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1 Article

2 ***N*-Heterocyclic Carbene Copper (I) Complexes Incorporating**
3 **Pyrene Chromophore: Synthesis, Crystal Structure, and Lumi-**
4 **nescent Properties**5 Yaping Cheng,¹ Geoffrey Gontard¹, Abderrahim Khatyr,² Michael Knorr,² and Hani Amouri^{1,*}6 ¹ Sorbonne Université- Campus Pierre et Marie Curie, Institut Parisien de Chimie Moléculaire (IPCM) UMR
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12 **Abstract:** Luminescent *N*-heterocyclic carbene chloride copper (I) complexes incorporating pyrene
13 chromophore (1-Pyrenyl-NHC-R)-Cu-Cl, (**3**, **4**) have been prepared and fully characterized. Two
14 complexes were prepared with R = methyl (**3**) and R = naphthyl groups (**4**) at the nitrogen center of
15 the carbene unit to tune their electronic properties. The molecular structures of **3** and **4** have been
16 elucidated by X-ray diffraction and confirm the formation of the target compounds. Preliminary
17 results reveal that all compounds including the imidazole-pyrenyl ligand **1** are emissive in the blue
18 region at room temperature in solution and in solid-state. All complexes display quantum yields
19 comparable or higher when compared to the parent pyrene molecule. Interestingly replacement of
20 the methyl by naphthyl group increases the quantum yield by almost two folds. These compounds
21 might show promise for applications as optical displays.22 **Keywords:** Luminescent copper complexes; *N*-heterocyclic carbenes; Blue emitters; X-ray struc-
23 tural determination
2425 **1. Introduction**

N-heterocyclic carbenes (NHCs) are strongly coordinating ligands and have proven themselves as the ligands of choice in a wide-range of the chemistry spectrum spanning from organometallics, catalysis to medicinal chemistry as well.[1-5] More recently they have been used with success to design stable luminescent organometallic and coordination complexes.[6-9] This is because they tend to push the ³dd dark states high in energy and thus avoiding the deactivation processes of the low-lying MC (metal-centered) transition states. In a previous work we demonstrated that cyclometalated octahedral iridium complexes containing NHC-NI (NI = Naphthalimide) are strongly phosphorescent emitters in the red to near IR regions. The introduction of the organic chromophore modifies the nature of the excited states from ³MLCT to ³LC centered on the naphthalimide chromophore.[10-12]

Pursuing our work in this area we sought to prepare another class of luminescent carbene complexes incorporating copper as inorganic chromophore and pyrene as organic chromophore. The high abundance of copper and its low cost compared to expensive third raw transition metals render this metal as an attractive choice to construct copper based luminescent materials.

Copper complexes display a small S₁-T₁ energy gap, ΔE_{ST} and thus enabling efficient triplet harvesting by reverse intersystem crossing (RISC). Such process is known as the aforementioned TADF mechanism.[13,14] The judicious placement of the pyrene

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luminophore *via* the carbene ligand in close proximity to the metal center provides access to novel class of stable luminescent complexes with rich excited states.[15]

In this work we describe the design of novel class of luminescent NHC-copper (I) complexes containing a pyrene chromophore. The effect of the alkyl substituent versus the naphthyl group on the carbene unit was investigated and showed that the latter increases the emissive properties of the compounds.

Interestingly all compounds showed comparable quantum yields to that of the parent pyrene molecule, remarkably the complex with naphthyl-group increases the quantum yields by almost two folds. Moreover, our complexes are strongly emissive when compared to classical *N*-heterocyclic coinage halogen complexes which are often weakly emissive.[16-19]

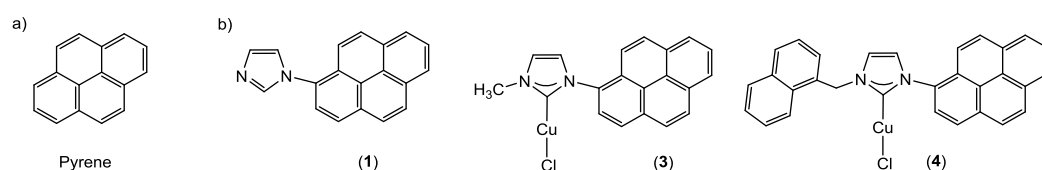
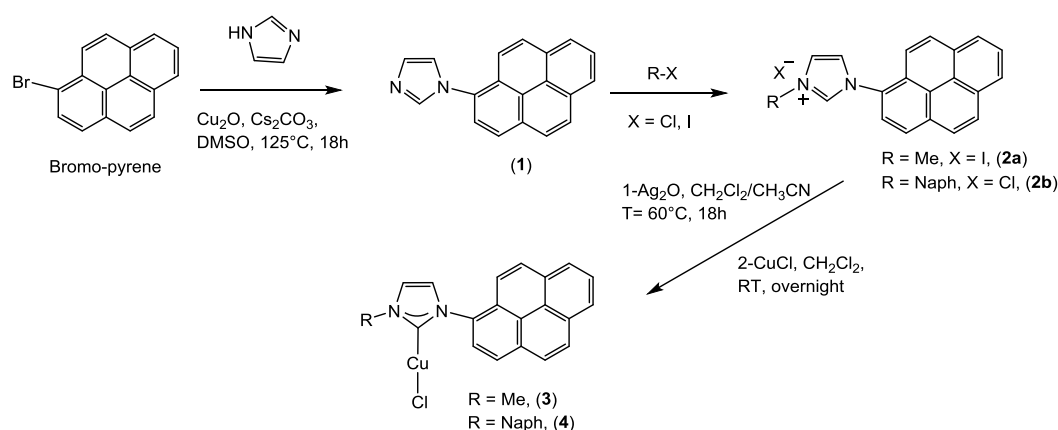


Figure 1. a) Pyrene. b) Imidazole-pyrenyl ligand (1) and the novel NHC-Cu(I) complexes (3) and (4) described in this work.

2. Results and Discussion

2.1. Synthesis and characterization

Complexes 3-4 were obtained in three steps, according to a synthetic procedure developed by our group. The first step consists in the preparation of imidazole-pyrenyl ligand 1 from the commercially available Br-pyrene as starting material, which is *N*-arylated upon treatment with imidazole under heating in the presence of Cs_2CO_3 and a catalytic amount of Cu_2O . Reaction work-up followed by column chromatography provided analytically pure 1 in 92% yield. The second step consists in alkylation of 1 with the appropriate alkyl halide in THF to give the corresponding azolium salts (2a, 2b) as pure white salts in 97% and 87% yields respectively. Finally, the target pyrenyl-NHC-Cu(I)-Cl complexes (3, 4) were obtained in 83% and 86% yields respectively by treatment of the azolium salts with CuCl using Ag_2O via the transfer reagent method. (Scheme 1).



Scheme 1. Synthesis of the imidazole-pyrene ligand and the related pyrenyl-NHC-Cu(I)-Cl (3-4) complexes containing pyrene luminophore.

