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# Four-coordinated copper(I) complexes containing variably substituted N-heterocyclic carbenes (NHCs): Synthesis, photophysical properties and theoretical investigation



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#### ABSTRACT

Three four-coordinated N-heterocyclic carbene (NHC) copper(I) complexes, [Cu(NaphIm-Py)(POP)]PF6 (1),  $[Cu(AnthrIm-Py)(POP)]PF_6$  (2), and  $[Cu(PhBenIm-c-Py)(POP)]PF_6$  (3) (NaphIm-Py = 3-(naphthalen-2-ylmethyl-1-(pyridin-2-yl)-1H-imidazolylidene, AnthrIm-Py = 3-(anthracen-9-ylmethyl)-1-(pyridin-2-ylmethylm2-yl)-1*H*-imidazolylidene, PhBenIm-*c*-Py = 3-benzyl-1-(pyridin-2-ylmethyl)-1*H*-benzo[*d*]imidazolylidene, POP = bis[2-diphenylphosphino]-phenyl)ether) have been synthesized and characterized. The effect of varying carbene ligands with different substituents on the structural aspects and photophysical properties of the complexes is systematically investigated. The lowest absorption bands of 1 at about 350 nm are assigned as metal-to-ligand charge transfer (MLCT) character with some contribution from ligand-to-ligand charge transfer (LLCT) character, while the  $\pi$ - $\pi$ \* transition of the anthryl group are responsible for the lowest absorption band of 2. For 3, no MLCT absorption band are observed in lower energy region. The emission wavelengths of all NHC-Cu(I) complexes are in the range of 520–550 nm with the phosphorescent origin in the solid state. 1 and 2 with naphthyl and anthryl groups show the lower photoluminescence efficiency due to the strong  $\pi$ - $\pi$  stacking interactions, whereas 3 exhibit good photoluminescence properties companying with the higher quantum yields and long excited-state lifetimes. Density functional theory (DFT) and time dependent density functional theory (TDDFT) calculations were employed to rationalize the photophysical properties of the NHC-Cu(I) complexes.

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#### 1. Introduction

N-heterocyclic carbene (NHC) has been widely used as a new class of ligands for the design of a wide variety of complexes because of its attractive feature, such as strong electron donation and complex stability [1]. Many NHC-based metal complexes have been reported and utilized in a wide range field of applications including catalysts [2–6] and medicinal fields [7–10]. Among them, NHC copper complexes have attracted considerable attention due to their inexpressive and relatively low toxicity [11–15]. However, their applications in other areas remain vast room to be explored [16,17].

Since Tsubomura and co-workers [18] first reported the photoluminescence properties of the NHC-Cu (I) complex in 2009, there has been a growing interest in the study of luminescent NHC-Cu(I) complexes. Thompson group in 2010 reported the photoluminescence behavior of the two NHC-Cu(I) complexes of the type [(NHC)Cu(L)] complexes (NHC=IPr = 1,3bis(2,6-diisopropylphenyl)imidazol-2-ylidene, L1 = Phen = 1,10-phenanthroline; L2 = pybim = 2-(2-pyridyl)benzimidazole), in which [(IPr)Cu(pybim)] complex exhibited high emission quantum yields ( $\phi = 0.58$ ) and long-lived triplet excited state lifetimes ( $\tau = 33.1 \text{ } \mu \text{s}$ ) [19]. Subsequent to this work, the same group in 2012 reported a series of analogous NHC-Cu(I) complexes containing various pyridyl-azolate ligands [20]. These complexes exhibited moderate to high quantum yields ( $\phi = 0.23-0.62$ ) with longer-lived excited lifetimes ( $\tau = 12-13$ μs). More recently, the [(NHC)Cu(py<sub>2</sub>BMe<sub>2</sub>)] complexes  $(py_2Bme_2 = di(2-pyridyl)dimethylborate)$  containing different



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NHC ligands were described. The color of these complexes was observed to turn from blue to red while retaining high emission efficiencies, depending on the type of the NHC ligands [21]. In 2014, Marion and Gaillard employed the dipyridylamine ligands to synthesize a series of  $[(NHC)Cu(N^N)]$  complexes, where N^N denotes a dipyridylamine ligand. These NHC-Cu(I) complexes display strong blue emission with the highest quantum yield of 0.88 and the excited state lifetime of 51 us [22]. These pioneering works have inspired us to turn our attention to the photophysical properties of NHC-Cu(I) complexes. However, a perusal of the literature for luminescent NHC-Cu(I) complexes shows that the three-coordinated species are widely studied and nearly all prior works have employed compound **IPr** as ligand to prepare this class of three-coordinated NHC-Cu(I) complexes. It is inconvenient to tune the photophysical properties for the corresponding NHC-Cu(I) complexes since the functionalization of **IPr** ligand or its derivatives is not simple.

On the other hand, from a conceptual point of view, the fourcoordinated NHC-Cu(I) complexes seem also interesting since they can allow a broader range of ligand selection to conveniently tune the photophysical properties. Surprisingly, studies on the luminescent properties of the four-coordinated NHC-Cu(I) complexes are very scarce. Wang and coworkers in 2016 reported the first study on the luminescence behavior of the fourcoordinated NHC-Cu(I) complexes, in which the photoluminescence band maximum was found to be blue-shifted from 570 to 520 nm with high emission intensity [23]. Most recently, our groups developed a efficient preparation method for this kind of complexes without transmetalation of Ag(I) complexes and the resulting complexes all exhibit good photoluminescence properties [24].

