Synthesis, characterization and photophysical properties of a new 2,5-di(aryl)phosphole derivative and their trigonal copper-phosphole complexes.

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Abstract

A new phosphole derivative 2,5-di(2-quinolyl)-1-phenylphosphole (**1**) was synthesized by using the Fagan–Nugent method. Phosphole **1** was obtained as an air stable solid in high yield (73%). Additionally, two new copper-phosphole complexes [CuX(Phosphole)$_2$] (X = Cl (**2a**), I (**2b**), Phosphole = **1**) have been synthesized by reaction of CuX (X = Cl, I) and phosphole derivative (**1**). All compound were characterized by NMR, ESI-MS, UV–Vis and fluorescence spectroscopy. The photophysical properties of all compounds were analyzed, UV-Vis spectra of the complexes **2a-b** shown π–π* transitions with shift very similar to the found in the free phosphole due to that their symmetrical structures inhibits efficient ILCT. We have found that the compounds **1**, **2a-b** exhibited fluorescence between 460 and 583 nm with quantum yields of Φ_f = 0.04 – 0.11. The emission energy of **2b** is higher than **2a**, suggesting that λ_{max} is affected by the ligand-field strength of the halogen ions in the complexes ($I^- < Cl^-$).

Keywords: phosphole, copper–phosphole complexes, bis(quinolyl)phosphole, photophysical properties, fluorescent Cu–complexes.

1. Introduction

Luminescent transition metal complexes have gained much attention due to their potential application in organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) [1–7]. Copper(I)-containing complexes have been extensively studied because of their relative abundance and low cost, moreover, they have demonstrated a wave variety of applications in solar energy conversion, luminescence-based sensors, catalysis and probes of biological systems [4,8–16]. Nowadays, it is well-know that the use of bulky and rigid ligands regulate the structure and configuration of copper (I) complexes, leading to effective suppression of the nonradiative processes, which is the key to synthesize highly efficient Cu(I)-complexes [17–20]. Additionally, different studies have reported that the nature of ligands, specifically halides and phosphines, affect the luminescence properties of Cu(I)-compounds [21–25]. Particularly, three-coordinate Cu(I) halide coordinated by phosphine ligands have showed high luminescent efficiency [26–30].

On the other hand, phosphole ligands have attracted growing interest for the development of complexes due to their ability to act as ⌠-ligands through the nucleophilic phosphorus atom [31–33], allowing a tuning of their photophysical properties which has been used in the development of multifunctional materials for OLEDs and catalytic reactions [16,34–38].

Based on the interesting electronic properties that present both phospholes-complexes and three-coordinate mononuclear Cu(I) halide with phosphine ligands, we have synthesized a new rigid phoshole with pi-conjugated system (**1**) and two trigonal copper-phosphole complexes (**2a-b**). Their spectroscopy characterization and photophysical properties are described.

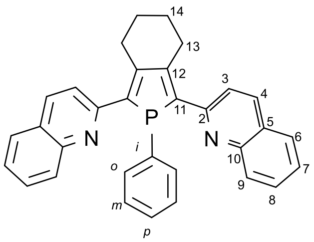
2. Experimental section

2.1. Materials and methods

All experiments were performed under an atmosphere of dry argon in the dark using a standard Schlenk technique. The solvents were previously dried and distilled following standard methods prior to use [39]. Dibromidephenylphosphine ($PhPBr_2$) was synthesized according to published procedures [40]. ^{31}P, ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Advance AM 300 and AM600 spectrometers. Mass spectra were acquired on a Thermo Scientific TSQ Quantum Ultra AM Triple Quadrupole mass spectrometer employing the Heated Electrospray Ionization (HESI) technique. The UV-Vis spectra were recorded on a PerkinElmer Lambda 2 spectrophotometer. All fluorescence spectra were recorded at room temperature at 10^{-6} M on a PerkinElmer L545 fluorescence spectrometer with a pulse xenon lamp, the fluorescence quantum yield was determined in CH_2Cl_2 on freshly prepared samples (air-equilibrated). Samples of tetraphenylporphyrin in CH_2Cl_2 were employed as a standard ($\Phi_f = 0.11$).