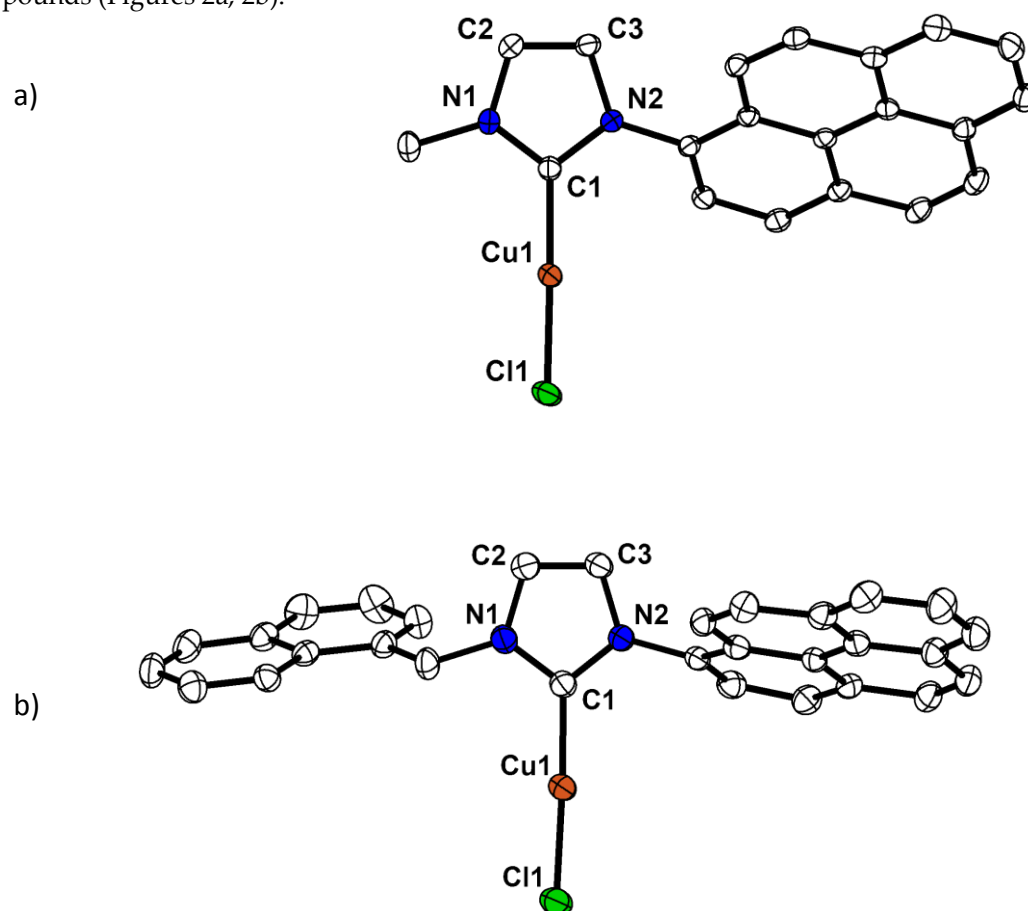
The $^1\text{H-NMR}$ spectra of 1 recorded in CDCl_3 confirm the formation of our imidazole-pyrenyl chromophore. Ligand 1 displays a multiple pattern for the aromatic protons of the pyrenyl-unit. The protons ascribed to the imidazolyl unit appear as two large singlets at δ 7.44 ppm and δ 7.83 ppm and show by integration 2H and 1H respectively. The

79 formation of the imidazolium salts **2a** and **2b**, is inferred by the appearance of the NCHN
80 proton, which occurs at δ 9.77 and δ 10.15 ppm, respectively (see also **Figures S1-S10**).
81 We also note that the crystal structure of pyrenyl-azolium salt containing a BF_4^- as a
82 counter anion was reported previously. However the preparation follows an
83 electrochemical procedure, which is completely different from the synthetic procedure,
84 described in this work.[20] The pyrenyl-NHC-Cu-Cl complexes **3** and **4** were found to be
85 stable in solution to allow full characterization. For instance the ^{13}C -NMR of the carbenic
86 carbon for these complexes display signals at around δ 179 ppm after prolonged acquisi-
87 tion. These compounds were kept under argon in the solid state for several weeks with-
88 out decomposition.

89 Moreover the identity of all molecules was ascertained by electrospray spectrometry.
90 Complete spectroscopic characterizations (^1H , ^{13}C , MS) are given in the experimental
91 section. Furthermore, the molecular structures of **3** and **4** were confirmed by single crys-
92 tal X-ray diffraction study (vide infra).

93 2.2. X-ray molecular structures of (Pyrenyl-NHC-R)-Cu-Cl, (R= Me, **3**; R = Naph, **4**).

94 Suitable crystals of **3** and **4** were obtained by slow diffusion of cyclohexane into a
95 solution of the complex in dichloromethane. The crystal structures were solved by X-ray
96 diffraction and confirmed the formation and molecular structures of the target com-
97 pounds (**Figures 2a, 2b**).



98
99 **Figure 2.** Crystal structures of **3** (a) and **4** (b). Thermal ellipsoids were drawn at 30% probability.
100 Hydrogens were omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Cu1-Cl1
101 2.095(1), Cu1-C1 1.876(2), C1-N1 1.346(3), C1-N2 1.367(3), N1-C2 1.377(3), N2-C3 1.393(3), C2-C3
102 1.336(4), Cl1-Cu1-C1 176.44(8), Cu1-C1-N1 128.2(2) and Cu1-C1-N2 127.6(2). Selected bond distan-
103 ces (Å) and angles (°) for **4**: Cu1-Cl1 2.101(2), Cu1-C1 1.881(4), C1-N1 1.350(5), C1-N2 1.357(5),
104 N1-C2 1.379(6), N2-C3 1.382(5), C2-C3 1.333(6), Cl1-Cu1-C1 176.6(2), Cu1-C1-N1 127.0(3),
105 Cu1-C1-N2 128.8(3).

Both structures show common features. For instance, the NHC-Cu-Cl moiety is indeed attached at the 1-position of the pyrene luminophore. The two-coordinate copper complexes display linear configurations around the metal center with angles of $176.44(8)^\circ$ for **3** and $176.6(2)^\circ$ for **4**, in line with those obtained for related two-coordinated NHC-Cu-Cl complexes.[21-23]. The carbene-Cu bond distances are $1.876(2) \text{ \AA}$ and $1.881(4) \text{ \AA}$ for **3** and **4** respectively and the Cu-Cl bond distances are of $2.095(1) \text{ \AA}$ and $2.101(2) \text{ \AA}$ respectively. These bond distances are similar to those found in related two-coordinate NHC-Cu(I) chloride compounds.[23,24]

Examining the packing of the molecules in the crystal of **3** revealed the presence of weak Cu(I)---Cu(I) contacts between two adjacent molecules at $d = 3.573(1) \text{ \AA}$ (Figure 3).[25] As for complex **4**, the packing shows a distance between the two Cu(I) centers at $d = 3.797(1) \text{ \AA}$ which precludes the presence of cuprophilic interactions.[26] This difference might be the consequence of the large naphthyl-group compared to the CH_3 -group on the carbene unit, which generates more steric hindrance and eventually move the molecules further away suppressing metal---metal interaction at the supramolecular level. Further weak secondary interactions occurring in the packing of **3** are an intermolecular C-H...Cl hydrogen bonding of 2.762 \AA between H22 of the pyrene cycle and the chlorido ligand of a neighbored molecule, thus generating a kind of 1D supramolecular ribbon.

