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A Novel Family of Luminescent Pyrenyl-(*N*-Heterocyclic Carbene)- Halogenated Coinage Metal Complexes: Synthesis, Crystal Structures, and Optical Properties

Yaping Cheng,^[a] Geoffrey Gontard,^[a] Marie Noelle Rager,^[b] Abderrahim Khatyr,^[c] Michael Knorr,^[c] and Hani Amouri*^[a]

A family of luminescent pyrenyl-(NHC)-M-Cl coinage metal complexes has been prepared and fully characterized (NHC = *N*-heterocyclic carbene). Two classes of complexes are described: (M=Cu (1 a), Ag (2 a), Au (3 a) where pyrenyl-(NHC) = 1-pyrenyl-3-methyl-imidazolin-2-ylidene and M=Cu (1 b), Ag (2 b), Au (3 b) with pyrenyl-(NHC) = 1-pyrenyl-3-naphthyl-imidazolin-2-ylidene. The molecular structures of the six complexes were confirmed by single crystal X-ray diffraction studies. All complexes were

found to be emissive both in solution and solid state. The use of the chromophoric-(NHC) ligand endows to these complexes emissive properties in solution in the blue region (376–397 nm). The presence of the naphthyl-substituent in the 1 b–3 b series enhances the quantum yields relative to the methyl-series 1 a–3 a. In particular, the carbene gold complexes were the most emissive and displayed the highest quantum yields.

Introduction

Coinage metal complexes bearing *N*-heterocyclic carbenes (NHCs) are one of the most investigated classes of compounds ligated by this type of ligand.^[1–4] For instance, NHC–M–X complexes (M=Cu, Ag, Au; X=halogen) have been successfully used as catalysts for multicomponent alkyne activation reactions, hydrosilylation of ketones and cycloisomerisation of alkynylfuran.^[5–7] On the other hand, silver-carbene complexes are known to act as very efficient carbene transfer agents to prepare other transition metal-NHC complexes.^[8] More recently, *N*-heterocyclic carbene ligands were used to prepare highly emissive complexes.^[9–12] These emissive properties are due to the strong donor ability of the carbene ligand which pushes the d-d metal centered (MC) dark states to higher energy, thus rendering them thermodynamically inaccessible and hence

enhancing the luminescent properties in such class of compounds.^[9,13,14]

In general, modification of the backbone of the carbene ligand^[15] or the substituents at the *N*-center of the imidazolyli-dene brings dramatic changes to the reactivity and properties of the coinage metal compounds. In our approach we sought to prepare a novel class of metal carbene compounds by judicious placement of a chromophoric ligand (pyrene) at the *N*-center of the imidazolyli-dene unit. The presence of the tetracyclic organic pyrene chromophore^[16,17] next to the NHC ligand should boost the luminescent properties of this family of halogenated carbene coinage metal complexes pyrenyl-(NHC)MCl (Figure 1). For instance, classical *N*-heterocyclic coinage halogen complexes are often described as weakly emissive or even non-emissive due to the weak donor character of the halogen ligand.^[18–21]

Pursuing our research program in the area of luminescent organometallic and coordination compounds,^[22–31] we recently communicated the synthesis and optical properties of some halogenated Cu(I) complexes bearing a pyrenyl-derived NHC ligand.^[32] In this paper we described the synthesis of two new series based on Ag(I) and Au(I) compounds. Two classes of complexes are described, bearing different substituent groups on the second *N*-atom with R=Me (1 a–3 a) and R=naphthyl (1 b–3 b). These alkyl and aryl groups are closely attached to the carbenic carbon center of the NHC-unit allowing to tune the electronic properties of these coinage metal complexes. All

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M = Cu(I) (1a); Ag(I) (2a); Au (3a)

M = Cu(I) (1b); Ag(I) (2b); Au (3b)

Figure 1. Complexes described in this work.

complexes were emissive in solution and solid state. Moreover, the naphthyl group series (1b–3b) confers higher quantum yields when compared to the Me-series (1a–3a) (Figure 1). Within these series, the novel carbene gold complexes 3a–3b were the most emissive and displayed the highest quantum yields.

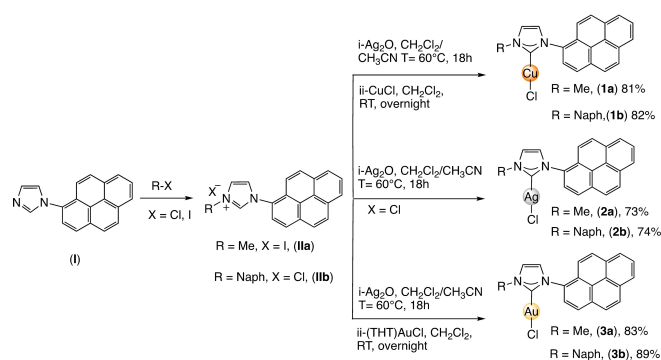
Results and Discussion

Synthesis and Characterization of the Carbene Metal Complexes 1a–3a and 1b–3b.

The synthesis of the imidazole-pyrene (I) and the related azolium salts IIa and IIb were performed following a synthetic procedure developed previously by our group.^[32] The related coinage metal complexes 1a–3a or 1b–3b were obtained by treatment of either IIa or IIb with the appropriate metal precursor according to Scheme 1.

The copper (I) and gold (I) complexes were obtained in two steps; the first step consists in the formation of the silver-carbene precursor which subsequently serves as carbene transfer agent to furnish the target complexes in good yields (81%–89%). The silver complexes 2a and 2b were directly obtained from treatment of the appropriate azolium salts with Ag₂O in a CH₂Cl₂/CH₃CN mixture at 60 °C for 18 hours. Subsequent reaction workup provided the target compounds in 73% and 74% yields. All complexes were fully characterized using ¹H- and ¹³C-NMR spectroscopy and electrospray MS-spectrometry including their X-ray molecular structures (vide infra). These compounds were found to be stable in solid state and solution and can be stored under argon for several weeks without decomposition.