In this paper, with the aim of further tuning the luminescent properties of this type of the four-coordinated NHC-Cu(I) complexes, we report the synthesis, structural characterization, and photophysical properties of the three four-coordinated NHC-Cu(I) complexes bearing variably substituted carbene ligands with various aryl groups (Fig. 1). The influence of the different structural carbene ligands on the luminescent behaviors of the NHC-Cu(I) complexes have been investigated. In addition, density functional theory (DFT) and time-dependent density functional theory (TDDFT) were employed to rationalize the photophysical properties of those NHC-Cu(I) complexes.

#### 2. Experimental

#### 2.1. Materials and methods

The known intermediates, 2-(1H-imidazol-1-yl)pyridine (Im-Py) and 1-(yridine-2-ylmethyl)-1H-benzo[*d*]imidazole (BenIm-*c*-Py), were prepared according to procedures previously reported [24]. Other chemicals with analytical grade regent were purchased from Sinopharm Chemical Reagent Co and used as received without further purification.

<sup>1</sup>H  $\hat{NMR}$ , <sup>13</sup>C NMR, and <sup>31</sup>P NMR spectra in DMSO- $d_6$  were performed in a Bruker AV400 MHz spectrometer. For <sup>1</sup>H and <sup>13</sup>C NMR, the chemical shifts were referenced to the residual signals of the deuterated solvent. <sup>31</sup>P NMR signals were referenced using 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. High-resolution mass spectra (HRMS) were obtained with the Agilent 6450 Q-TOF mass spectrometer using electrospray ionization (ESI). Elemental analyses of the complexes were carried out on an Elementar VarioEL cube analyzer. UV-vis absorption spectra were measured using a Perkin Elmer Lambda-900 spectrophotometer. Fluorescence spectra were determined with a Hitachi F-4600 fluorescence spectrophotometer. Photoluminescence (PL) quantum yields were determined using a Hamamatsu system for absolute PL quantum yield measurements (type C11347). Fluorescent lifetimes were measured with a compact fluorescent lifetime spectrometer (Hamamatsu, C11367, Japan). The X-ray experiment of the single-crystal was done on a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique and Mo K $\alpha$  radiation. The structure was solved using the SHELXTL-97 program. Crystallographic data for the structure of 1 have been deposited as supplemental material at the Cambridge Crystallographic Data Center CCDC 1523539.

#### 2.2. Synthetic procedure

**(NaphIm-Py)(PF<sub>6</sub>).** A mixture of compound ImPy (1.45 g, 10 mmol) and 1-(chloromethyl)naphthalene (1.77 g, 10 mmol) in toluene (20 mL) was refluxed for 24 h under N<sub>2</sub>. The solvent was removed by filtration, and the crude product was dried. NH<sub>4</sub>PF<sub>6</sub> (1.73 g, 10 mmol) was added into the aqueous solutions of the product. And the mixture was stirred for 10min. The precipitate was obtained, and recrystallized with CH<sub>3</sub>CN and ether. The product was obtained as a white solid. Yield: 2.76 g, 64%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  10.31 (d, *J* = 12.4 Hz, 1H), 8.68 (s, 1H), 8.57



Fig. 1. Molecular structures of the four-coordinated NHC-Cu(I) complexes containing different groups and their abbreviations in this study.

(s, 1H), 8.28 (d, J = 8.1 Hz, 1H), 8.26–8.19 (m, 1H), 8.15–7.99 (m, 4H), 7.78–7.57 (m, 5H), 6.14 (d, J = 37.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  149.62, 140.98, 135.78, 133.88, 130.86, 130.18, 129.38, 128.17, 127.75, 126.94, 126.16, 125.72, 124.23, 123.37, 120.19, 114.83, 50.95.

(AnthrIm-Py)(PF<sub>6</sub>). This compound was prepared via a similar procedure for (NaphIm-Py)(PF<sub>6</sub>) from ImPy (1.45 g, 10 mmol) and 9-(chloromethyl)anthracene (2.27 g, 10 mmol). The product was obtained as a pale yellow solid. Yield: 2.89 g, 60%. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  10.11 (s, 1H), 8.88 (s, 1H), 8.64 (d, *J* = 4.5 Hz, 1H), 8.58 (d, *J* = 4.7 Hz, 1H), 8.56 (s, 1H), 8.45 (s, 1H), 8.27 (s, 1H), 8.24 (s, 1H), 8.17 (t, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.78–7.71 (m, 2H), 7.64 (dd, *J* = 14.4, 7.7 Hz, 4H), 6.63 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  148.01, 145.13, 139.34, 133.36, 129.95, 129.67, 129.23, 128.31, 126.76, 124.48, 124.12, 122.25, 122.02, 121.70, 118.49, 113.31, 44.37.

(**PhBenIm-c-Py)(PF6).** This compound was prepared via a similar procedure for (NaphIm-Py)(PF6) from 1-(2-picolyl)benzimidazole (2.09 g, 10 mmol) and benzyl bromide (1.71 g, 10 mmol). The product was obtained as a white solid. Yield: 3.61 g, 81%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*6):  $\delta$  9.95 (s, 1H), 8.46 (d, *J* = 4.4 Hz, 1H), 8.18 (t, *J* = 13.6 Hz, 1H), 8.06 (t, *J* = 6.8 Hz, 3H), 7.99 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.72–7.62 (m, 5H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.42–7.32 (m, 1H), 6.39 (s, 2H), 5.96 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  152.83, 149.59, 143.94, 143.45, 137.54, 133.87, 131.55, 131.29, 130.86, 129.04, 128.76, 128.26, 128.14, 126.85, 126.73, 123.71, 122.72, 113.88, 50.96, 50.02.