For complex **4**, the chlorido ligand even triply interacts with H10 (2.828 \AA), H17 (2.902 \AA), and H22 (2.762 \AA) of the aryl cycles.

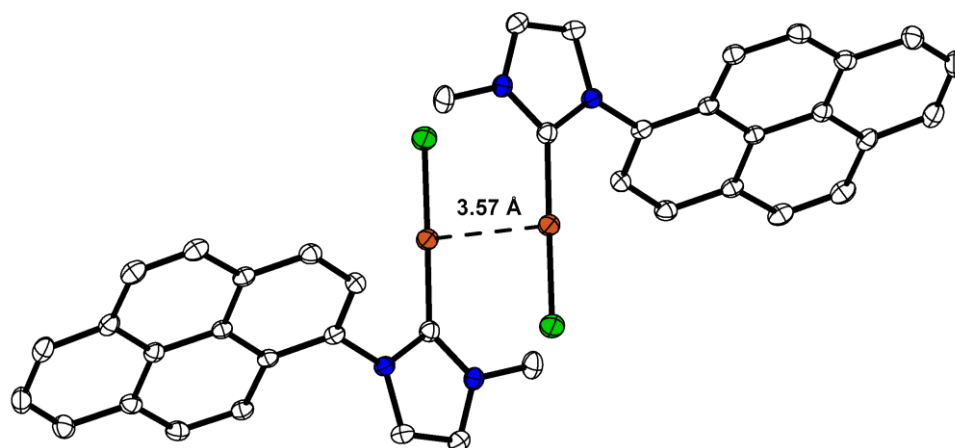


Figure 3. Packing of **3** showing weak Cu---Cu contact between two adjacent molecules at the supramolecular level.

2.3. Absorption properties

The UV absorption profiles of ligand **1** and complexes **3-4** in dilute CH_2Cl_2 solution at room temperature are shown in Figure 4, and pertinent absorption data are presented in Table 1.

The ligand **1** exhibits vibronically resolved intense absorption bands with $\lambda_{\text{max}} = 343 \text{ nm}$ assigned to $^1\pi\text{-}\pi^*$ transitions centered at the pyrene chromophore.[27] The presence of the imidazole moiety at the C1-position induces a bathochromic shift of all bands by about 2-6 nm indicating a lowering of the energy difference between the HOMO-LUMO orbitals when compared to the free pyrene (Figure 4). This might indicate that attachment of the imidazole to the pyrene extends the π -conjugation in ligand **1**.

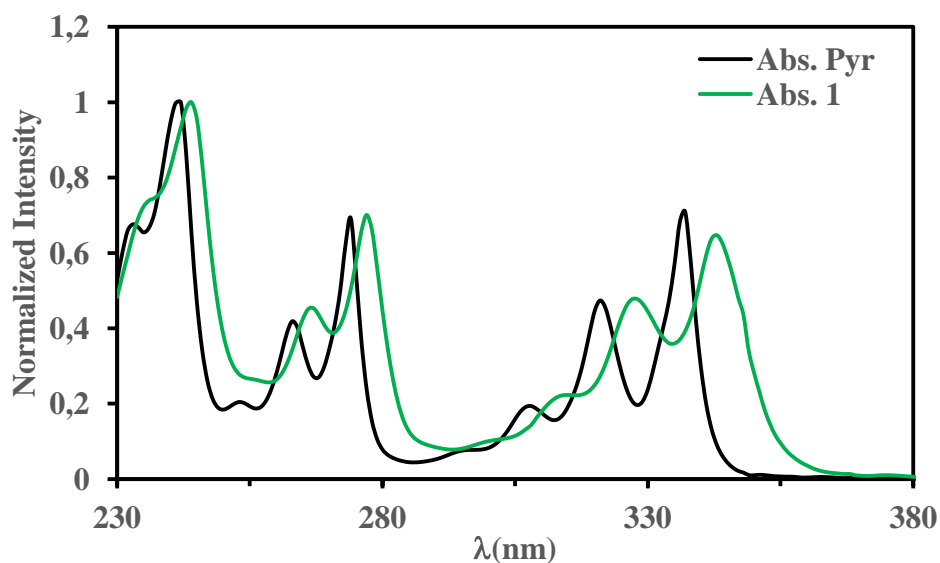


Figure 4. Absorption spectra of pyrene (Pyr) and **1** in CH₂Cl₂ solution at rt.

The Cu(I) complexes **3-4** present similar vibronic absorption bands to that of **1** in the UV region with $\lambda_{\text{max}} = 344$ nm for **3** and for **4** as well (Figure 5). These absorption bands are again associated with the spin-allowed π - π^* ligand-centered (LC) transitions from the pyrene ligand.[27]

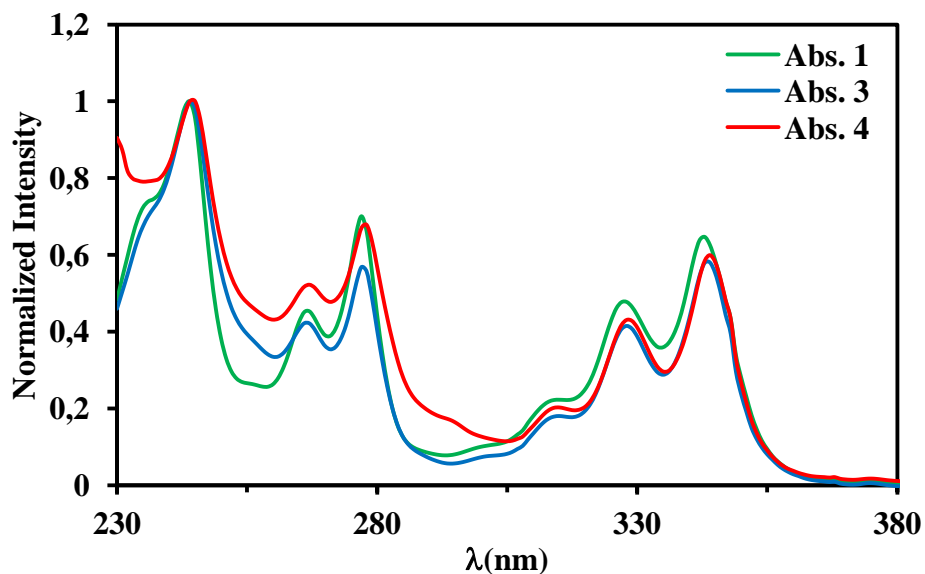


Figure 5. Absorption spectra of ligand **1** and complexes **3-4** in CH₂Cl₂ solution at rt.