The ¹³C-NMR spectra of the above complexes were very informative notably concerning the chemical shift of the carbenic carbon signals. For instance, the ¹³C_{carbene} signals of the gold complexes 3a and 3b displayed up-field shift with $\delta = 173.4$ ppm and $\delta = 173.6$ ppm when compared to those of the copper 1a and 1b with $\delta = 179.0$ ppm for both compounds, and silver compounds 2a and 2b with $\delta = 182.6$ ppm and $\delta = 182.9$ ppm respectively. This chemical shift is related to the Lewis acidity of the metal center.^[8] The greater the Lewis acidity



Scheme 1. Synthesis of the coinage metal halogenated compounds 1a–3a and 1b–3b.

of the metal center,^[33] the more up-field shifted is the carbene resonance. Complete characterization data of all compounds are given in the experimental section and in SI (Figures S1–S12).

X-Ray Molecular Structures of 1a–3a, and 1b–3b.

Suitable crystals of the six compounds were grown at room temperature by slow diffusion of cyclohexane into a CH₂Cl₂ solution of the respective complex. The crystal structures confirm the formation of the desired compounds. The molecular structures of 1a–3a and 1b–3b are shown in Figure 2. Refinement data are given in Table 1 and comparative bond distances and angles are depicted in Table 2. In each series, the mean M–C1 bond distances lengthens when going from Cu(I) (1.879 Å) to Ag(I) (2.076 Å), and then shortens below 2 Å (1.990 Å) in the case of the respective Au(I) complexes. These bond lengths may be compared with those reported for chloro-(1,3-dimesityl-2,3-dihydro-1H-imidazol-2-yl)-copper(I) (1.897(7) Å), chloro-(1,3-bis(2-oxo-2-(phenylamino)ethyl)-1H-imidazol-2-ylidene)silver (2.061(5) Å) and chloro-(1-mesityl-3-methyl-2,3-dihydro-1H-imidazol-2-yl)-gold (1.975(4) Å).^[7,34,35] One exception with a particular elongated C1–Cu distance is chloro-(N,N'-dicyclohexylimidazol-2-ylidene)-copper (2.114(11) Å).^[6]

A common feature of the (NHC–M–Cl) moiety is the attachment of the pyrene chromophore at the 1-position. All coinage metals adopt a two-coordinate linear geometry with angles ranging from 176.4° to 178.5°, similar to related complexes reported in the literature.^[36,37]

An examination of the packing of the above complexes in the crystal structure reveals the formation of dimeric species in the case of the copper (I) and gold (I) complexes 1a and 3a with Cu(I)—Cu(I) and Au(I)—Au(I) contacts at $d = 3.573(1)$ Å and $d = 3.585(1)$ Å respectively. Auophilic interactions between closed shell d¹⁰ metal ions of gold have long been recognized,^[38,39] due to numerous examples while those occur-

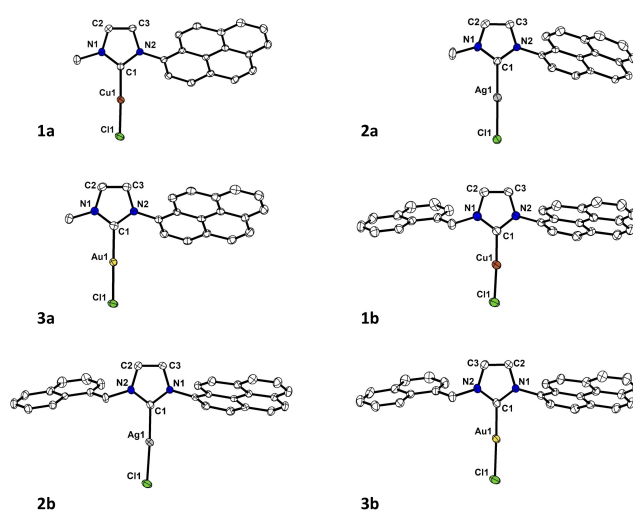


Figure 2. ORTEP drawings of 1a–3a, and 1b–3b with partial numbering system showing the M-carbene unit attached to the 1-position of the organic pyrene-chromophore. Thermal ellipsoids at 30% probability level, hydrogen atoms are omitted for clarity.

Table 1. Refinement data for complexes 1a–3a and 1b–3b.