2.2. Synthesis of 1-phenyl-2,5-di(2-quinolyl)phosphole (1)

A solution of n-BuLi in hexane (1.6 M, 1.9 mL; 3.05 mmol) was added dropwise to a solution of 1,8-di(2-quinolyl)octa-1,7-diyne (500.0 mg; 1.39 mmol) and [Cp_2ZrCl_2] (405.6 mg; 1.39 mmol) in THF (25 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. Freshly distilled $PhPBr_2$ (383.6 mg; 1.43 mmol) was added to this solution at –78 °C. The solution was allowed to warm to room temperature and stirred for 24 h. The solution was filtered, and the volatile materials were removed under vacuum. After purification on basic alumina (4 x 25 mL THF) and the washing on pentane, **1** was obtained as a yellow solid (yield: 472.9 mg; 73%). **NMR-^{31}P{^{1}H} (200 MHz, $CDCl_3$):** δ = 12.36 (s). **NMR-^{1}H (600 MHz, $(CD_3)_2CO$):** δ = 7.80 (2H; d; $J_{H^{4}\text{-}H^{3}}$ = 8.40 Hz; H^{4}); 7.50 (2H; d; $J_{H^{9}\text{-}H^{6}}$ = 7.80 Hz; H^{9}); 7.42 (2H; d; $J_{H^{6}\text{-}H^{9}}$ = 7.80 Hz; H^{6}); 7.31 (2H; d; $J_{H^{3}\text{-}H^{4}}$ = 8.40 Hz; H^{3}); 7.26 (2H; t; $J_{H^{8}\text{-}H^{7}}$ = 7.20 Hz; H^{8}); 7.06 (2H; t; $J_{H^{7}\text{-}H^{8}}$ = 7.20 Hz; H^{7}); 6.93 (2H; m; H^{o}); 6.63 (3H; m; H^{p} and H^{m}) 3.12 (2H; m; H^{13a}); 2.47 (2H; m; H^{13b}); 1.45 (2H; m; H^{14a}); 1.28 (2H; m; H^{14b}). **NMR-^{13}C{^{1}H} (200 MHz, $(CD_3)_2CO$):** δ = 145.42 (d; $^{2}J_{PC}$ = 18.00 Hz; C^{2}); 139.25 (d; $^{2}J_{PC}$ = 10.60 Hz; C^{12}); 137.85 (s; C^{5}); 135.48 (s; C^{11}); 126.40 (s; C^{4}); 124.77 (s; C^{i}); 123.86 (d; $^{2}J_{PC}$ = 17.70 Hz; C^{o}); 120,08 (s; C^{8}); 118.89 (s; C^{9}); 118.76 (s; C^{p}); 118.70 (s; C^{m}); 117.97 (s; C^{6}); 116.36 (s; C^{7}); 116.21 (s; C^{10}); 112.17 (d; $^{3}J_{PC}$ = 8.90 Hz; C^{3}); 18.94 (s; C^{13}); 12.81 (s; C^{14}). MS (CH_2Cl_2, ESI): m/z: 469.19 [$C_{32}H_{25}N_2PH$]$^{+}$. UV-Vis (CH_2Cl_2), λ_{max} (nm): 240 nm (ε = 775023 M $^{-1}$cm^{-1}), 402 (ε = 279991 M $^{-1}$cm^{-1}). Fluorescence (CH_2Cl_2), λ_{max} (nm): 460 nm, Φ_f = 0.04.