Table 1. Absorption data.

	λ_{max} , nm ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$) ^a
1	235 sh (45), 244 (62.2), 267 (28.4), 277 (43.6), 313 (13.5), 327 (30.1), 343 (40.6), 374 (0.6)
3	236 sh (35), 244 (49.6), 267 (21.1), 277 (28.3), 314 (8.9), 328 (20.6), 344 (29.2), 375 (0.5)
4	245 (52.4), 268 (27.2), 278 (35.4), 314 (10.8), 328 (22.5), 344 (21.2), 375 (1.1)

^a In CH₂Cl₂ solution at rt; sh is shoulder.

2.4. Luminescence properties

The photoluminescence properties of ligand **1** and the complexes **3-4** were investigated in CH₂Cl₂ solution at room temperature (298 K) and in CH₃OH: C₂H₅OH (1 : 4) glassy solution at 77 K. The normalized emission spectra of the ligand and complexes at 298 K are shown in Figure 5, and the spectra at 77 K are given in Figure 8. The emission maxima (λ_{max}), photoluminescence quantum yields (φ) and lifetimes (τ) are collected in Table 2.

The ligand **1** exhibits at room temperature a relatively broad and structured emission bands, with λ_{max} at 379 nm (Figure 5) with quantum yield ($\varphi = 39\%$), and short lifetimes in the nanosecond regime $\tau = 32.13$ ns. This behavior can be assigned to the fluorescence of the pyrene unit of the molecule. For comparison purposes, the parent pyrene molecule under similar experimental condition display a lower quantum yield in CH₂Cl₂ ($\varphi = 27\%$).[28]

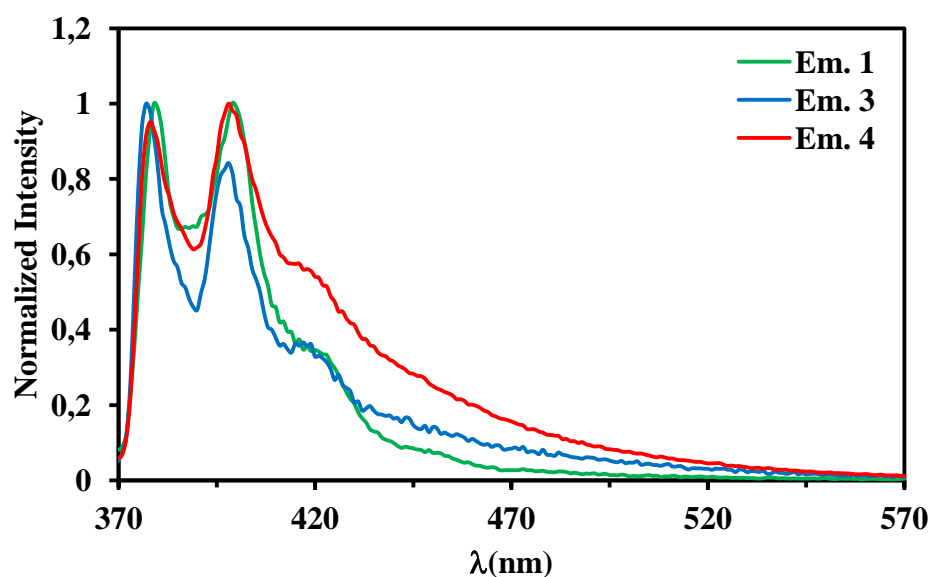


Figure 6. Normalized emission spectra of ligand **1** and carbene complexes **3-4** in de-aerated CH₂Cl₂ solution at rt.

The emission spectrum of **1** in a CH₃OH : C₂H₅OH glassy solution at 77 K is reported in Figure 7. In comparison with its spectrum recorded at rt, we notice the presence of a similar pattern but with sharper bands.

The Cu(I) carbene complexes **3-4** display in CH₂Cl₂ solution at room temperature a similar broad and structured emission bands in comparison to the free ligand **1** (Figure 6), with λ_{max} at 377 nm for both complexes with lifetimes $\tau = 8.72$ ns and $\tau = 7.79$ ns respectively indicating that the observed emissions are fluorescence in nature. The displayed vibronic structure indicates a predominantly ¹LC π - π^* character of the emissive excited state centered at the pyrenyl chromophore. This is in line with the photoluminescence behavior of other metalated complexes containing pyrene motifs.[17] The emission spectra of the Cu(I) carbene complexes **3** and **4** at room temperature also show a longer tail that extend into the visible region when compared to ligand **1**.

It is worth mentioning that the photoluminescence quantum yields of our complexes **3, 4** are ($\varphi = 28\%$) and ($\varphi = 42\%$), (Table 2) which are higher than that observed for the pyrene parent molecule suggesting that the presence of the "NHC-Cu-Cl" unit provides extra rigidity to the system and hence increases the emission efficiency. Moreover, it should be mentioned that mononuclear-NHC-halogenated complexes have been investigated in the literature and are often described as weakly or even non-emissive.[16,17,19,29]

The photograph of ligand **1** and carbene complexes **3, 4** in CH₂Cl₂ and in solid state upon irradiation with a UV lamp in the dark at 365 nm is given in Figure 7.

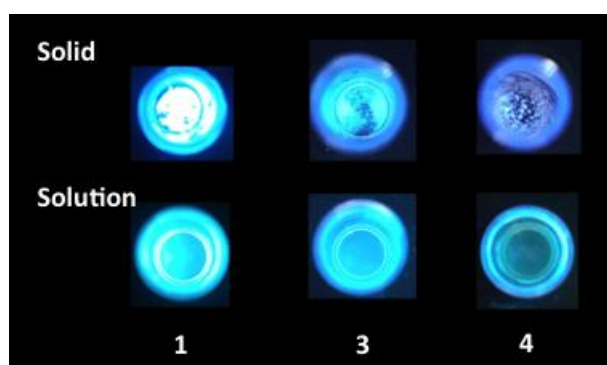


Figure 7. Photograph of ligand 1 and complexes 3, 4 upon irradiation with a UV lamp in the dark at 365 nm.

At low temperature in $\text{CH}_3\text{OH} : \text{C}_2\text{H}_5\text{OH}$ glassy solution at 77 K, complexes 3 and 4 were found to be luminescent (Figure 8). The spectra of the two complexes 3 and 4 show sharper bands at 77 K when compared to those recorded at rt, and they are slightly blue shifted relative the r.t. emissions. No phosphorescence was detected at 77 K.

The solid-state emission spectra of ligand 1 and complexes 3-4 recorded at room temperature displayed broad structureless bands for all compounds with λ_{max} at 470 nm, 457 nm and 462 nm and lifetimes of $\tau = 27.23$ ns and $\tau = 1.13$ ns and $\tau = 7.79$ ns respectively (Figure S11). This type of broad emission can be tentatively assigned to the excimers formed between pyrene molecules in the solid state.[30,31] The spectra of 1 and complexes 3-4 were also recorded at 77K and provided similar large bands pattern.