General procedure for preparation of NHC-Cu(I) complexes. NHC-Cu(I) complexes 1-3 were synthesized by the following route: a solution of imidazolium salt (0.4 mmol), copper powder (0.032 g, 0.5 mmol) and POP (0.22 g, 0.4 mmol) reacted in CH<sub>3</sub>CN (5 mL) at 60 °C for 24 h. The resulting mixture was filtered through a plug of Celite and concentrated to ca. 1 mL. Addition of Et<sub>2</sub>O (10 ml) to the filtrate afforded a pale yellow precipitate, which was collected and washed with Et<sub>3</sub>O. And the product was recrystallized with ethanol.

 $[Cu(NaphIm-Py)(POP)](PF_6)$ , **1**. The product was a pale yellow powder. Yield: 0.34 g, 88%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.54 (d, J = 15.2 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 8.13 (t, J = 7.5 Hz, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.65–7.60 (m, 1H), 7.59–7.49 (m, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.29 (dd, J = 14.1, 6.9 Hz, 8H), 7.23–7.18 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.02 (dd, J = 13.5, 6.0 Hz, 5H), 6.97 (d, J = 7.5 Hz, 1H), 6.86 (d, J = 3.9 Hz, 4H), 6.74 (dd, *J* = 18.7, 6.1 Hz, 5H), 6.48 (d, *J* = 2.8 Hz, 2H), 6.34 (d, *J* = 7.0 Hz, 1H), 5.48 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 158.34, 158.28, 150.30, 148.50, 141.30, 134.34, 133.53, 133.13, 132.84, 132.51, 132.34, 132.19, 132.12, 130.60, 130.33, 130.11, 129.28, 129.02, 128.26, 127.04, 126.68, 125.67, 125.46, 124.93, 123.71, 123.62, 123.49, 123.28, 122.69, 120.76, 118.11, 113.04, 52.43. <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>): δ –9.39 (s), -143.61 (quint). HRMS (*m/z*, ESI<sup>+</sup>): calcd. For C<sub>55</sub>H<sub>43</sub>CuN<sub>3</sub>OP<sub>2</sub> ([M]<sup>+</sup>) 886.2177: found 886.2142. Anal. Calcd. For C<sub>55</sub>H<sub>43</sub>CuF<sub>6</sub>N<sub>3</sub>OP<sub>3</sub> (1032.40): C 63.99, H 4.20, N 4.07; found: C 63.81, H 4.09, N 4.32.

[*Cu*(*AnthrIm-Py*)(*POP*)](*PF*<sub>6</sub>), **2**. The product was a pale yellow powder. Yield: 0.34 g, 88%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.77 (s, 1H), 8.32 (d, *J* = 4.6 Hz, 1H), 8.21 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 13.7 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.53–7.47 (m, 5H), 7.45 (s, 1H), 7.44–7.34 (m, 9H), 7.33 (s, 1H), 7.32–7.23 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 8H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 2.8 Hz, 2H), 6.41 (s, 1H), 5.57 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  157.94, 157.89, 149.77, 148.51, 140.65, 133.77, 132.97, 132.18, 132.00, 131.77, 131.61, 130.88, 130.28, 130.17, 129.54, 129.35, 128.96, 127.25, 125.25, 123.86, 123.77, 122.80, 122.37, 121.60, 120.55, 117.59, 112.66, 46.59. <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  –8.88 (s), –143.52 (quint). HRMS (*m*/*z*,

ESI<sup>+</sup>): calcd. For C<sub>59</sub>H<sub>45</sub>CuN<sub>3</sub>OP<sub>2</sub> ([M]<sup>+</sup>) 936.2334; found 936.2359. Anal. Calcd. For C<sub>59</sub>H<sub>45</sub>CuF<sub>6</sub>N<sub>3</sub>OP<sub>3</sub> (1082.47): C 65.46, H 4.19, N 3.88; found: C 65.11, H 4.21, N 3.83.

[*Cu*(*PhBenIm-c-Py*)(*POP*)](*PF*<sub>6</sub>), **3**. The product was a pale yellow powder. Yield: 0.34 g, 88%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.77 (s, 1H), 8.32 (d, *J* = 4.6 Hz, 1H), 8.21 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 13.7 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.53–7.47 (m, 5H), 7.45 (s, 1H), 7.44–7.34 (m, 9H), 7.33 (s, 1H), 7.32–7.23 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 8H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 2.8 Hz, 2H), 6.41 (s, 1H), 5.57 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 156.93, 154.29, 148.59, 145.88, 141.36, 137.93, 135.48, 134.50, 133.77, 133.02, 132.66, 132.34, 131.29, 130.90, 130.55, 129.56, 129.17, 127.68, 125.74, 123.87, 122.57, 121.00, 119.35, 116.77, 112.69, 111.96, 50.24, 48.25. <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>): δ -8.99 (s), -143.69 (quint). HRMS (*m/z*, ESI<sup>+</sup>): calcd. For C<sub>52</sub>H<sub>43</sub>CuF<sub>6</sub>N<sub>3</sub>OP<sub>3</sub> (996.38): C 62.68, H 4.35, N 4.22; found: C 62.51, H 4.21, N 4.13.