2.3. Synthesis of [CuCl(1-phenyl-2,5-di(2-quinolyl)phosphole)$_2$] (2a)

A solution of **1** (157.7 mg; 0.34 mmol) and CuCl (16.9 mg; 0.17 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature under argon for 24 h. The solvent was removed under vacuum and the remaining solid washed on pentane (4 x 10 mL) to give **2a** as a red solid (yield: 151.3 mg; 87%). **NMR-^{31}P{^{1}H} (200 MHz, $CDCl_3$):** δ = 4.57 (s) **NMR-^{1}H (600 MHz, $CDCl_3$):** δ = 8.23 (4H; m; H^{4}); 7.86 (4H; d; H^{9}); 7.53 (8H; m; H^{6} y H^{3}); 7.46 (8H; m; H^{8} and H^{7}); 7.36 (4H; m; H^{o}); 7.11 (6H; m; H^{p} and H^{m}); 3.34 (4H; m; H^{13a}); 2.72 (4H; m; H^{13b}); 1.74 (4H; m; H^{14a}); 1.69 (4H; m; H^{14b}). **NMR-^{13}C{^{1}H} (200 MHz, $CDCl_3$):** δ = 154.13 (s; C^{2}); 152.37 (s; C^{12}); 147.77 (s; C^{5}); 135.72 (d; C^{11}); 133.70 (s; C^{4}); 130.15 (s; C^{i}); 129.75

(s; C^{o}); 129.50 (s; C^{8}); 129.34 (s; C^{9}); 127.42 (s; C^{p}); 127.21 (s; C^{m}); 126.26 (s; C^{6}); 126.05 (s; C^{7}); 124.24 (s; C^{10}); 122.36 (s; C^{3}); 29.74 (s; C^{13}); 22.63 (s; C^{14}). MS (CH_2Cl_2, ESI): m/z: 999.31 $[C_{64}H_{50}N_4P_2Cu]^+$. UV-Vis (CH_2Cl_2), λ_{max} (nm): 240 nm (ε = 909294 $M^{-1}cm^{-1}$), 403 (ε = 322051 $M^{-1}cm^{-1}$). Fluorescence (CH_2Cl_2), λ_{max} (nm): 583 nm, $\Phi_f = 0.07$.

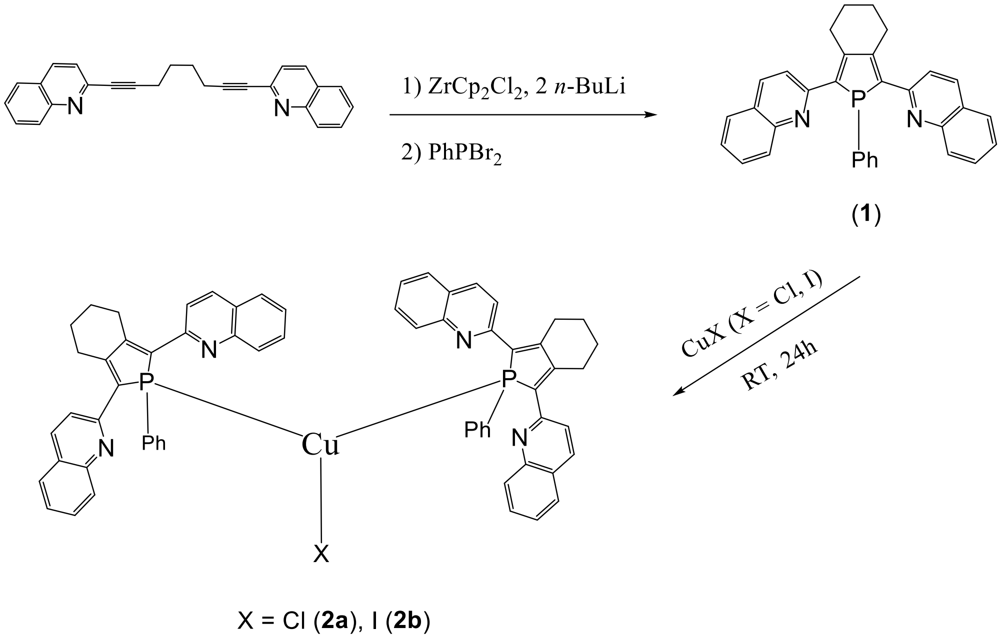
2.4. Synthesis of [CuI(1-phenyl-2,5-di(2-quinolyl)phosphole)$_2$] (2b)