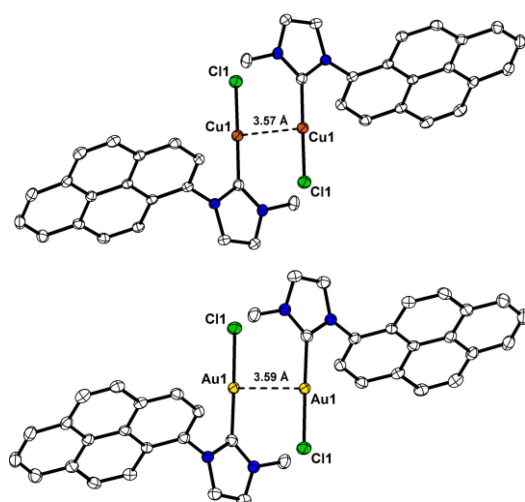
Compound	1a	1b	2a	2b	3a	3b
Formula unit	C ₂₀ H ₁₄ ClCuN ₂	C ₃₀ H ₂₆ ClCuN ₂	C ₂₀ H ₁₄ AgClN ₂	C ₃₀ H ₂₆ AgClN ₂	C ₂₀ H ₁₄ AuClN ₂	C ₃₀ H ₂₆ AuClN ₂
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /n	P 2 ₁ /c	P 2 ₁ /n	P 2 ₁ /c	P 2 ₁ /n
Unit cell	a = 13.1563(5) Å b = 16.1523(6) Å c = 7.7591(3) Å α = 90° β = 102.650(2)° γ = 90° v = 1608.82(11) Å ³	a = 7.6040(6) Å b = 23.8164(19) Å c = 14.3051(13) Å α = 90° β = 94.615(5)° γ = 90° v = 2582.3(4) Å ³	a = 11.5210(3) Å b = 12.2658(3) Å c = 12.0431(3) Å α = 90° β = 95.848(2)° γ = 90° v = 1693.01(7) Å ³	a = 7.5508(2) Å b = 24.0732(6) Å c = 14.3550(4) Å α = 90° β = 94.840(2)° γ = 90° v = 2600.03(12) Å ³	a = 13.1193(4) Å b = 16.4661(5) Å c = 7.6829(2) Å α = 90° β = 101.400(2)° γ = 90° v = 1626.94(8) Å ³	a = 7.5882(2) Å b = 23.9006(6) Å c = 14.4315(4) Å α = 90° β = 95.040(2)° γ = 90° v = 2607.21(12) Å ³
Units per cell	4	4	4	4	4	4
Crystal description	colourless needle	colourless needle	yellow prism	colourless needle	yellow prism	colourless needle
Crystal size	0.25×0.05×0.03 mm ³	0.76×0.04×0.03 mm ³	0.3×0.3×0.2 mm ³	1.16×0.07×0.04 mm ³	0.12×0.12×0.07 mm ³	0.58×0.05×0.02 mm ³
Absorption coefficient	3.447 mm ⁻¹	2.287 mm ⁻¹	11.008 mm ⁻¹	7.307 mm ⁻¹	18.512 mm ⁻¹	11.690 mm ⁻¹
Min and max transmission	0.67 and 0.96	0.50 and 1.00	0.15 and 0.35	0.12 and 0.79	0.22 and 0.42	0.16 and 0.93
Temperature	200(1) K	200(1) K	200(1) K	200(1) K	200(1) K	200(1) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å
θ range	4.40° to 66.58°	3.62° to 66.58°	3.86° to 66.57°	3.67° to 66.59°	4.36° to 66.58°	3.59° to 66.68°
Reflections measured	10915	17321	12618	22838	11830	19491
Independent reflections	2833	4540	2990	4567	2879	4530
R(int)	0.0318	0.1090	0.0228	0.0464	0.0223	0.0468
Completeness	0.995	0.998	0.999	0.999	0.999	0.985
Parameters	217	307	218	307	217	307
Restraints	0	0	0	0	0	0
R1 [I > 2σ(I)]	0.0348	0.0563	0.0291	0.0263	0.0234	0.0391
wR2 (all data)	0.0961	0.1481	0.0776	0.0670	0.0587	0.0869
Goodness-of-fit	1.024	0.957	1.060	1.052	1.119	1.112
Largest difference peak	0.42 e.Å ⁻³	0.33 e.Å ⁻³	0.91 e.Å ⁻³	0.45 e.Å ⁻³	1.08 e.Å ⁻³	1.92 e.Å ⁻³
Largest difference hole	-0.36 e.Å ⁻³	-0.54 e.Å ⁻³	-0.77 e.Å ⁻³	-0.47 e.Å ⁻³	-0.67 e.Å ⁻³	-1.21 e.Å ⁻³

Table 2. Selected bond distances (Å) and distortion angles (°) in **1a–3a** and **1b–3b**.

	1a	2a	3a	1b	2b	3b
M1-Cl	2.095(1)	2.350(1)	2.273(2)	2.101(2)	2.312(1)	2.280(2)
M1-C1	1.876(2)	2.085(3)	1.993(4)	1.881(4)	2.066(2)	1.987(6)
C1-N1	1.346(3)	1.352(3)	1.336(5)	1.350(5)	1.354(3)	1.335(7)
C1-N2	1.367(3)	1.350(3)	1.356(5)	1.357(5)	1.343(3)	1.346(8)
N1-C2	1.377(3)	1.373(4)	1.387(6)	1.379(6)	1.386(3)	1.387(8)
N2-C3	1.393(3)	1.379(3)	1.388(6)	1.382(5)	1.375(3)	1.362(8)
C2-C3	1.336(4)	1.342(4)	1.342(6)	1.333(6)	1.338(4)	1.336(9)
Cl1-M1-C1	176.4(1)	176.7(1)	178.1(2)	176.6(2)	177.0(1)	178.5(2)
M1-C1-N1	128.2(2)	128.5(2)	126.7(3)	127.0(3)	128.5(2)	127.8(4)
M1-C1-N2	127.6(2)	127.3(2)	126.8(3)	128.8(3)	127.0(2)	127.1(4)

ring between closed-shell Cu(I) ion pairs are less investigated due to relatively limited examples.^[40,41] Thus in complex **1a**, the unsupported cuprophilic interaction is comparable to the intermolecular Cu—Cu interaction (3.58 Å) encountered in the trimeric {[3,5-(Me)2-4-(Ph)Pz]Cu}₃, (Pz = pyrazole). Interestingly the authors demonstrated that such interactions contributed to the phosphorescence behavior of the trimeric species.^[42]

In contrast, the naphthyl series **1b–3b** did not display any close metal—metal contact relative to the methyl series **1a–3a** perhaps due to steric hindrance. Furthermore, both silver(I) complexes **2a** or **2b** did neither exhibit relativistic metal-metal interactions,^[21] nor any dimerization through μ_2 -halide bridging as encountered for bis(μ_2 -chloro)-(1-mesityl-3-(pyridin-2-ylmethyl)-2,3-dihydro-1H-imidazol-2-ylidene)-disilver and bis(μ_2 -chloro)-bis(1-(*N,N*-diethylcarbamoylmethyl)-3-mesitylimidazol-2-ylidene)-disilver.^[43,44] [Figure 3]

**Figure 3.** Solid-state packing shows dimer formation through Cu—Cu in **1a** and Au—Au contacts in **3a**.

Absorption and Emission Properties

Absorption

The absorption spectra of the investigated pyrenyl-(NHC)-M—Cl complexes, (M=Cu, Ag, Au; R=Me (**1a–3a**) and R=Naph (**1b–3b**)) recorded in CH₂Cl₂ are reported in Figure 4 and relevant data are collected in Table 3. The absorption profiles of the Me-series (**1a–3a**) and Naph-series (**1b–3b**) show a similar envelope of intense vibronic bands (Figure 2) in the spectral region of 240–370 nm. They originate from spin-allowed ¹ π - π^* centered (¹LC) ligand transitions of the pyrene chromophore.^[45,46] The absorption bands of coinage metal complexes **1a–3a** and **1b–3b** are all red shifted relative to those of the parent pyrene molecule (Figure S1). Such red shifts were also observed by introducing alkyl groups at the pyrene-1 position, which tends to narrow the HOMO-LUMO gap.^[47]

