 127.59, 83.85, 33.92, 24.86. The NMR spectra were consistent with literature values.³⁵

Diphenyl(2-(4,4,5,5,-tetramethyl-1,3,2-dioxaboralan-2-yl)benzyl)phosphine oxide (A-3).

Sodium hydride (60%) (0.16 g, 4 mmol) was dissolved in DMF (10 mL) and cooled to 0 $^{\circ}$ C before diphenylphosphine oxide (0.41 g, 2 mmol) was added. The mixture was stirred at this temperature for 2 h and then A-2 (0.59 g, 2 mmol) in soln in anhyd DMF (3 mL) was added dropwise to the white mixture at room temperature. After completion of the reaction (TLC), adding a few drops saturated ammonium chloride aqueous solution slowly at 0 °C, the reaction was considered to be complete when the generation of more gas was no longer observed. The mixture was washed by water, and the crude product was extracted with dichloromethane (3 x 30 mL). The combined organic fractions were dried with anhydrous magnesium sulfate, followed by filtration and removal of the solvent in vacuo. Then the concentrated mixture was directly purified by silica-gel column chromatography using ethyl acetate/hexane as eluent in increasing polarity to yield a colorless solid (0.66, 79 % yield). ¹H NMR (500 MHz, CDCl₃) & 7.77 - 7.72 (m, 1H), 7.67 (m, 4H), 7.50 – 7.44 (m, 2H), 7.42 – 7.28 (m, 6H), 7.19 (tt, *J* = 7.4, 1.5 Hz, 1H), 4.21 (s, 1H), 4.18 (s, 1H), 1.27 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 138.07 (d, J_P =8.7 Hz), 136.38 (d, J_P =2.5 Hz), 132.62 (d, $J_P = 97.5$ Hz), 131.47(d, $J_P = 2.5$ Hz), 131.39 (d, $J_P = 8.7$ Hz), 130.95 (d, $J_P = 2.5$ Hz), 130.57 (d, J_P =5 Hz), 128.17(d, J_P =11.2 Hz), 125.97 (d, J_P =2.5 Hz), 83.61, 37.06 (d, J_P =65 Hz), 24.94. ³¹P NMR (500 MHz, CDCl₃) δ 30.68. ESI-MS: [M+H]⁺=419.20.

(((4,7-diphenyl-1,10-phenanthroline-2,9-diyl)bis(2,1 phenylene) bis (methylene) bis

(diphenylphosphine oxide) (A-4).

To a round-bottom schlenk flask (10 ml) equipped with a condenser was added the degassed solution ($V_{C6H5CH3}/V_{CH3CH2OH}/V_{H2O}=1/1/1$, 9 ml) of Na₂CO₃ (0.848 g, 8 mmol), Pd(PPh₃)₄ (58 mg, 0.05 mmol), **A-3** (1.82 g, 2 mmol) and 2,9-dibromo-4,7-diphenyl-1,10-phenanthroline (0.48 g, 1 mmol). After 12 h under reflux, the reaction mixture was cooled to room temperature, during which process, a precipitate appeared. The crude mixture was purified by silica-gel column chromatography (petroleum ether/ ethyl acetate 1:1) to yield a yellow solid **A-4** (0.69 g, 76 % yield). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.74 (m, 2H), 7.62 – 7.56 (m, 2H), 7.57 – 7.50 (m, 5H), 7.37 (s, 4H), 7.27 (s, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.61 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 158.46, 148.93, 145.29, 138.14 (d, *J*_P=5), 137.90, 134.91(d, *J*_P=5), 132.60 (d, *J*_P=97.5 Hz), 131.20 (d, *J*_P=8.7 Hz), 131.12(d, *J*_P=2.5 Hz), 130.85, 130.78, 129.64, 129.46 (d, *J*_P=2.5 Hz), 128.71, 128.62, 127.55 (d, *J*_P=11.2 Hz), 127.43 (d, *J*_P=2.5 Hz), 125.07, 123.57 (d, *J*_P=15 Hz), 123.63, 123.51, 34.13 (d, *J*_P=62.5 Hz). ³¹P NMR (500 MHz, CDCl₃) δ 28.46. ESI-MS: [M+H]⁺=913.30.

The complex **A**.