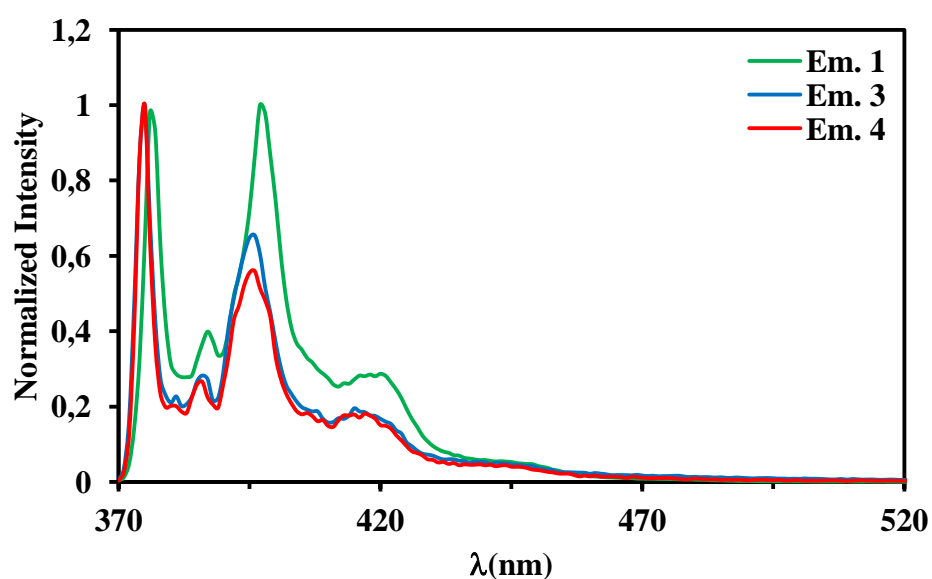


Figure 8. Normalized emission spectra of ligand 1 and complexes 3-4 in $\text{CH}_3\text{OH} : \text{C}_2\text{H}_5\text{OH}$ (1 : 4) glassy solution at 77 K.

Table 2. Emission data.

	rt			77 K
	λ_{max} , nm ^a	ϕ (%) ^a	τ , ns ^a	λ_{max} , nm ^b
1	379	39	32.13	397
3	377	28	8.72	375
4	377	42	7.79	375

^a In CH_2Cl_2 solution at rt. ^b In $\text{CH}_3\text{OH} : \text{C}_2\text{H}_5\text{OH}$ (1 : 4) glassy solution at 77 K.

3. Conclusions

In this paper we have described the synthesis of a novel fluorescent imidazole-pyrenyl ligand **1** which allowed the preparation of some stable *N*-heterocyclic carbene chloride copper (I) complexes (**3-4**) containing a pyrenyl chromophore. The X-ray molecular structures of both complexes are described and confirm the identity of the target molecules. These complexes represent the first examples of such compounds and pave the way to the placement of other inorganic metal chromophores to the pyrene fluorophore. At room temperature, ligand **1** and the Cu(I) complexes **3-4** display blue fluorescence at 379 nm and 377 nm originating mainly from the pyrene ligand. All of our molecules were found to be strongly emissive. Remarkably, the quantum yields of **1**, **3** and **4** in solution were found to be higher than that of the pyrene parent molecule under same experimental conditions. These results highlight the importance of the NHC-Cu-Cl moiety, which brings extra rigidity to the system and enhances its emission properties and this should be also compared to the known mononuclear-NHC-halogenated complexes, which are often weakly or even non-emissive.

4. Materials and Methods

Apart from the chlorides/anions metathesis workup, which has been performed under air, all other experimental manipulations were carried out under argon atmosphere using Schlenk tube techniques. Standard techniques were used for the solvents purification. Deuterated solvents and commercially available reagents were used as received unless otherwise specified. A Bruker Avance 300 NMR or Avance NEO 400 spectrometer was used for recording the ¹H NMR and ¹³C NMR spectra in CD₂Cl₂ or CDCl₃. For the UV-Vis spectra, a VARIAN-Cary 300 array spectrophotometer was used. Chemical shifts are reported in ppm downfield from tetramethylsilane and are referenced to the residual hydrogen signal of deuterated solvents (CHD₂NO₂ at 4.33 ppm, CHDCl₂ at 5.32 ppm) and the residual solvent carbon signal (CD₃NO₂ at 61.4 ppm, CD₂Cl₂ at 53.5 ppm) for ¹³C NMR. A Jobin-Yvon Fluoro Log 3 spectrofluorometer equipped with a R928P detector was employed for recording the steady state excitation and emission spectra both in the solid state (298 K and 77 K) and in solution at room temperature.

Synthesis of 1-(pyren-1-yl)-1*H*-imidazole (**1**)

Under argon atmosphere, 1-bromo-pyrene (1.5 g, 1.0 equiv.), imidazole (546 mg, 1.5 equiv.), Cs₂CO₃ (3.45 g, 2.0 equiv.), 2,2,6,6-tetramethyl-3,5-heptanedione (DPM) (197 mg, 0.2 equiv), and Cu₂O (153 mg, 0.2 equiv.) were introduced into a Schlenk tube equipped with magnetic stirrer. Then DMSO (6 mL) was added with vigorous stirring at room temperature. The reaction mixture was sealed and heated at 100 °C, for 18 hours. Then mixture was cooled to room temperature and water (30 mL) was added and extracted with ethyl acetate. The organic phase was separated and dried with anhydrous MgSO₄. Subsequently, the product was purified using column chromatography to obtain a white solid (1.317 g, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.20 (m, 3H, H_{py}), 8.21 – 8.05 (m, 4H, H_{py}), 7.95 (dd, J = 8.0, 2.4 Hz, 2H, H_{py}), 7.83 (d, J = 9.2 Hz, 1H, H_{im}), 7.44 (s, 2H, H_{im}). ¹³C NMR (400 MHz, CDCl₃) δ 131.51, 131.18, 130.88, 130.72, 129.40, 128.52, 126.98, 126.75, 126.72, 126.19, 125.85, 125.07, 124.79, 124.25, 123.87, 121.05, 77.37, 77.26, 77.06, 76.74. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₂N₂H 269.1073. Found 269.106.

Synthesis of 3-methyl-1-(pyren-1-yl)-1*H*-imidazole-3-ium iodine (**2a**).