A solution of **1** (170.8 mg; 0.36 mmol) and CuI (33.9 mg; 0.18 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature under argon for 24 h. The solvent was removed under vacuum and the remaining solid washed on pentane (4 x 10 mL) to give **2b** as an orange solid (yield: 187.8 mg; 88%). **NMR- $^{31}P\{^1H\}$ (121,4 MHz, CD_2Cl_2):** δ = 2.22. **NMR-^1H (600 MHz, $CDCl_3$):** δ = 8,20 (4H; m; H^{4}); 7.87 (4H; d; H^{9}); 7.51 (8H; m; H^{6} and H^{3}); 7.45 (4H; m; H^{8}) 7.41 (4H; m; H^{7}); 7.31 (4H; m; H^{o}); 7.09 (6H; m; H^{p} and H^{m}); 3.34 (4H; m; H^{13a}); 2.82 (4H; m; H^{13b}); 1.75 (8H; m; $H^{14a,b}$). **NMR-$^{13}C\{^1H\}$ (150,8 MHz, $CDCl_3$):** δ = 154.64 (s; C^{2}); 154.09 (s; C^{12}); 152.12 (s; C^{5}); 148.09 (s; C^{11}); 147.67 (s; C^{4}); 136.01 (s; C^{i}); 135.62 (s; C^{o}); 133.70 (s; C^{8}); 129.98 (s; C^{9}); 129.50 (s; C^{p}); 129.25 (s; C^{m}); 128.52 (s; C^{6}); 127.16 (s; C^{7}); 126.23 (s; C^{10}); 125.93 (d; C^{3}); 29.65 (s; C^{13}); 22.70 (s; C^{14}). MS (CH_2Cl_2, ESI): m/z: 999.31 $[C_{64}H_{50}N_4P_2Cu]^+$. UV-Vis (CH_2Cl_2), λ_{max} (nm): 239 nm (ε = 572282 $M^{-1}cm^{-1}$), 403 (ε = 196877 $M^{-1}cm^{-1}$). Fluorescence (CH_2Cl_2), λ_{max} (nm): 490 nm, $\Phi_f = 0.11$.

3. Results and discussion

3.1. Synthesis and characterization of 1-phenyl-2,5-di(2-quinolyl)phosphole (1)

The new phosphole derivative (**1**) was obtained employing the Fagan–Nugent method [41,42], which involve the oxidative coupling of 1,8-di(2-quinolyl)octa-1,7-diyne [43] with $[Cl_2ZrCp_2]$ followed by treatment with dibromidephenylphosphine ($PhPBr_2$) (Scheme 1). The phosphole derivative is purified by flash column chromatography (Al_2O_3 basic, eluant: THF) and isolated as air-stable yellow solid in high yield (73%). The new phosphole (**1**) was stable in different solvents such as THF, CH_2Cl_2, $CHCl_3$, DMSO and acetone. The ESI-MS spectrum of compound **1** displayed a peak at m/z 469.19, which matches with the molecular ion [**1** + H]$^+$ = $[C_{32}H_{25}N_2PH]^+$]. Its $^{31}P\{^1H\}$NMR spectrum showed only a singlet at ™ +12.36 ppm, whose shift is similar to that found for related symmetrical 2,5-disubstituted 1-phenylphospholes [31]. On the other hand, all ^1H and $^{13}C\{^1H\}$ NMR signals were unequivocally assigned on the basis of 1D and 2D, correlation spectroscopy (COSY), heteronuclear multiple quantum correlation (HMQC) and heteronuclear multiple bond correlation (HMBC) experiments (for complete NMR data see experimental section). Thus, their ^{1}H and ^{13}C{^{1}H} NMR spectra showed signals consistent with the structure of the phosphole **1**.



(**1**)

X = Cl (**2a**), I (**2b**)

Scheme 1. Synthesis of phosphole **1** and their complexes **2a-b**.