#### 2.3. DFT calculations

All calculations were performed using the Gaussian 09 [25] program package. The B3LYP exchange-correlation function [26,27] was used to optimize the ground state ( $S_0$  state) geometries of complexes **1**–**4** using the polarized continuum model (PCM) [28] in CH<sub>2</sub>Cl<sub>2</sub> media. The 6-31G\* basis set [29,30] was used for the C, H, N, O, and P atoms. The LANL2DZ basis set [31] was adopted for the Cu atom. On the basis of the optimized ground geometries, TDDFT method [32,33] associated with PCM in CH<sub>2</sub>Cl<sub>2</sub> media were used to simulate the absorption spectra of complexes studied. The first 200 singlet vertical excitations were obtained form the TDDFT output file to construct the calculated absorption spectra. Calculated electronic density plots for the frontier molecular orbitals were prepared using Multiwfn analyzer soft [34] and VMD program [35].

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthetic pathways for the NHC precursors and the corresponding four-coordinate NHC-Cu(I) complexes are shown in Scheme 1. The imidazolium salt (NaphIm-Py)(PF<sub>2</sub>), (AnthrIm-Py)(PF<sub>2</sub>) and (PhBenIm-c-Py)(PF<sub>2</sub>) were prepared according to the literature procedure [36]. The four-coordinate NHC-Cu(I) complexes was prepared by the established synthetic method [24]. Spectroscopic data of <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P NMR, HRMS and MS confirmed the formation of the desired NHC-Cu(I) complexes (see Experimental Section). The <sup>1</sup>H NMR spectra of the imidazolium salt (Naph-ImPy)(PF<sub>2</sub>), (Anth-ImPy)(PF<sub>2</sub>) and (PhBenIm-c-Py)(PF<sub>2</sub>) exhibit pro-carbenic proton resonance signals at 10.31, 10.11 and 9.95 ppm, respectively. As expected, upon coordination of the NHC ligands, the signal of pro-carbenic proton resonances was absent from the <sup>1</sup>H NMR spectra illustrating that Cu-C<sub>carbene</sub> bonds are formed. In the <sup>13</sup>C NMR spectra, the signals for the carbon atoms of **1–3** appear at 158.34, 157.94 and 156.93 ppm, respectively. Usually the <sup>13</sup>C chemical shifts of known carbonic carbon atom of NHC-Cu(I) complexes appear in the range 150–204 ppm depending the ancillary ligands [19-23,37-39]. Additionally, the <sup>31</sup>P NMR spectra are consistent with the presence of POP ligand, a singlet at -9.39, -8.88 and -8.99 ppm for 1-3, respectively. The presence of the  $[PF_6]^-$  counterion was confirmed by the observation of a characteristic quintet at -143.61, -143.52 and -143.69 ppm for 1–3, respectively [40].



Scheme 1. The synthetic pathways of the NHC precursors and the corresponding NHC-Cu(I) complexes.

Single crystal of **1** suitable for X-ray diffraction analysis was obtained by slow evaporation of dichloromethane/ethanol solution of the complexes. The crystal structures and the detailed crystallographic data are provided in Fig. 1S and Table 1S in the Supporting Information. The Cu-N bond lengths (2.176 Å) and Cu-P bond lengths (2.240–2.256 Å) are normal for the four-coordinate Cu(I) complexes. The dihedral angles defined by P-Cu-P and C-Cu-N planes are  $80.96^{\circ}$  for **1**. It is clearly seen that the short C-H···F contacts are in the range of 2.701–2.691 Å, probably indicating the present of intramolecular hydrogen-bonding interactions between the two atoms. However, the present of a [PF6]<sup>-</sup> counterion has little effect on the electrical structure and absorption spectra of the complexes, as demonstrated theoretically by Lu et al. [41,42]. Additionally, it is worthwhile noticing that the bond lengths of Cu-C<sub>carbene</sub> of **1** is 1.970 Å, which is obviously shorter than those of Cu-N bond of the similar structural tetrahedral Cu(I) complexes (2.070–2.141 Å) [43], suggesting that the carbon atom of the NHC ligand forms stronger bond to the Cu center. These important bond lengths and angles have been anticipated by DFT calculations (see below).



Fig. 2. Absorption spectra in dichloromethane at 298 K of 1–3.

Table 1Photophysical properties of 1–3.

Complex	$\lambda_{abs}/nm$	$\lambda_{em}/nm$	τ/μs	$\Phi$ /%	$k_{\rm r}/10^4 {\rm s}^{-1}$	$k_{\rm nr}/10^4 {\rm s}^{-1}$
1	350	540	75.3	6.10	0.08	1.25
2	352/370/391	550	20.9	3.30	0.16	4.62
3	/	526	33.42	46.7	1.40	1.59

#### 3.2. Photophysical properties

UV-Vis spectra of complexes 1-3 in CH<sub>2</sub>Cl<sub>2</sub> solution were shown in Fig. 2 at room temperature and the corresponding absorption maxima of the relevant bands were summarized in Table 1. Absorption spectra for all NHC-Cu(I) complexes showed intense absorption bands in the region of 230-280 nm, which was assigned to the ligand-centered  ${}^{1}\pi\pi^{*}$  transitions of both NHC and POP ligands. In the lower-energy region, the less intense absorption shoulders at around 350 nm for complex 1, not present in the free NHC and POP ligands, may be tentatively assigned to metal Cu to ligand charge transfer (MLCT) characters. Complex 2 in the lower-energy region showed the vibrationally structured bands at 352, 370, 391 nm. These bands were assigned as the characteristic  ${}^{1}\pi\pi^{*}$  transition of the anthryl moiety [44]. Additionally, it is worth noting that the typical weak MLCT bands for complex 2 were overlapped under the considerably intense  ${}^{1}\pi\pi^{*}$  transition of the anthryl moiety, which precludes the visualization of this bands in the spectrum. For complex 3, the conjugation between the pyridine ring and imidazolylidene ring is broken owing to the present of a single methyl group, giving an increase of the energy gap. Therefore, the lower energy side of the absorption spectrum is blue-shifted compared with that of complex 1 and 2.