Emission

The emission spectra of all complexes recorded in CH₂Cl₂ at room temperature are shown in Figure 5 and relevant parameters are given in Table 3. All complexes were found to be emissive and displayed good quantum yields even higher than that of the parent pyrene chromophore. For instance, all pyrenyl-coinage metal complexes displayed broad structured emission bands similar to that of the imidazole-pyrenyl ligand (**1**). The observed lifetimes in the nanosecond range support that this type of emissions is fluorescent in nature and suggest that they originate from π - π^* transitions of the metal perturbed pyrene chromophore.^[47,48] Comparison between the Me-series (**1a–3a**) and Naph-series (**1b–3b**), show that the latter display higher quantum yields. Moreover, within the same series, the (pyrenyl-NHC)-Au—Cl complexes **3a** and **3b** were the most emissive compounds. It is noteworthy that mononuclear-NHC-halogenated complexes without organic chromophore have been investigated in the literature and were described as weakly or even non-emissive.^[18–21]

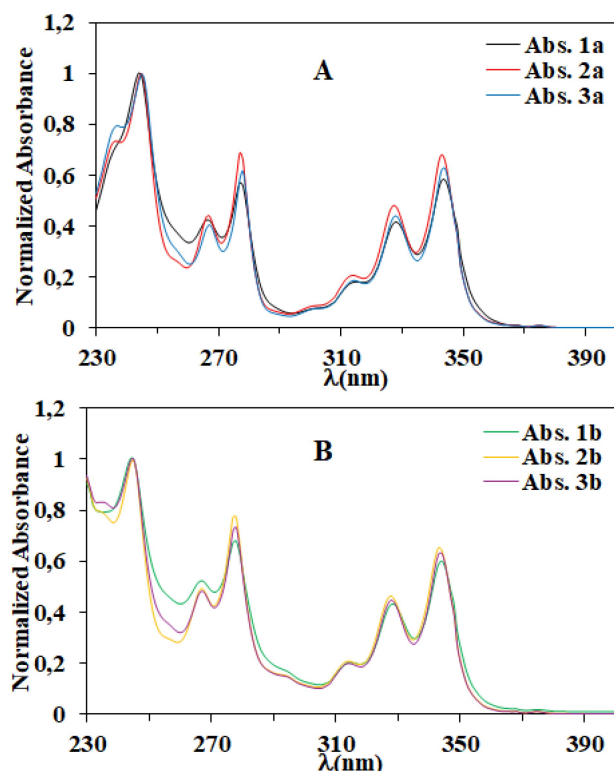


Figure 4. Absorption spectra of complexes **1a–3a** and **1b–3b** in CH_2Cl_2 solutions.

The emission spectra of the pyrenyl coinage metal complexes (**1a–3a**) and Naph-series (**1b–3b**), were recorded in $\text{CH}_3\text{OH}:\text{C}_2\text{H}_5\text{OH}$ at room temperature and at 77 K and were found to be luminescent (Figure 6). At room temperature all compounds displayed vibronic band emissions within the range of $\lambda \approx 370\text{--}450\text{ nm}$ similar to those observed in CH_2Cl_2 . Furthermore, the spectra of all complexes display sharper bands at 77 K when compared to those recorded at room temperature, and appear slightly blue shifted. No phosphorescence

was detected at 77 K. It is commonly observed that phosphorescent molecules display temperature-dependent emission. For instance, upon cooling triplet emission activates, as reported previously for some pyrene-gold complexes.^[49]

The solid-state emission of the pyrenyl coinage metal complexes **1a–3a** and **1b–3b** recorded at room temperature displayed broad structureless bands for all compounds with λ_{max} in the range of 447–466 nm, (Figure S3) and lifetimes in the nanosecond regime (Table S1). This type of broad emission can be tentatively assigned to the excimers formed between pyrene molecules in the solid state.^[50–52]

Conclusions

In this work we reported a novel family of luminescent pyrenyl-(NHC)-M–Cl coinage metal complexes. Two types of compounds were prepared, namely those containing methyl-substituent at the nitrogen of the carbene unit **1a–3a** and those bearing a naphthyl-group **1b–3b**. The structures of all complexes were ascertained by single crystal X-ray diffraction study. The use of the chromophoric-(NHC) ligand endows to these complexes emissive properties in solution and solid state in the blue region. The measured lifetimes are in the nanosecond regime, which suggest that the emission arises presumably from $\pi\text{-}\pi^*$ states of the aromatic core of the pyrenyl-unit. Our future efforts involve the replacement of the weakly-donor halogenated ligands by strongly σ -donor acetylides to engineer multi-emissive compounds.

Experimental Section

General 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 solvent purification. The ^1H NMR spectra were routinely recorded on a

Table 3. Photophysical data of pyrene, imidazole-pyrene (I) and the investigated complexes in CH_2Cl_2 .

Compound	Absorption CH_2Cl_2 at 298 K λ_{abs} nm ($\epsilon\text{M}^{-1}\text{cm}^{-1}$)	Emission CH_2Cl_2 at 298 K		
		λ_{max} , nm	Φ (%)	τ (ns)
Pyrene	235 (49800), 242 (75200), 256 (15500), 263 (32100), 274 (53100), 296 sh (600), 309 (14200), 322 (34400), 337 (54000)	394	27 ^[46]	29.17
(I)	235 sh (45000), 244 (62200), 267 (28400), 277 (43600), 313 (13500), 327 (30100), 343 (40600), 374 (600)	379	39	32,13
1a	236 (35000), 244 (49600), 267 (21100), 277 (28300), 314 (8850), 328 (20600), 344 (29200), 375 (450)	377	28	8,72
2a	237 (36000), 246 (48900), 267 (21700), 277 (33800), 300 sh (4200), 314 (9900), 328 (22800), 343 (5200), 375 (650)	377	25	7,25
3a	237 (39500), 245 (49300), 267 (20200), 278 (30400), 300 (3400), 314 (9100), 328 (21900), 344 (31300), 375 (100)	376	31	8,20
1b	245 (52400), 268 (27200), 278 (35400), 314 (10800), 328 (22500), 344 (21200), 375 (1050)	398	42	7,79
2b	245 (53100), 267 (26400), 278 (41750), 294 sh (8300), 314 (11000), 328 (25000), 343 (34550), 375 (700)	377	48	9,12
3b	245 (55200), 268 (26400), 278 (40400), 294 sh (8300), 314 (10900), 328 (24300), 344 (35000), 375 (800)	398	56	25,91