To a mixture of A-4 (182 mg, 0.20 mmol), titanium isopropoxide (34 mg, 0.12 mmol) and triethoxy silane (77 mg, 1.2 mmol) were added 5 mL of anhydrous benzene under nitrogen. The pale brown slurry was heated to reflux, and the solid dissolved and the solution turned gray-green 0.5 h later. The reaction was stopped, cooled to rt and the solvent was removed by cold hydrazine to give a brown solid. Then the degassed dichloromethane (10 mL) and $Cu(CH_3CN)_4PF_6$ (74 mg, 0.20 mmol) were added. The mixture was stirred for 12 h at room temperature. Subsequently, the reaction mixture was evaporated to dryness and the crude material was purified by column chromatography using dichloromethane as eluent to afford a yellow solid (82 mg, 38 % yield). ¹H NMR (500 MHz, CDCl₃) δ 8.21 (s, 1H), 7.94 (s, 1H), 7.69 – 7.57 (m, 5H), 7.36 – 7.27 (m, 4H), 7.23 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.5 Hz, 2H), 7.02 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.90 (q, J = 6.2 Hz, 2H), 6.80 – 6.75 (m, 2H), 3.76 (m, 1H), 3.05 (d, J = 13.2 Hz, 1H). ¹³C NMR $(125 \text{ MHz}, \text{CDCl}_3) \delta 159.47, 151.55, 143.09, 139.57, 136.00, 134.30, 133.77 (t, <math>J_P$ =7.5, 8.7 Hz), 133.30, 133.18, 131.50, 131.01 (t, J_P=7.5, 7.5 Hz), 130.67 (d, J_P=7.5, 8.7 Hz), 130.06, 129.78, 129.42, 129.21, 128.64 (t, $J_P = 5.0$, 5.0 Hz), 128.32 (t, $J_P = 3.7$, 5.0 Hz), 127.05 (d, $J_P = 95$ Hz), 126.51, 125.18, 77.28, 32.07 (t, $J_P = 7.5$, 7.5 Hz), 30.93. ³¹P NMR (500 MHz, CDCl₃) δ 9.72. ESI-MS: [M+H]⁺=943.30. HRMS m/z (ESI+): Calculated for C62H46CuN2P2 (M⁺): 943.2427, Found 943.2445.

4,4,5,5-Tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane (B-1).

The synthetic process of the compound **B-1** was similar to the compound **A-1**.

¹H NMR (500 MHz, CDCl₃) δ 8.10 (dd, J = 8.3, 1.1 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.44 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.37 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 2.62 (s, 3H), 1.48 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 141.36, 136.64, 131.39, 129.57, 128.48, 128.12, 127.50, 125.99, 124.54, 83.98, 25.10, 22.62.The NMR spectra were consistent with literature values.³⁶

2-(2-(Bromomethyl)naphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (B-2).

The synthetic process of the compound **B-2** was similar to the compound **A-1**.

¹H NMR (500 MHz, CDCl₃) δ 8.30 (m, 1H), 7.86 – 7.75 (m, 2H), 7.51 – 7.41 (m, 3H), 4.96 (s, 2H), 1.50 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 141.68, 136.62, 132.65, 130.76, 128.47, 128.23, 127.62, 126.56, 126.11, 84.38, 34.39, 25.12. The NMR spectra were consistent with literature

values.36

Diphenyl((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene-2 yl)methyl)phosphine oxide (B-3).

The synthetic process of the compound **B-3** was similar to the compound **A-2**.

¹H NMR (500 MHz, CDCl₃) δ 8.44 (d, J = 8.4 Hz, 1H), 7.74 – 7.65 (m, 6H), 7.47 – 7.36 (m, 9H), 4.28 (s, 1H), 4.25 (s, 1H), 1.40 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 137.08 (d, $J_P = 1.2$ Hz), 136.41(d, $J_P = 7.5$ Hz), 132.64 (d, $J_P = 97.5$ Hz), 131.92(d, $J_P = 1.2$ Hz), 131.59 (d, $J_P = 2.5$ Hz), 131.31 (d, $J_P = 8.7$ Hz), 130.18 (d, $J_P = 1.2$ Hz), 128.30 (d, $J_P = 11.2$ Hz), 128.31, 128.17(d, $J_P = 7.5$ Hz), 126.13, 125.17, 83.91, 38.27 (d, $J_P = 65$ Hz), 25.14. ³¹P NMR (500 MHz, CDCl₃) δ 30.10. ESI-MS: [M+H]⁺=469.20.

(((4,7-diphenyl-1,10-phenanthroline2,9-diyl)bis(naphthalene-1,2 diyl)) bis(methylene)) bis (diphenylphosphine oxide) (B-4).

The synthetic process of the compound B-4 was similar to the compound B-3.

¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, J = 15.0 Hz, 1H), 7.76 (dd, J = 8.6, 3.5 Hz, 3H), 7.72 (m, 1H), 7.59 (d, J = 9.2 Hz, 3H), 7.54 (dd, J = 15.0, 6.4 Hz, 2H), 7.45 (d, J = 9.3 Hz, 2H), 7.30 (dd, J = 24.7, 10.5 Hz, 4H), 7.24 – 7.03 (m, 2H), 6.99 (d, J = 7.4 Hz, 2H), 6.91 (d, J = 8.1 Hz, 3H), 4.39 (t, J = 14.7 Hz, 1H), 3.72 (t, J = 14.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 157.75, 148.08, 146.97, 146.41, 143.91, 137.99, 137.65, 137.50, 132.16 (d, $J_P = 106.2$ Hz), 131.47 (d, $J_P = 10.0$ Hz), 131.26 (d, $J_P = 8.7$ Hz), 131.17, 130.94, 130.60 (d, $J_P = 10$ Hz), 129.99, 128.68, 128.35 (d, $J_P = 11.2$ Hz), 128.5 (d, $J_P = 11.2$ Hz), 126.95, 126.76, 126.00, 125.84, 125.36, 124.23, 35.26 (d, $J_P = 63.7$ Hz). ³¹P NMR (500 MHz, CDCl₃) δ 29.93. ESI-MS: [M+H]⁺=1013.30.

The complex **B**.

The synthetic process of the compound **B** was similar to the compound **A**.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.97 (s, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.74 – 7.69 (m, 3H), 7.65 – 7.55 (m, 3H), 7.47 (t, J = 7.4 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.18 (m, 3H), 6.90 – 6.77 (m, 5H), 6.64 (q, J = 6.4, 5.9 Hz, 2H), 6.53 (q, J = 6.9, 6.0 Hz, 2H), 3.72 (m, 1H), 3.15 (d, J = 12.8 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 157.66, 150.26, 144.05, 135.89, 135.21, 133.71 (t, $J_P = 7.5$, 7.5 Hz), 132.47(d, $J_P = 3.5$ Hz), 131.88,130.77 (t, $J_P = 7.5$, 7.5 Hz), 130.49, 129.89, 129.79, 129.39, 129.22, 128.94 (t, $J_P = 3.7$, 5.0 Hz), 128.85, 128.64, 128.53, 128.08 (t, $J_P = 5.0$, 5.0), 127.39 (d, $J_P = 101.2$ Hz), 126.07, 125.55, 124.83, 33.50 (t, $J_P = 6.2$, 12.5 Hz), 30.95. ³¹P NMR (500 MHz, CDCl₃) δ 10.80. ESI-MS: [M+H]⁺=1043.30. HRMS m/z (ESI+): Calculated for C70H50CuN2P2 (M⁺): 1043.2740, Found 1043.2738.

Characterization

¹H, ¹³C and ³¹P spectra were recorded on Bruker AVANCE III 500 MHz using CDCl₃ as solvent with TMS as internal standard. HRMS were recorded on Agilent 6210 TOF LC/MS mass spectrometer. UV–vis absorption spectra were recorded using a Cary 500 UV–vis spectrophotometer. Steady-state photoluminescence (PL) was recorded using a SENS-9000 spectrophotometer. Time-resolved PL was carried out using QM4 with time correlated single-photon counting capability. Cyclic voltammetry (CV) measurements were performed using a BASi Epsilon-EC workstation with anhydrous acetonitrile solvent, glass carbon as the working electrode, platinum wire as the counter electrode, Ag/AgCl as the reference electrode, an *n*-Bu₄NPF₆(0.1 M) electrolyte and a ferrocene standard at a scan rate of 100 mV • s⁻¹. Application software was Gaussian 16. A time-dependent-DFT approach (TDDFT) was used to interpret the absorption and emission spectra in this system based on the optimized geometries at the

B3LYP/LANL2DZ and PCM levels of theory.

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Mononuclear Copper(I) Complexes Based on Phenanthroline derivatives P^N^NP Tetradentate Ligands: Syntheses, Crystal Structure, Photochemical **Properties**

Highlights

- 1. The novel P^N^N^P-type ligands and the mononuclear tetradentate phenanthroline Cu(I) complexes were designed and prepared.
- 2. Compared with the typical Cu(P^P)(N^N) complexes, they showed a wider excitation wavelength and a red-shifted about 100 nm emission peak.
- 3. The copper complex **B** having the naphthyl link groups displayed high red-emissive photoluminescence quantum efficiency, which was up to 3.8 %.

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