Emission spectra of the NHC-Cu(I) complexes **1–3** in PMMA film as 20% dopant are shown in Fig. 3 and the relevant emission data are also provided in Table 1. All complexes show broad and unstructured shapes, which is a characteristic feature of triplet charge-transfer (<sup>3</sup>CT) nature of the emitting state. The maximum emission wavelengths for **1** and **2** are located at 540 and 550 nm, indicating that the substituent from naphthyl to anthryl group at N3 position of the imidazolylidene ring has the slight influences on the emissive properties of the complexes. In contrast, the emission band of **3**, located at 526 nm, is blue-shifted compared with the maxima of **1** and **2**. The blue shifted emission of **3** is because of the broken of  $\pi$ -conjugation system in the carbene ligands. Here, the



Fig. 3. Normalized emission spectra of 1-3 in PMMA films (10%).

emission bands of **1** and **3** are assigned to a  $d\pi(Cu) \rightarrow \pi^*(\text{ligand})$  excited state (<sup>3</sup>MLCT), whereas that of **3** can be regard as triplet ligand-localized (intraligand, <sup>3</sup>IL) excited state inside the anthryl moiety, which are corroborated by the spin density distributions (see below).

To gain a deeper understanding of the emitting states of complexes **1**–**3**, the photoluminescence quantum yields ( $\phi$ ) and excited state lifetimes ( $\tau$ ) were also measured. As shown in Table **1**, the  $\phi$  values of **1** and **2** are 6.1 and 3.3%, respectively. These  $\phi$  values are significantly smaller to the values reported for the similar NHC-Cu(I) complexes [19], which may be rationalized by the strong intermolecular  $\pi$ - $\pi$  stacking interactions caused by the large planar structures of naphthyl group in **1** and anthryl groups in **2**. The  $\phi$  values decrease in the order **1** > **2**, in accordance with the increase of the  $\pi$ - $\pi$  stacking ability of the substituents (naphthyl < anthryl). In contrast, an increase in  $\phi$  for **3** ( $\phi$  = 46.7%) is observed as compared to **1** and **2**, presumably because of the presence of a nonplanar form of the carbene ligand with the smaller planar structure of phenyl group in **3**.

The  $\tau$  values of all complexes are in the range of 20–76 µs, confirming their phosphorescence origin in nature. Based on the known  $\phi$  and  $\tau$  values, the radiative rate constant ( $k_r$ ) and non-radiative rate constant ( $k_{nr}$ ) are calculated and summarized in

#### Table 2

Selected parameters of the optimized geometric structures of **1–3** in  $CH_2Cl_2$  solvent in the ground and lowest-lying triplet excited states at the (B3LYP)/6-31g\*/LANL2DZ level.

	1			2		3	
	S0	T1	Exptl <sup>a</sup>	S0	T1	S0	T1
Bond length(Å)							
Cu-P1	2.392	2.497	2.256	2.390	2.390	2.411	2.537
Cu-P2	2.416	2.489	2.240	2.418	2.419	2.460	2.556
Cu-N1	2.331	2.035	2.176	2.332	2.323	2.353	2.020
Cu-C1	2.027	1.983	1.970	2.026	2.027	2.045	2.028
Bond angle (deg)							
P1-Cu-P2	112.57	104.19	111.59	111.66	111.65	111.82	101.78
P1-Cu-N1	110.74	132.94	118.15	105.85	106.16	112.15	137.61
P1-Cu-C1	115.56	101.42	110.50	126.93	127.22	117.13	96.85
P2-Cu-N1	111.32	100.89	109.85	105.00	104.60	104.23	103.74
P2-Cu-C1	123.75	141.82	123.85	118.76	118.44	118.16	134.30
N1-Cu-C1	76.66	81.14	79.90	76.79	76.96	90.29	88.90
Distortion Parameter (deg)							
$\theta_{x}$	78.6	83.8		66.6	66.6	79.1	85.2
$\theta_y$	87.1	87.7		87.0	86.6	87.2	88.0
$\theta_z$	87.5	58.7		88.4	88.7	85.9	60.1
ξ <sub>CD</sub>	0.909	0.787		0.848	0.847	0.904	0.803

<sup>a</sup> In this work.

Table 1. A comparison of the  $k_n$  and  $\phi$  shows a simple trend that the photoluminescence quantum yield is mainly determined by the radiative decay. It may be noted that the values of  $k_{nr}$  for **1** and **3** are roughly the same ( $1.25 \times 10^4$  for **1** and  $1.59 \times 10^4$  for **3**), while that of **2** ( $4.62 \times 10^4$ ) is much larger than those of the other two complexes. This is additional evidence that the nature of the emitting state of **2** is difference from that of **1** and **3**.