1-(pyren-1-yl)-1*H*-imidazole (800 mg, 1.0 equiv) was introduced into a round bottom flask equipped with magnet stirrer, and a rubber stopper. THF (8 mL) was added to the reaction mixture, then MeI (3.6 mL, 2.0 equiv), was added dropwise and the system was sealed. The reaction mixture was heated at 60 °C for 48 h. Addition of Et₂O (20 mL) to the reaction mixture, provided a white precipitate which was filtered off and washed with Et₂O (2x 5 mL), and then dried under vacuum. (1.189 g, 97% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.77 (s, 1H, H_{im}), 8.54 (d, J = 8.2 Hz, 1H, H_{im}), 8.49 (dd, J = 7.6, 3.1 Hz, 1H, H_{py}), 8.46 – 8.37 (m, 2H, H_{py}), 8.39 – 8.28 (m, 3H, H_{py}), 8.23 (t, J = 7.7 Hz, 1H, H_{py}), 8.15 (t, J = 1.8 Hz, 1H, H_{py}), 7.93 (d, J = 9.2 Hz, 1H, H_{im}), 4.10 (s, 3H, H_{Me}). ¹³C NMR (400 MHz, DMSO-*d*₆)

258 δ 139.17, 132.64, 131.05, 130.63, 130.53, 129.75, 128.49, 127.81, 127.45, 127.39, 126.97, 126.13,
259 125.61, 125.36, 124.93, 124.85, 124.68, 124.36, 123.53, 120.73, 36.86. HRMS (ESI) m/z : $[M]^+$
260 Calcd for $C_{20}H_{15}N_2$ 283.1226. Found 283.1230.

261 **Synthesis of 3-(naphthalen-1-ylmethyl)-1-(pyren-1-yl)-1H-imidazole-3-ium chloride** 262 **(2b).**

263 A round bottom flask equipped with a stirrer bar was charged with
264 1-(pyren-1-yl)-1H-imidazole (1.0 g, 1.0 equiv) and 1-(chloromethyl)naphthalene (985 mg,
265 1.5 equiv). Dioxane (20 mL) was added and the reaction mixture was heated at 100 °C for
266 48 h in a sealed system. During which a white precipitate was formed. The solid was
267 filtered and washed with dioxane (2x 10 mL), then with Et₂O (2x 10 mL), and dried under
268 vacuum to give a white microcrystalline solid (1.450 g, 87% yield). ¹H NMR (400 MHz,
269 DMSO-*d*₆) δ 10.15 (t, *J* = 1.6 Hz, 1H, H_{im}), 8.57 – 8.45 (m, 3H, H_{py}), 8.45 – 8.32 (m, 6H, H_{py}),
270 8.28 – 8.19 (m, 2H, H_{naph}), 8.09 (d, *J* = 8.2 Hz, 2H, H_{im}), 7.84 – 7.61 (m, 4H, H_{naph}), 6.20 (s, 2H,
271 H_{CH2}). ¹³C NMR (400 MHz, DMSO- *d*₆) δ 139.15, 133.97, 132.68, 131.06, 131.02, 130.70,
272 130.51, 130.30, 130.26, 129.78, 129.45, 128.54, 128.45, 127.84, 127.76, 127.48, 127.00, 126.97,
273 126.24, 126.07, 125.96, 125.59, 125.05, 124.34, 123.83, 123.54, 123.50, 120.47, 66.81. HRMS
274 (ESI) m/z : $[M]^+$ Calcd for $C_{30}H_{21}N_2$ 409.1699. Found 409.1699.

275 **General procedure for the preparation of Cu(I) N-heterocyclic carbene complexes (3, 4).**

276 The azolium salt either **2a** or **2b** was introduced into a dry Schlenk tube kept under
277 argon. Then degassed dried solvents CH₂Cl₂ and CH₃CN (1V:1V = 8 mL/8 mL) were in-
278 troduced with Ag₂O (2.0 eq.). The solution was refluxed at 60 °C for overnight under
279 light protection using aluminum foil. The mixture was cooled and an appropriate
280 amount of charcoal was introduced and the reaction mixture was filtered to another
281 Schlenk tube containing CuCl (2.0 eq.). CH₂Cl₂ (16 ml) was added and the reaction mix-
282 ture was heated for overnight at 60° C. Then CuCl (1eq) was introduced and the reaction
283 was left to stir for 24 hours. The mixture was cooled then filtered through celite in order
284 to remove a grey precipitate and washed with CH₂Cl₂. The crude product was extracted
285 by CH₂Cl₂. The solvent was removed under vacuum and the precipitate was recrystal-
286 lized from CH₂Cl₂/cyclohexane to give microcrystalline solids, which was filtered and
287 dried, under vacuum.

288 Compound **3** was obtained as off-white microcrystalline solid (144mg, 83%) using
289 (200mg, 0.4878 mmol) of **2a**. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.41 – 8.30 (m, 3H, H_{py}), 8.31 –
290 8.19 (m, 3H, H_{py}), 8.20 – 8.10 (m, 2H, H_{py}), 7.85 (d, *J* = 9.2 Hz, 1H, H_{py}), 7.42 (s, 1H_m, H_{im}),
291 7.30 (s, 1H, H_{im}), 4.10 (s, 3H, H_{Me}). ¹³C NMR (400 MHz, CD₂Cl₂) δ 178.95 (C-Carbenic),
292 131.97, 131.20, 130.67, 129.39, 128.65, 127.06, 126.76, 126.34, 125.96, 125.03, 124.90, 124.72,
293 124.15, 120.77, 38.6 (CH₃-). HRMS (ESI) m/z : $[M]^+$ Calcd for (C₂₀H₁₄N₂)₂Cu 627.1604.
294 Found 627.159.

295 Compound **4** was also obtained as white microcrystalline solid using (200mg, 0.4494
296 mmol) of **2b** (196 mg, 86%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.34 (dd, *J* = 13.5, 7.7 Hz, 3H,
297 H_{naph}), 8.29 – 8.10 (m, 6H, H_{py}), 8.02 (d, *J* = 6.4 Hz, 2H, H_{naph}), 7.83 (d, *J* = 9.2 Hz, 1H, H_{naph}),
298 7.75 – 7.59 (m, 4H, H_{naph}), 7.36 (s, 1H, H_{im}), 7.14 (s, 1H, H_{im}), 6.02 (s, 2H, H_{CH2}). ¹³C NMR
299 (400 MHz, CD₂Cl₂) δ 179.03 (C-Carbenic), 134.05, 132.04, 131.20, 131.12, 130.84, 130.66,
300 129.80, 129.48, 129.03, 128.69, 127.85, 127.18, 127.05, 126.78, 126.39, 126.00, 125.50, 125.04,
301 124.91, 124.73, 124.14, 123.08, 120.68, 65.65, 15.08. HRMS (APCI) m/z : $[M]^+$ Calcd for
302 C₃₀H₂₀CuN₂ 471.0917. Found 471.0927.

303 **X-Ray crystal structure determination.** Single crystals were selected, mounted and
304 transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker
305 Kappa APEX II system using micro-source Cu-K α radiation. Unit-cell parameters de-
306 termination, data collection strategy, integration and absorption correction were carried
307 out with the Bruker APEX3 suite of programs. The structures were solved with SHELXT
308 and refined anisotropically by full-matrix least-squares methods with SHELXL using
309 WinGX. The structures were deposited at the Cambridge Crystallographic Data Centre
310 with numbers CCDC 2249001 and CCDC 2249002 and can be obtained free of charge via
311 www.ccdc.cam.ac.uk.