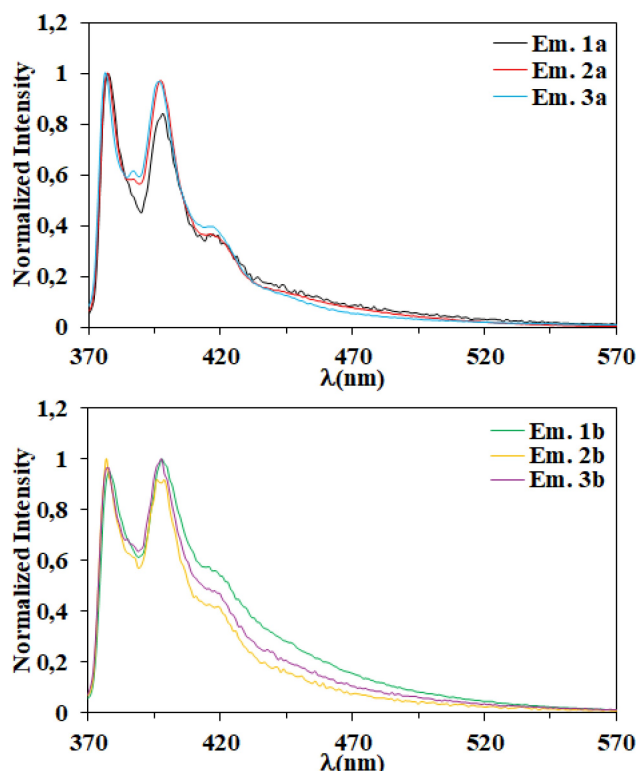
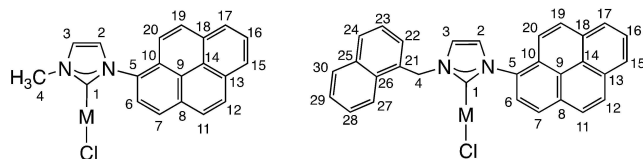


Figure 5. Emission spectra of complexes 1a–3a and 1b–3b recorded in CH_2Cl_2 solutions.

Bruker Avance NEO 400 spectrometer. Full ^1H and ^{13}C NMR characterization were acquired on Bruker Avance NEO 500 spectrometer in CD_2Cl_2 at 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR. The ^{13}C -NMR signals of the carbenic carbon required between 3 and 14 hours of acquisition on the 500 spectrometer to become visible. NMR chemical shifts are reported in parts per million referenced to the residual solvent proton ($\delta = 5.32$ ppm) for ^1H NMR and carbon ($\delta = 53.5$ ppm) for ^{13}C NMR. For the UV-Vis spectra, a VARIAN-Cary 300 array spectrophotometer was used. 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 at ambient temperature. The synthesis of the pyrene-imidazole (I) and the related azolium salts (IIa) and (IIb) were prepared according to our published synthetic procedure.^[32]



M = Cu(I) (1a); Ag(I) (2a); Au (3a)

M = Cu(I) (1b); Ag(I) (2b); Au (3b)

Atom numbering system used to assign the ^1H and ^{13}C -NMR signals for 1a–3a and 1b–3b.

General Synthetic Procedure for the Coinage Metal Carbene Complexes 1a–3a and 1b–3b.

The silver complexes 2a and 2b were obtained straightforward, and were used as carbene transfer agents to provide the copper

carbene complexes 1a and 1b as well as the gold complexes 3a and 3b respectively.

Silver complexes 2a, 2b. A dry Schlenk tube, containing a magnetic bar, was charged with the appropriated azolium salt IIa or IIb (1.0 equiv), and Ag_2O (2.0 equiv). The solids were suspended in a mixture of CH_2Cl_2 and CH_3CN (8 mL: 8 mL). The reaction mixture was refluxed at 60°C overnight under light protection using aluminum foil. Then the mixture was cooled to room temperature followed by addition of an appropriate amount of charcoal and stirred for 5 minutes. Subsequently the mixture was filtered through cotton-celite-cotton and the filtrate was evaporated to dryness. Recrystallization from CH_2Cl_2 /cyclohexane provided the silver complexes 2a and 2b.

Copper and gold complexes 1a, 2a and 3a, 3b. A dry Schlenk tube, containing a magnetic bar, was charged with the appropriated azolium salt IIa or IIb (1.0 equiv.), and Ag_2O (2.0 equiv). The solids were suspended in a mixture of CH_2Cl_2 and CH_3CN (8 mL: 8 mL). The reaction mixture was refluxed at 60°C overnight under light protection using aluminum foil. Then the mixture was cooled to room temperature followed by addition of an appropriate amount of charcoal and stirred for 5 minutes. The mixture was filtered into another Schlenk tube, containing the desired metal complex CuCl (1.0 equiv) or (THT)AuCl (1.0 equiv) in CH_2Cl_2 (16 mL). The reaction mixture was placed at 60°C in oil bath overnight for the copper complexes and at room temperature for the gold complexes. Charcoal was added to the reaction mixture at room temperature and was allowed to stir for 5 minutes, then the mixture was filtered off using a frit equipped with cotton-celite-cotton. The filtrate was evaporated to dryness and recrystallized from CH_2Cl_2 /cyclohexane to give the desired compounds 1a, 1b or 3a, 3b.

Complex 1a. IIa (200 mg, 0.4878 mmol), Ag_2O (226 mg, 0.9756 mmol), CH_2Cl_2 : CH_3CN (8 mL: 8 mL); CuCl (96 mg, mmol.) CH_2Cl_2 (16 mL). The compound was obtained as off-white microcrystalline (144 mg, 83% yield).