#### 3.3. Theoretical calculations

## 3.3.1. Ground state geometries, molecular orbital properties, and singlet-singlet excited states

The optimized ground state geometric structures in CH<sub>2</sub>Cl<sub>2</sub> solvent for complexes **1**–**3** are shown in Fig. 4 and selected bond lengths and angles are summarized in Table 2. The optimized structural parameters of the complexes **1** are in general agreement with the corresponding experimental values. The geometry for all the complexes is best described as a distorted tetrahedral geometry around the Cu(1) center. In general, the degree of distortion in the Cu coordination often be assessed as the flattening distortion expressed by the dihedral angles ( $\theta_{LL}$ ) between the two chelate ligand planes ( $\theta_{LL} = 90.0^{\circ}$  for the ideal tetrahedral geometry).



Fig. 4. The optimized ground state geometric structures in CH<sub>2</sub>Cl<sub>2</sub> solvent for 1-3.



**Fig. 5.** The energy levels and atomic orbital compositions calculated for the HOMO and LUMO of **1–3.** 

Herein, these dihedral angles are defined by P1-Cu-P2 and C1-Cu-N3 planes and are 88.2° for **1**, 88.5° for **2**, and 85.9° for **3**, respectively. Obviously, the distortion of the geometry for **3** is slightly larger than that of **1** and **2** owing to the present of the flexible methylene spacer between the pyridine moiety and the benzo[*d*] imidazolylidene ring. The bond lengths of Cu-C<sub>carbene</sub> of **1**–**3** are calculated to be 2.027, 2.026, and 2.045 Å, respectively, which are in good agreement with the shorter Cu-C<sub>carbene</sub> bond lengths in experiments.

To gain a comprehensive description of the distortion of the Cu(I) center from the ideal tetrahedral geometry, the overall distortions around Cu(I) center in the three-dimensional space are highly desired. In 1984, White and coworkers firstly reported the effective approach to describe the distortions in terms of the angles  $\theta_x$ ,  $\theta_y$ , and  $\theta_z$  [45]. The  $\theta_z$  value is generally similar to the dihedral angle  $(\theta_{LL})$  usually reported in the literature, corresponding the flattening distortion; while the  $\theta_x$  and  $\theta_y$  are regarded as the 'rocking' and 'waggling' distortions, respectively [46]. For the ideal tetrahedral geometry,  $\theta_x = \theta_y = \theta_z = 90.0^\circ$ . Based on the six angles around the Cu(I) center (see Table 2), the calculation of  $\theta_x$ ,  $\theta_y$ , and  $\theta_z$  was done and the corresponding data are detailed in Table 2. As shown in Table 2, the rocking distortion with the  $\theta_x$ values in the range of 66.6°-79.1° are much greater than the waggling and flattening distortions with the  $\theta_{v}$  and  $\theta_{z}$  values in the range of 85.9°-89.0° for all the complexes. The longer Cu-N1 bonds compared to the Cu-Ccarbene bonds provide further evidences for this distortion, as the rocking moves one bond toward the axial position. The  $\theta_z$  values ( $\theta_z = 87.5^\circ$ ,  $88.4^\circ$ ,  $85.9^\circ$  for **1–3**, respectively) is approximately the same with the  $\theta_{LL}$  values mentioned above. In 2004, Coppens and coworkers employed a single parameter  $\xi$  to conveniently quantify the degree of overall distortion as follows [47]:

$$\xi = \frac{(90 + \theta_x) (90 + \theta_y) (90 + \theta_z)}{180^3}$$

As seen in Table 2, the  $\xi$  value for 1 can reach as high as 0.909, which means that the distortion of molecular structure of 1 is very small. For 2, the degree of overall distortion is slightly increased ( $\xi = 0.848$ ), owing to the larger anthryl group inserted into the N3 position of the benzo[*d*]imidazolylidene ring. With respect to 3, the degree of overall distortion is smaller compared to 2 since the small size of the phenyl group is introduced into the N3 position. Thus, the overall distortion of the complex studied away from an ideal tetrahedral geometry is in the order: 2 > 3>1.

Table 3

Electronic absorptions of 1-3 in CH<sub>2</sub>Cl<sub>2</sub> based on TDDFT calculations at the (B3LYP)/6-31g\*/LANL2DZ level, together with the experimental values.