Crystal data for 3. C₂₀H₁₄ClCuN₂, monoclinic P 2₁/c, a = 13.1563(5) Å, b = 16.1523(6) Å, c = 7.7591(3) Å, α = γ = 90°, β = 102.650(2)°, V = 1608.82(11) Å³, Z = 4, colourless needle 0.25 × 0.05 × 0.03 mm³, μ = 3.447 mm⁻¹, min / max transmission = 0.67 / 0.96, T = 200(1) K, λ = 1.54178 Å, θ range = 4.40° to 66.58°, 10915 reflections measured, 2833 independent, R_{int} = 0.0318, completeness = 0.995, 217 parameters, 0 restraints, final R indices R1 [I > 2σ(I)] = 0.0348 and wR2 (all data) = 0.0961, GOF on F² = 1.024, largest difference peak / hole = 0.42 / -0.36 e·Å⁻³.

Crystal data for 4. C₃₀H₂₀ClCuN₂, monoclinic P 2₁/n, a = 7.6040(6) Å, b = 23.8164(19) Å, c = 14.3051(13) Å, α = γ = 90°, β = 94.615(5)°, V = 2582.3(4) Å³, Z = 4, colourless needle 0.76 × 0.04 × 0.03 mm³, μ = 2.287 mm⁻¹, min / max transmission = 0.50 / 1.00, T = 200(1) K, λ = 1.54178 Å, θ range = 3.62° to 66.58°, 17321 reflections measured, 4540 independent, R_{int} = 0.1090, completeness = 0.998, 307 parameters, 0 restraints, final R indices R1 [I > 2σ(I)] = 0.0563 and wR2 (all data) = 0.1481, GOF on F² = 0.957, largest difference peak / hole = 0.33 / -0.54 e·Å⁻³.

Photophysical measurements. Steady state excitation and emission spectra in the solid state (298 K and 77 K) and in solution at room temperature were recorded on a Jobin-Yvon Fluoro Log 3 spectrofluorometer equipped with a R928P detector. Luminescence quantum yields Φ_L of complexes at 298 K were determined using pyrene ($\Phi_L = 27\%$) as a luminescence quantum yield standard because its fluorescence emission is in the same range as our samples.[28] Solid-state photophysical studies were carried out with solid samples contained in a quartz tube inside a quartz-walled Dewar flask. Measurements of the solid-state sample at 77 K were similarly conducted with liquid nitrogen filled in the optical Dewar flask. All solutions for photophysical studies were prepared in dry dichloromethane spectrophotometric grade. Luminescence decay signals were recorded using a FL-R928P-TCSPC apparatus equipped with a deltadiode source. Analysis of luminescence decay profiles against time was accomplished using the Decay Analysis Software DAS6.

Supporting Information: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1. Figures S1-S10: ¹H and ¹³C NMR spectra of all novel compounds **1**, **2a**, **2b**, **3** and **4**. Normalized emission spectra of ligand **1** and complexes **3** and **4** in solid state at room temperature (Figure S11). Emission decay (S12-S14) of compounds **1**, **3** and **4** in CH₂Cl₂ at room temperature. Emission decay (S15-S17) of compounds **1**, **3** and **4** in solid-state at room temperature.

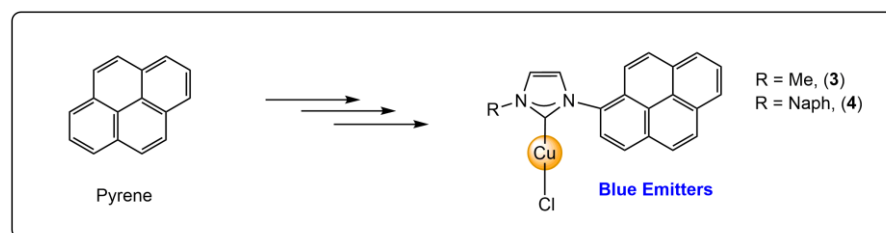
Author Contributions: The synthesis and spectroscopic characterization of the new complexes were performed by Y. Cheng. The X-ray structural determination was carried out by G. Gontard. A. Khatyr and M. Knorr performed the photophysical characterization. All authors participated in the discussion. Preparation and writing of the manuscript were made by H. Amouri who also directed the project.

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Conflicts of Interest: The authors declare no conflict of interest.

Figure Caption.