^1H NMR (500 MHz, CD_2Cl_2) δ 8.32–8.28 (m, 2H, H_7 and H_{15}), 8.27 (d, $J = 7.6$ Hz, 1H, H_{17}), 8.20 (d, $J = 9.0$ Hz, 1H, H_{12}), 8.17 (d, $J = 9.2$ Hz, 1H, H_{19}), 8.16 (d, $J = 9.0$ Hz, 1H, H_{11}), 8.12–8.07 (m, 2H, H_6 and H_{16}), 7.80 (d, $J = 9.2$ Hz, 1H, H_{20}), 7.37 (br s, 1H, H_2), 7.27 (br s, 1H, H_3), 4.03 (s, 3H, H_4). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 179.0 (C_1), 132.9 (C_5), 132.0 (C_8), 131.2 (C_{13}), 130.7 (C_{18}), 129.4 (C_{19}), 128.7 (C_{12}), 127.1 (C_{11}), 126.81 (C_{16}), 126.79 (C_{10}), 126.4 (C_{15}), 126.0 (C_{17}), 125.1 (C_9), 124.9 (C_7), 124.8 (C_6), 124.2 (C_{14}), 124.1 (C_2), 122.0 (C_3), 120.8 (C_{20}), 38.6 (C_4).

HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $(\text{C}_{20}\text{H}_{14}\text{N}_2)_2\text{Cu}$ 627.1604. Found 627.1597.

Complex 2a. IIa (100.0 mg, 0.3137 mmol), Ag_2O (145.0 mg, 0.6274 mmol), CH_2Cl_2 : CH_3CN (4 mL:4 mL). This compound was obtained as off-white microcrystalline, Yield (93.8 mg, 70%).

^1H NMR (500 MHz, CD_2Cl_2) δ 8.32 (dd, $J = 7.6$; 0.9 Hz, 1H, H_{15}), 8.27 (d, $J = 7.6$ Hz, 1H, H_{17}), 8.26 (d, $J = 8.1$ Hz, 1H, H_7), 8.21 (d, $J = 9.0$ Hz, 1H, H_{12}), 8.16 (d, $J = 9.2$ Hz, 1H, H_{19}), 8.14 (d, $J = 9.0$ Hz, 1H, H_{11}), 8.11 (t, $J = 7.6$ Hz, 1H, H_{16}), 8.01 (d, $J = 8.1$ Hz, 1H, H_6), 7.73 (d, $J = 9.2$ Hz, 1H, H_{20}), 7.40 (d, $J = 1.8$ Hz, 1H, H_2), 7.31 (d, $J = 1.8$ Hz, 1H, H_3), 3.99 (s, 3H, H_4). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 182.6 (C_1), 133.0 (C_5), 132.1 (C_8), 131.2 (C_{13}), 130.7 (C_{18}), 129.5 (C_{19}), 128.8 (C_{12}), 127.1 (C_{11}), 126.9 (C_{10}), 126.9 (C_{16}), 126.5 (C_{15}), 126.1 (C_{17}), 125.0 (C_9), 124.9 (C_7), 124.7 (C_6), 124.5 (C_2), 124.1 (C_{14}), 122.3 (C_3), 120.7 (C_{20}), 39.0 (C_4).

HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $(\text{C}_{20}\text{H}_{14}\text{N}_2)_2\text{Ag}$ 671.1359. Found 671.1352

Complex 3a. IIa (200 mg, 0.4874 mmol), Ag_2O (169.4 mg, 0.3656 mmol), CH_2Cl_2 / CH_3CN (8 mL: 8 mL), [(THT)-Au-Cl] (156.8 mg,