3.2. Synthesis and characterization of [CuX(1-phenyl-2,5-di(2-quinolyl)phosphole)$_2$] (X = Cl (2a), I (2b))

The reaction of CuX (X = Cl, Br, I) with two equivalent of phosphole **1** in dichloromethane as solvent at RT for 24 h lead to the complexes [CuX(Phosphole)$_2$] (X = Cl (**2a**), I (**2b**), Phosphole = **1**), the complex with bromide not was observed. **2a-b** were isolated in good yields as air stables red and orange solids, respectively (87% **2a**, 88% **2b** yields). Both complexes **2a-b** were stable in different solution such as CH_2Cl_2, $CHCl_3$, DMSO; slightly soluble in Et_2O, THF; and insoluble in pentane and H_2O.

The ESI-MS spectra of the complexes **2a-b** depict a peak of high intensity corresponding to the molecular ion $[C_{64}H_{50}N_4P_2Cu]^+$ at m/z 999.31 in both cases. These are consistent with a copper atom and two phosphole ligands, suggesting that the compounds obtained are of the type [M-X-Phosphole]. The ^{31}P, ^{1}H and ^{13}C signals showed variations in their chemical shifts with respect to those of the free phosphole, being the Δ™ used as a parameter to deduce the binding mode of **1** to the metal center. The $^{31}P\{^{1}H\}$NMR spectra of both complexes exhibit only a singlet signal high-field shifted in comparison to the free phosphole (™ = 4.57 (**2a**) and 2.22 (**2b**) ppm), indicating that each compound correspond to a disubstituted Cu-complex with two equivalent phosphorus atoms. Their ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra showed very small differences compared to those of the free ligand, suggesting that each complex present a ⌠-coordination of the two phosphole ligands and a symmetrical structure. Based on the available data, the structures shown for **2a-b** in Scheme 1 are the most likely. Thus, the compounds **2a-b** correspond to 16-electron symmetric Cu(I)-complexes in the usual d^{10} trigonal planar coordination geometry as we have been previously reported for [Cu{1-phenyl-2,5-bis(2-thienyl)phosphole}$_2$Cl] [44].

3.3. Photophysical properties

Phosphole ligand and their complexes were analyzed by UV-Vis and fluorescence spectroscopy to evaluate and compare their electronic properties. The spectroscopic data are summarized in Table X. The measured absorption and emission spectra of all compounds were recorded in CH_2Cl_2 at room temperature. These spectra were measured at an identical molar concentration (1×10^{-6} M), so that a direct comparison of absorbance could be made.

The phosphole ligand (**1**) exhibit an absorption at 402 nm in the visible region of its UV–vis spectrum, that is attributed to the π–π* transitions of the extended p-conjugated system of the phosphole ligand [31,45,46]. UV-Vis spectra of both complexes **2a-b** (Figure 1) showed π–π* transitions with shift very similar to the observed in the free phosphole, which can be due to the symmetrical structure of the complexes, that inhibits efficient ILCT [31].