References

- 357
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- 361 1. Huynh, H.V. *The Organometallic Chemistry of N-Heterocyclic Carbenes* Wiley: Chichester, UK, 2017.
 - 362 2. Bourissou, D.; Guerret, O.; Gabbai, F.P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* **2000**, *100*, 39-91.
 - 363 3. Herrmann, W.A. N-heterocyclic carbenes: A new concept in organometallic catalysis. *Angew. Chem. Int. Ed.* **2002**, *41*,
364 1290-1309.
 - 365 4. Meier-Menches, S.M.; Neuditschko, B.; Zappe, K.; Schaier, M.; Gerner, M.C.; Schmetterer, K.G.; Del Favero, G.; Bonsignore,
366 R.; Cichna-Markl, M.; Koellensperger, G., *et al.* An Organometallic Gold(I) Bis-N-Heterocyclic Carbene Complex with
367 Multimodal Activity in Ovarian Cancer Cells. *Chem. Eur. J.* **2020**, *26*, 15528-15537.
 - 368 5. Nelson, D.J.; Nolan, S.P. Quantifying and understanding the electronic properties of N-heterocyclic carbenes. *Chem. Soc.*
369 *Rev.* **2013**, *42*, 6723-6753.
 - 370 6. Visbal, R.; Gimeno, M.C. N-heterocyclic carbene metal complexes: photoluminescence and applications. *Chem. Soc. Rev.*
371 **2014**, *43*, 3551-3574.
 - 372 7. Strassner, T. Phosphorescent Platinum(II) Complexes with CC Cyclometalated NHC Ligands. *Acc. Chem. Res.* **2016**, *49*,
373 2680-2689.
 - 374 8. Hossain, J.; Akhtar, R.; Khan, S. Luminescent coinage metal complexes of carbenes. *Polyhedron* **2021**, *201*, 115151-115187.
 - 375 9. Amouri, H. Luminescent Complexes of Platinum, Iridium, and Coinage Metals Containing N-Heterocyclic Carbene
376 Ligands: Design, Structural Diversity, and Photophysical Properties. *Chem. Rev.* **2023**, *123*, 230-270.
 - 377 10. Groue, A.; Montier-Sorkine, E.; Cheng, Y.P.; Rager, M.N.; Jean, M.; Vanthuyne, N.; Crassous, J.; Lopez, A.C.; Moncada,
378 A.S.; Barbieri, A., *et al.* Enantiopure, luminescent, cyclometalated Ir(III) complexes with N-heterocyclic
379 carbene-naphthalimide chromophore: design, vibrational circular dichroism and TD-DFT calculations. *Dalton Trans.* **2022**,
380 *51*, 2750-2759.
 - 381 11. Lanoe, P.-H.; Chan, J.; Groue, A.; Gontard, G.; Jutand, A.; Rager, M.-N.; Armaroli, N.; Monti, F.; Barbieri, A.; Amouri, H.
382 Cyclometalated N-heterocyclic carbene iridium(III) complexes with naphthalimide chromophores: a novel class of
383 phosphorescent heteroleptic compounds. *Dalton Trans.* **2018**, *47*, 3440-3451.
 - 384 12. Lanoe, P.-H.; Chan, J.; Gontard, G.; Monti, F.; Armaroli, N.; Barbieri, A.; Amouri, H. Deep-Red Phosphorescent Iridium(III)
385 Complexes with Chromophoric N-Heterocyclic Carbene Ligands: Design, Photophysical Properties, and DFT Calculations.
386 *Eur. J. Inorg. Chem.* **2016**, 1631-1634.
 - 387 13. Czerwieniec, R.; Leitzl, M.J.; Homeier, H.H.H.; Yersin, H. Cu(I) complexes - Thermally activated delayed fluorescence.
388 Photophysical approach and material design. *Coord. Chem. Rev.* **2016**, *325*, 2-28.
 - 389 14. Leitzl, M.J.; Zink, D.M.; Schinabeck, A.; Baumann, T.; Volz, D.; Yersin, H. Copper(I) Complexes for Thermally Activated
390 Delayed Fluorescence: From Photophysical to Device Properties. *Topics in Current Chemistry* **2016**, *374*, 141-147.
 - 391 15. Lanoe, P.-H.; Najjari, B.; Hallez, F.; Gontard, G.; Amouri, H. N-heterocyclic carbene coinage metal complexes containing
392 naphthalimide chromophore: design, structure, and photophysical properties. *Inorganics* **2017**, *5*, 58.
 - 393 16. Romanov, A.S.; Di, D.; Yang, L.; Fernandez-Cestau, J.; Becker, C.R.; James, C.E.; Zhu, B.; Linnolahti, M.; Credgington, D.;
394 Bochmann, M. Highly photoluminescent copper carbene complexes based on prompt rather than delayed fluorescence.
395 *Chem. Commun.* **2016**, *52*, 6379-6382.
 - 396 17. Gutierrez-Blanco, A.; Fernandez-Moreira, V.; Gimeno, M.C.; Peris, E.; Poyatos, M. Tetra-Au(I) Complexes Bearing a
397 Pyrene Tetraalkynyl Connector Behave as Fluorescence Torches. *Organometallics* **2018**, *37*, 1795-1800.
 - 398 18. Vogler, A. Luminescence of (NHC)Cu(I)Cl with NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene under ambient
399 conditions. UV phosphorescence in solution and in the solid state. *Inorg. Chem. Commun.* **2017**, *84*, 81-83.

- 400 19. Gernert, M.; Muller, U.; Haehnel, M.; Pflaum, J.; Steffen, A. A Cyclic Alkyl(amino)carbene as Two-Atom pi-Chromophore
401 Leading to the First Phosphorescent Linear Cu-I Complexes. *Chem. Eur. J.* **2017**, *23*, 2206-2216.
- 402 20. de Robillard, G.; Makni, O.; Cattey, H.; Andrieu, J.; Devillers, C.H. Towards sustainable synthesis of pyren-1-yl azoliums
403 via electrochemical oxidative C-N coupling. *Green Chemistry* **2015**, *17*, 4669-4679.
- 404 21. Pinto, A.; Echeverri, M.; Gomez-Lor, B.; Rodriguez, L. Highly emissive supramolecular gold(I)-BTD materials. *Dalton*
405 *Trans.* **2022**, *51*, 8340-8349.
- 406 22. Gauthier, E.S.; Kaczmarczyk, D.; Del Fre, S.; Favereau, L.; Caytan, E.; Cordier, M.; Vanthuyne, N.; Williams, J.A.G.;
407 Srebro-Hooper, M.; Crassous, J. Helicenic N-heterocyclic carbene copper(I) complex displaying circularly polarized blue
408 fluorescence. *Dalton Trans.* **2022**, *51*, 15571-15578.
- 409 23. Ren, X.; Wesolek, M.; Braunstein, P. Cu(I), Ag(I), Ni(II), Cr(III) and Ir(I) complexes with tritopic NimineCNHCNamine
410 pincer ligands and catalytic ethylene oligomerization. *Dalton Trans.* **2019**, *48*, 12895-12909.
- 411 24. Liu, C.; Shen, H.-Q.; Chen, M.-W.; Zhou, Y.-G. C₂-Symmetric Hindered "Sandwich" Chiral N-Heterocyclic Carbene
412 Precursors and Their Transition Metal Complexes: Expedient Syntheses, Structural Authentication, and Catalytic
413 Properties. *Organometallics* **2018**, *37*, 3756-3769.
- 414 25. Hermann, H.L.; Boche, G.; Schwerdtfeger, P. Metallophilic interactions in closed-shell copper(I) compounds - A theoretical
415 study. *Chem. Eur. J.* **2001**, *7*, 5333-5342.
- 416 26. Harisomayajula, N.V.S.; Makovetskyi, S.; Tsai, Y.-C. Cuprophilic Interactions in and between Molecular Entities. *Chem. -*
417 *Eur. J.* **2019**, *25*, 8936-8954.
- 418 27. Niko, Y.; Kawauchi, S.; Otsu, S.; Tokumaru, K.; Konishi, G.-i. Fluorescence Enhancement of Pyrene Chromophores
419 Induced by Alkyl Groups through sigma-pi Conjugation: Systematic Synthesis of Primary, Secondary, and Tertiary
420 Alkylated Pyrenes at the 1, 3, 6, and 8 Positions and Their Photophysical Properties. *Journal of Organic Chemistry* **2013**, *78*,
421 3196-3207.
- 422 28. Sriyab, S.; Jorn-Iat, K.; Prompinit, P.; Wolschann, P.; Hannongbua, S.; Suramitr, S. Photophysical properties of
423 1-pyrene-based derivatives for nitroaromatic explosives detection: Experimental and theoretical studies. *Journal of*
424 *Luminescence* **2018**, *203*, 492-499.
- 425 29. Chow, A.L.-F.; So, M.-H.; Lu, W.; Zhu, N.-Y.; Che, C.-M. Synthesis, Photophysical Properties, and Molecular Aggregation
426 of Gold(I) Complexes Containing Carbon-Donor Ligands. *Chem. - Asian J.* **2011**, *6*, 544-553.
- 427 30. Birks, J.B. Excimers. *Reports on Progress in Physics* **1975**, *38*, 903-974.
- 428 31. Wang, J.; Dang, Q.; Gong, Y.; Liao, Q.; Song, G.; Li, Q.; Li, Z. Precise Regulation of Distance between Associated Pyrene
429 Units and Control of Emission Energy and Kinetics in Solid State. *Ccs Chemistry* **2021**, *3*, 274-286.
- 430