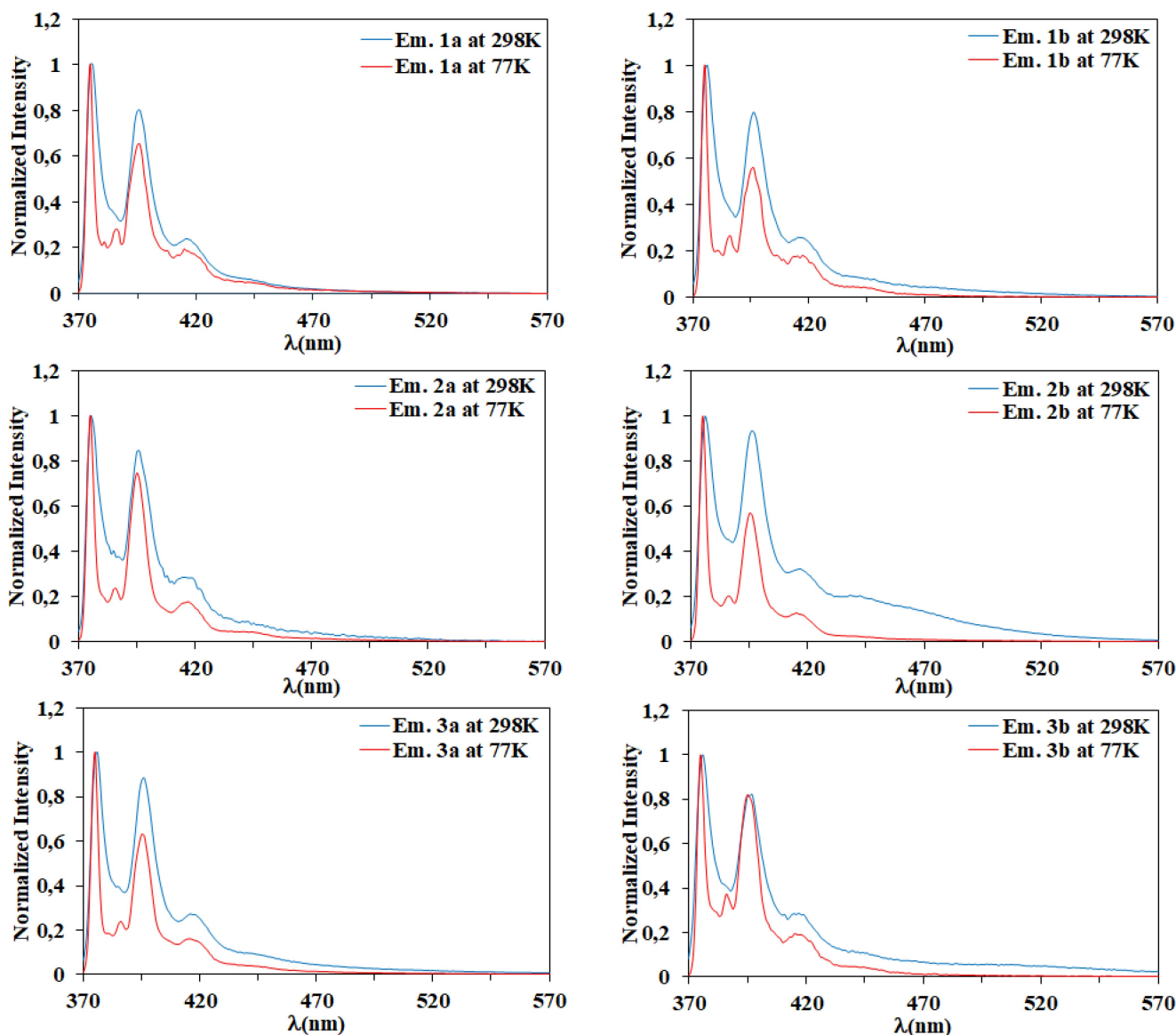


Figure 6. Emission spectra of complexes 1a–3a and 1b–3b recorded in CH₃OH:C₂H₅OH solution at 77 K (Red) and 298 K (Blue).

0.4874 mmol), CH₂Cl₂ (16 mL). The product was obtained as off-white powder. Yield (203.6 mg, 81.1 %).

¹H NMR (500 MHz, CD₂Cl₂) δ 8.33 (d, *J* = 7.6; 0.9 Hz, 1H, H₁₅), 8.32 (d, *J* = 8.1 Hz, 1H, H₇), 8.30 (dd, *J* = 7.6; 0.9 Hz, 1H, H₁₇), 8.24 (d, *J* = 9.0 Hz, 1H, H₁₂), 8.20 (d, *J* = 9.2 Hz, 1H, H₁₉), 8.19 (d, *J* = 9.0 Hz, 1H, H₁₁), 8.12 (t, *J* = 7.6 Hz, 1H, H₆), 8.12 (d, *J* = 8.1 Hz, 1H, H₆), 7.72 (d, *J* = 9.2 Hz, 1H, H₂₀), 7.36 (d, *J* = 1.9 Hz, 1H, H₂), 7.30 (d, *J* = 1.9 Hz, 1H, H₃), 4.04 (s, 3H, H₄). ¹³C NMR (125 MHz, CD₂Cl₂) δ 173.4 (C₁), 132.3 (C₈), 132.2 (C₅), 131.3 (C₁₃), 130.7 (C₁₈), 129.6 (C₁₉), 128.9 (C₁₂), 127.18 (C₁₀), 127.16 (C₁₁), 126.9 (C₁₆), 126.5 (C₁₅), 126.2 (C₁₇), 125.1 (C₆), 125.0 (C₉), 124.9 (C₇), 124.2 (C₁₄), 124.1 (C₂), 122.0 (C₃), 120.8 (C₂₀), 38.6 (C₄).

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₁₄N₂ClAuNa 537.0403. Found 537.0398.

Compound 1b. **1b** (200 mg, 0.4494 mmol), Ag₂O (208 mg, 0.8989 mmol), CH₂Cl₂:CH₃CN (8 mL:8 mL); CuCl (89.0 mg, 0.8989 mmol) and CH₂Cl₂ (16 mL). The product was obtained as white powder. Yield (187.5 mg, 82.2 % yield).

¹H NMR (500 MHz, CD₂Cl₂) δ 8.32–8.30 (m, 2H, H₇ and H₁₅), 8.28 (d, *J* = 7.6 Hz, 1H, H₁₇), 8.23–8.20 (m, 1H, H₂₇), 8.20 (d, *J* = 9.0 Hz, 1H, H₁₂), 8.18 (d, *J* = 9.2 Hz, 1H, H₁₉), 8.16 (d, *J* = 9.0 Hz, H₁₁), 8.13 (d, *J* = 8.1 Hz, 1H, H₆), 8.11 (t, *J* = 7.6 Hz, 1H, H₆), 8.00–7.96 (m, 2H, H₂₄ and H₃₀), 7.79 (d, *J* = 9.2 Hz, 1H, H₂₀), 7.68–7.64 (m, 1H, H₂₈), 7.63–7.59 (m, 1H, H₂₉), 7.59–7.57 (m, 2H, H₂₂ and H₂₃), 7.32 (d, *J* = 1.5 Hz, 1H, H₂), 7.10 (d, *J* = 1.5 Hz, 1H, H₃), 6.01–5.93 (m, 2H, H₄). ¹³C NMR (125 MHz, CD₂Cl₂) δ 179.0 (C₁), 134.1 (C₂₅), 132.8 (C₅), 132.0 (C₈), 131.2 (C₁₃), 131.1 (C₂₆), 130.86 (C₂₁), 130.66 (C₁₈), 129.8 (C₂₄), 129.5 (C₁₉), 129.0 (C₃₀), 128.7 (C₁₂), 127.9 (C₂₂), 127.2 (C₂₈), 127.1 (C₁₁), 126.79 (C₁₆), 126.75 (C₁₀), 126.4 (C₁₅ and C₂₉), 126.0 (C₁₇), 125.5 (C₂₃), 125.0 (C₉), 124.9 (C₇), 124.7 (C₆), 124.2 (C₂), 124.1 (C₁₄), 123.1 (C₂₇), 120.69 (C₂₀), 120.65 (C₃), 53.5 (C₄).

HRMS (APCI) *m/z*: [M]⁺ Calcd for C₃₀H₂₀CuN₂ 471.0917. Found 471.0927.

Compound 2b. **1b** (200.0 mg, 0.4494 mmol), Ag₂O (208 mg, 0.8989 mmol), CH₂Cl₂:CH₃CN (8 mL:8 mL). The product was obtained as white powder. Yield (183.5 mg, 74 %).