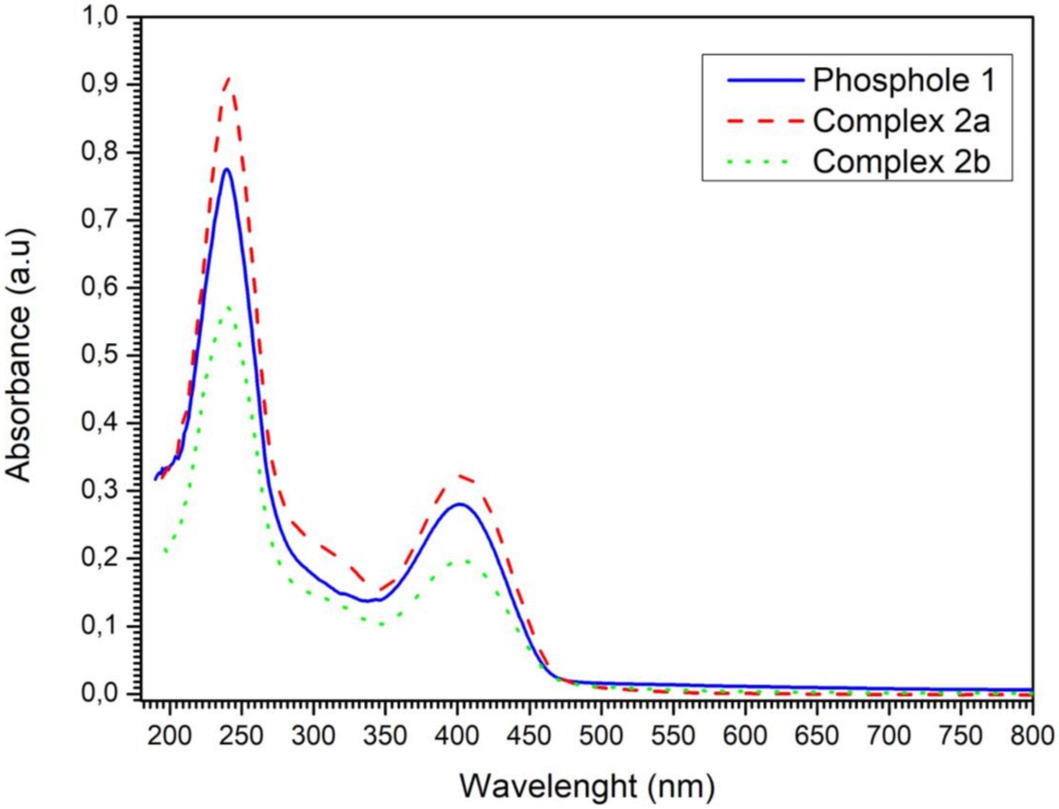


Figure 1. UV-Vis absorption spectra for the phosphole **1** and their complexes **2a-b** in CH_2Cl_2 at room temperature and [c] = 10^{-6} M.

The measured UV-excited (**λ**= 240 nm) fluorescence spectra have shown that phosphole ligand and their corresponding complexes exhibit emission between 460 and 583 nm (Figure 2). A wide range of Stokes shifts were found for all compound (Table 1), in which complex **2a** displays the largest Δλ value (180 nm) and the phosphole **1** displays the shortest one (Δλ = 58 nm). The emission bands of the complexes are broad and unstructured, suggesting that the emissive excited states have charge-transfer character [26,47]. The emission energy of **2b** is higher than **2a**, suggesting that λ_{max} is affected by the ligand-field strength of the halogen ions in the complexes ($I^- < Cl^-$). Presumably the electronic nature of the triplet excited state of **2a-b** is influenced to some extent by $X^- \rightarrow \pi^*$(**1**) charge-transfer transitions [25–27,47–49].