	Excited state	Transition	Coeff	E(eV)/(nm)	Oscillator	Assign	Exptl/nm
1	S <sub>2</sub>	$H-2 \rightarrow L$	0.47842(45.8%)	3.58/346	0.0401	$MLCT_{(Cu \rightarrow NHC)}/ILCT_{(NHC)}$	350
		$H \rightarrow L$	0.44380(39.4%)			$MLCT_{(Cu \rightarrow NHC)}/LLCT_{(POP \rightarrow NHC)}$	
	S <sub>13</sub>	$H-1 \rightarrow L+1$	0.58494(68.4%)	4.33/286	0.1660	ILCT <sub>(Naph)</sub>	272
		$H-2 \rightarrow L+1$	0.34409(23.7%)			$MLCT_{(Cu \rightarrow Naph)}/LLCT_{(NHC \rightarrow Naph)}$	
	S <sub>161</sub>	$H-1 \rightarrow L+16$	0.25266(12.8%)	5.74/216	0.2284	$LLCT_{(Naph \rightarrow NHC, POP)}$	237
		$H-1 \rightarrow L+10$	-0.24507(12.0%)			ILCT <sub>(Naph)</sub>	
		$H-5 \rightarrow L+1$	0.19754(7.80%)			ILCT <sub>(Naph)</sub>	
		$H-3 \rightarrow L+15$	-0.18898(7.14%)			$MLCT_{(Cu \rightarrow POP)}/LLCT_{(NHC \rightarrow POP)}$	
	S <sub>171</sub>	$H-1 \rightarrow L+16$	0.37322(27.9%)	5.79/214	0.2496	$LLCT_{(Naph \rightarrow NHC, POP)}$	232
2	S <sub>1</sub>	$H \rightarrow L$	0.70148(98.4%)	3.15/393	0.1521	ILCT <sub>(Anth)</sub>	391/370/352
	S <sub>6</sub>	$H-1 \rightarrow L+1$	0.52195(54.5%)	3.66/338	0.0725	$MLCT_{(Cu \rightarrow NHC)}/LLCT_{(POP \rightarrow NHC)}$	335
		$H-2 \rightarrow L+1$	0.39830(31.7%)			$MLCT_{(Cu \rightarrow NHC)}/ILCT_{(NHC)}$	
	S <sub>21</sub>	$H-1 \rightarrow L+6$	0.66500(88.4%)	4.34/286	0.0744	$MLCT_{(Cu \rightarrow POP)}/ILCT_{(POP)}$	274
	S <sub>71</sub>	$H \rightarrow L+8$	0.34141(23.3%)	4.99/248	0.9646	ILCT <sub>(Anth)</sub>	235-262
		$H-5 \rightarrow L$	-0.33764(22.8%)			ILCT <sub>(Anth)</sub>	
		$H-16 \rightarrow L$	-0.30612(18.7%)			$MLCT_{(Cu \rightarrow Anth)}/LLCT_{(POP \rightarrow Anth)}$	
3	S <sub>1</sub>	$H \rightarrow L$	0.63568(80.8%)	3.73/332	0.0496	$MLCT_{(Cu \rightarrow NHC)}/LLCT_{(POP \rightarrow NHC)}$	/
	S <sub>7</sub>	$H \rightarrow L+4$	0.64506(83.2%)	4.23/293	0.0745	$MLCT_{(Cu \rightarrow POP)}/ILCT_{(POP)}$	290
	S <sub>8</sub>	$H \rightarrow L+3$	0.44058(38.8%)	4.25/292	0.0835	$MLCT_{(Cu \rightarrow NHC)}/LLCT_{(POP \rightarrow NHC)}/ILCT_{(POP)}$	279
		$H-1 \rightarrow L+1$	-0.36868(27.2%)			$MLCT_{(Cu \rightarrow POP)}/LLCT_{(NHC \rightarrow POP)}/ILCT_{(POP)}$	
		$H-1 \rightarrow L+2$	0.34364(23.6%)			$MLCT_{(Cu \rightarrow POP)}/LLCT_{(NHC \rightarrow POP)}/ILCT_{(POP)}$	
	S <sub>130</sub>	$H \rightarrow L+18$	0.28763(16.5%)	5.62/221	0.0526	$MLCT_{(Cu \rightarrow NHC)}/ILCT_{(POP)}/LLCT_{(POP \rightarrow NHC)}$	234
		$H-13 \rightarrow L+4$	-0.21317(9.09%)			$MLCT_{(Cu \rightarrow POP)}/ILCT_{(POP)}$	
	S <sub>166</sub>	$H-1 \rightarrow L+18$	0.44445(39.5%)	5.79/214	0.0496	$MLCT_{(Cu \rightarrow NHC)}/ILCT_{(POP)}/ILCT_{(NHC)}$	234

Fig. 5 shows the energy levels and atomic orbital compositions calculated for the HOMO and LUMO of **1–3**. The HOMO of **1** and **3** is mainly localized on the Cu atom and the lone pair electrons on the P atoms in POP ligands. Therefore, the HOMO energy remains almost unchanged (–5.96 eV for **1**; –5.94 eV for **3**). On the other hand, the



**Fig. 6.** Comparison of the calculated (red line) and experimental (black line) absorption spectra in  $CH_2Cl_2$  solution for **1** (a), **2** (b), and **3** (c). Red vertical lines correspond to oscillator strength of calculated singlet-singlet transitions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

LUMO of **1** and **3** is predominately localized on the carbene ligands. However, the LUMO energy level of **3** is destabilized by 0.14 eV compared with **1**, due to the broken of  $\pi$ -conjuction between the pyridine moiety and the benzo[*d*]imidazolylidene ring. Unlike **1** and **3**, the HOMO and LUMO of **2** are mainly distributed on the anthryl moiety. The HOMO energy is calculated to be -5.68 eV, which is less stable than those of **1** and **3**. The LUMO energy (-2.19 eV) is calculated to be more stable compared to **1** and **3**. The HOMO-LUMO energy gap can be obtained in the order **3** (4.40 eV) > **1** (4.28 eV) > **2** (3.49 eV), in reasonably good agreement with the blue-shifted lowest-lying absorption onset observed in the experiments.

The low-lying singlet-singlet transitions of all the complexes were calculated by using the TDDFT approach to provide insight into the nature of the electronic transitions. Table 3 shows the transition energies to the low-lying singlet excited states for 1-3 associated with the dominant singlet-singlet vertical excitations, their oscillator strengths, assignment configurations, along with the corresponding experimental values. To conveniently discuss the electronic transition characters, the relative frontier molecular orbital compositions of complexes 1-3, which are expressed in terms of the molecular fragments, in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 2S and Table 2S (see Supporting Information).