^1H NMR (500 MHz, CD_2Cl_2) δ 8.30 (d, $J=7.6$ Hz, 1H, H_{15}), 8.27–8.23 (m, 2H, H_7 and H_{17}), 8.18 (d, $J=9.0$ Hz, 1H, H_{12}), 8.16 (d, $J=9.2$ Hz, 1H, H_{19}), 8.14–8.10 (m, 1H, H_{11}), 8.09 (t, $J=7.6$ Hz, 1H, H_{16}), 8.06 (d, $J=8.1$ Hz, 1H, H_6), 8.07–8.01 (m, 1H, H_{27}), 7.98–7.94 (m, 2H, H_{24} and H_{30}), 7.72 (d, $J=9.2$ Hz, 1H, H_{20}), 7.62–7.57 (m, 2H, H_{28} and H_{29}), 7.54 (t, $J=7.6$ Hz, 1H, H_{23}), 7.51–7.45 (m, 1H, H_{22}), 7.35 (d, $J=1.8$ Hz, 1H, H_2), 7.12 (d, $J=1.8$ Hz, 1H, H_3), 5.85 (br.s, 2H, H_4). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 182.9 (C_1), 134.1 (C_{25}), 132.9 (C_5), 132.2 (C_8), 131.2 (C_{13}), 131.1 (C_{26}), 130.65 (C_{18}), 130.63 (C_{21}), 129.9 (C_{24}), 129.7 (C_{19}), 129.1 (C_{30}), 128.8 (C_{12}), 127.8 (C_{22}), 127.2 (C_{28}), 127.1 (C_{11}), 127.0 (C_{10}), 126.9 (C_{16}), 126.5 (C_{15}), 126.4 (C_{29}), 126.1 (C_{17}), 125.5 (C_{23}), 125.1 (C_9), 125.0 (C_7), 124.72 (C_2), 124.69 (C_6), 124.1 (C_{14}), 122.9 (C_{27}), 121.1 (C_3), 120.6 (C_{20}), 54.0 (C_4).

HRMS (APCI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{20}\text{AgClN}_2\text{H}$ 551.0444. Found 551.0439.

Compound 3b. IIB (200.0 mg, 0.4494 mmol), Ag_2O (208.0 mg, 0.8989 mmol), $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (8 mL:8 mL). $[(\text{THT})\text{-Au-Cl}]$ (158.6 mg, 0.4494 mmol), CH_2Cl_2 (16 mL). The product was obtained as white powder. Yield (268.3 mg, 92.8%).

^1H NMR (500 MHz, CD_2Cl_2) δ 8.34 (d, $J=8.1$ Hz, 1H, H_7), 8.33 (d, $J=7.6$ Hz, 1H, H_{15}), 8.30 (d, $J=7.6$ Hz, 1H, H_{17}), 8.27 (d, $J=8.4$ Hz, 1H, H_{27}), 8.24 (d, $J=9.0$ Hz, 1H, H_{12}), 8.21 (d, $J=9.2$ Hz, 1H, H_{19}), 8.20–8.17 (m, 1H, H_{11}), 8.18 (d, $J=8.1$ Hz, 1H, H_6), 8.12 (t, $J=7.6$ Hz, 1H, H_{16}), 8.00–7.98 (m, 2H, H_{24} and H_{30}), 7.72 (d, $J=9.2$ Hz, 1H, H_{20}), 7.70–7.66 (m, 1H, H_{28}), 7.64–7.60 (m, 1H, H_{29}), 7.61–7.57 (m, 2H, H_{22} and H_{23}), 7.28 (d, $J=2.0$ Hz, 1H, H_2), 7.06 (d, $J=2.0$ Hz, 1H, H_3), 6.09 (d, $J=14.9$ Hz, 1H, H_4), 6.02 (d, $J=14.9$ Hz, 1H, H_4). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 173.6 (C_1), 134.1 (C_{25}), 132.4 (C_8), 132.2 (C_5), 131.3 (C_{13} and C_{26}), 130.7 (C_{18}), 130.4 (C_{21}), 130.0 (C_{24}), 129.7 (C_{19}), 129.1 (C_{30}), 128.9 (C_{12}), 128.1 (C_{22}), 127.4 (C_{28}), 127.20 (C_{10}), 127.16 (C_{11}), 126.9 (C_{16}), 126.5 (C_{15} and C_{29}), 126.2 (C_{17}), 125.5 (C_{23}), 125.15 (C_6), 125.07 (C_9), 124.9 (C_7), 124.4 (C_2), 124.2 (C_{14}), 123.3 (C_{27}), 120.8 (C_{20}), 120.4 (C_3), 53.5 (C_4).

HRMS (ESI) m/z : $[\text{M}+\text{NH}_4]^+$ Calcd for $\text{C}_{30}\text{H}_{20}\text{AuClN}_2\text{NH}_4$ 658.1319. Found 658.132;

X-Ray Structural Determination of Compounds 2–3, 5 and 6

Crystal structures of **1a** and **1b** were previously published in the Cambridge Structural Database with references XIZTOT and XIZTUZ.

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa APEX II system using micro-source Cu- $K\alpha$ radiation. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structure was solved with SHELXT and refined anisotropically by full-matrix least-squares methods with SHELXL using WinGX.

The structures of **2a**, **2b**, **3a** and **3b** were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 2333085–2333088 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Photophysical Measurements

UV-Visible spectra were obtained on a VARIAN-Cary 300 array spectrophotometer. Steady state excitation and emission spectra in solution and in the solid state 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.^[25] 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. Solutions for photophysical studies were prepared in dry dichloromethane spectrophotometric grade or in a mixture of methanol/ethanol (1/4). 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.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

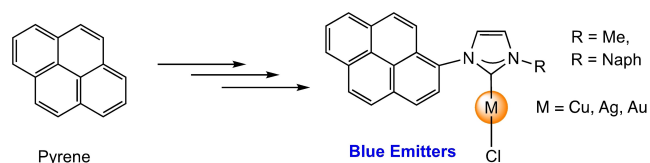
Keywords: Coinage metals · N-heterocyclic carbene · X-ray molecular structure · Chromophore · Luminescence

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studies The use of the chromophoric-(NHC) ligand endows to these complexes emissive properties in the blue region.

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1 – 10

A Novel Family of Luminescent Pyrenyl-(N-Heterocyclic Carbene)-Halogenated Coinage Metal Complexes: Synthesis, Crystal Structures, and Optical Properties