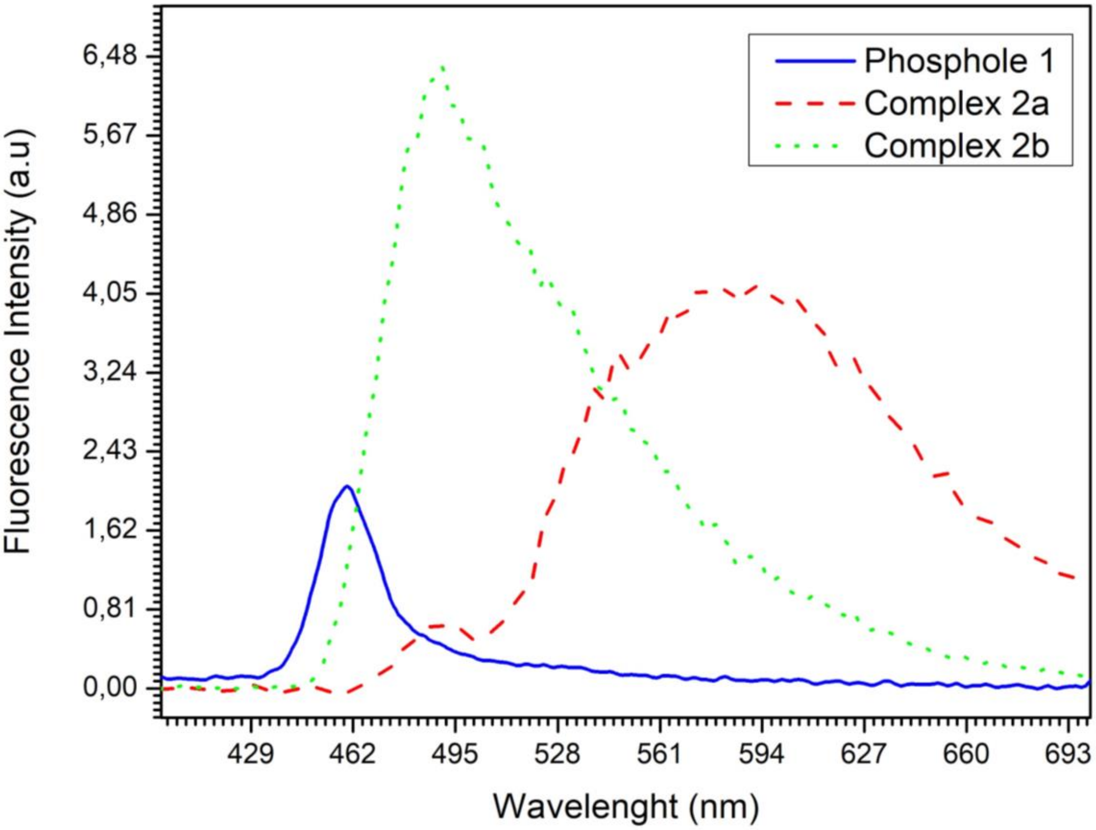


Figure 2. Fluorescence emission spectra (λ= 240 nm) for the phosphole **1** and their complexes **2a-b** in CH_2Cl_2 at room temperature and [c] = 10^{-6} M.

Phosphole **1** showed a quantum yield low (Φ_f = 0.04) due to chromophores that present λ^3-P centers generally exhibit almost no fluorescence as a result of quenching by the lone pair of the phosphorus atom [32,36,50–53]. Coordination of the phosphole ligands to metal center has an impact in the quantum yields [31,32,54], showing in the complexes **2a-b** values higher than those of the corresponding free phosphole (Φ_f = 0.07 (**2a**); 0.11 (**2b**)). It is also noteworthy that the complex **2b** exhibiting the highest value in solution. The values of fluorescence quantum yield of these complexes are highest that the found in trigonal Cu(I)-phosphine halide complexes [26,29].

Table 1. UV-Vis and fluorescence spectra of phosphole (1) and their complexes (2a-b).

Compound	UV-Vis λ_{max}/nm[a]	ε/M^{-1} cm^{-1}	F λ_{max}/nm[b]	Φ_f[c]	Stokes Shift $\Delta\lambda$
1	240	775023	460	0.04	58
	402	279991			
2a	240	909294	583	0.07	180
	403	322051			
2b	239	572282	491	0.11	88
	403	196877			

[a] At room temperature in CH_2Cl_2.

[b] At room temperature in CH_2Cl_2. [**1, 2a-b**] = 10^{-6} M

[c] Fluorescence quantum yield in CH_2Cl_2 relative to tetraphenylporphyrin (Φ_f = 0.11).

4. Conclusions

We have synthesized a new 2,5-di(aryl)phosphole derivative (**1**) by the Fagan–Nugent method in high yield. Additionally, we have obtained two new three-coordinate mononuclear Cu(I) halide complexes (**2a-b**) through the reaction of CuX (X = Cl, I) with two equivalent of **1**. All the compounds were characterized by analytical and spectroscopic techniques. The photophysical studies showed that all complexes exhibit fluorescence with quantum yields Φ_f = 0.04 – 0.11, being the highest value for complex **2b**. These new complexes open up the possibility of new researches in catalytic applications or studies of their biological activities as we have previously reported [16,44].

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Supplementary data

NMR and MS spectra of all compounds are found in supplementary material.

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