For **1**, the second low-lying singlet-singlet excited state S<sub>2</sub>, calculated at 346 nm, is mainly composed of HOMO-2→LUMO (45.8%) and HOMO  $\rightarrow$  LUMO (39.4%) transitions, in good agreement with the experimental values of 350 nm. An composition analysis of the HOMO. HOMO-1, and LUMO (see Table 2S. Supporting Information) clearly shows that this excitation can be ascribed as metalto-ligand charge transfer (MLCT)/ligand-to-ligand charge transfer (LLCT)/intraligand (ILCT) charge transfer character. For 2, the lowest-lying singlet-singlet excited state S<sub>1</sub>, calculated at 393 nm, is dominantly originated from HOMO[ $\pi$ (anthryl)] $\rightarrow$ LUMO  $[\pi^*(anthryl)]$  transition with  $\pi\pi^*$ character, corresponding to the experimental absorption bands in the range of 350-400 nm even though the calculated spectra do not display vibronic fine structure of anthryl group. For 3, the calculated lowest-lying absorption band at 332 nm from the S<sub>1</sub> state, not observed in experiments, is dominated by the HOMO→LUMO transition with MLCT/LLCT character. In addition, other transitions with the larger oscillator strengths are also presented in Table 2. A comparison of the shapes of calculated and experimental absorption spectra for 1-3 is presented in Fig. 6. It is found that the experimental spectra are overall well reproduced by the calculations.

#### 3.3.2. Triplet state geometries and emission properties

To gain insight into the nature of the emission properties of **1–3**, their lowest-lying triplet excited-state geometries (T<sub>1</sub>) were optimized at the spin-unrestricted UB3LYP/6-31G\*/LANL2DZ level with a spin multiplicity of 3 and selected bond lengths and angles are also presented in Table 2. Where stated, toluene was chosen as the solvent, because it is the less polar solvent and thus acts as the similar case to compare with the doped PMMA films. The calculated results show that the triplet geometrical parameters around Cu(I) center of 1 and 3 have large differences from the corresponding ground state structures, meaning that the metal character is involved in the excited state. The Cu-P1 and Cu-P2 bond lengths are relatively longer than that in the corresponding ground states, while the Cu-N1 and Cu-C1 bond lengths are shorted, indicating electron transfer from the POP ligand to NHC ligand in the excited states. The similar variation trend in the excited states suggests that 1 and 3 are emitting from the same excited state. For 2, the main geometric parameters around Cu(I) center did not change significantly in the lowest-lying triplet state compared to the ground state, which provides the additional



**Fig. 7.** Spin density distribution contours (isovalue = 0.004) for the lowest triplet state T<sub>1</sub> of **1–3**. The values of the unpaired-electron spin-density population are depicted together with the electronic nature of the states.

evidence of non-metal character involved in the excited state. It is worth noting that the dihedral angles between P1-Cu-P2 and C1-Cu-N3 planes are seriously flatten for **1** and **3** ( $\theta_z = 58.7^{\circ}$  and 60.1°, respectively). The  $\xi$  values gradually increase in the following order: **1** (0.787) < **3** (0.803). This order is correlated with the emission energy: the smaller the distortion in the excited state, the higher the emission energy. For **2**, although the distortion ( $\xi = 0.847$ ) in the excited state is smaller compared with **1** and **3**, its emission energy is red-shifted. This is due to the fact that the nature of the emitting excited state of **2** is different from that of **1** and **3**.

The nature of the emitting excited state of each complex can be quantitatively identified by the unpaired-electron spin-density distribution, as shown in Fig. 7. The unpaired electron spin-density distributions in the T<sub>1</sub> state are very similar for **1** and **3** (Cu, 0.61e; POP, 0.27e; NHC, 1.11e for **1**; Cu, 0.57e; POP, 0.26e; NHC, 1.17e for **3**) and confirm the emission behavior of  ${}^{3}MLCT/{}^{3}LLCT$  characters and illustrates the higher contribution of the d(Cu) to the NHC ligand with some contribution of POP ligand to the NHC ligand. The significant difference for **2** compared with **1** and **3** is that for the former a ligand-localized ( ${}^{3}IL$ ) excited state, in which the anthryl moiety accumulates almost all of the unpaired electrons (Cu, 0.002e; POP, 0.002e; NHC, 0.03e, Anthryl, 1.97e for **2**). These theoretical results provide further support of assignments of the nature of the emitting excited state.

#### 4. Conclusion

In this paper, three four-coordinated NHC-Cu(I) complexes,  $[Cu(NaphIm-Py)(POP)]PF_6$  (1),  $[Cu(AnthrIm-Py)(POP)]PF_6$  (2), and  $[Cu(PhBenIm-c-Py)(POP)]PF_6$  (3) have been synthesized by the previously reported method. The aryl substituents including phenyl, naphthyl, and anthryl groups are introduced into the NHC ligands. The photophysical properties of the resulting NHC-Cu(I) complexes have been systemically investigated both experimentally and theoretically. Complexes 1 and 2 exhibit poor photoluminescence efficiencies owing to the  $\pi$ - $\pi$  stacking interactions, whereas complex 3 shows good photoluminescence properties with the higher quantum yields and long excited-state lifetimes. It likely seems that the four-coordinate NHC-Cu(I) complexes will be probably promising candidates for the field of photosensitizers by judicious choice of NHC ligands.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.07.016.

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