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Luminescent Complexes of Platinum, Iridium and Coinage Metals Containing *N*-Heterocyclic Carbene Ligands: Design, Structural Diversity, and Photophysical Properties

Hani AMOURI [#] *

[#] *Sorbonne Université-Faculté des Sciences et Ingénerie Campus Pierre et Marie Curie, CNRS, IPCM (UMR 8232), 4 place Jussieu, 75252 Paris cedex 05, France. E-mail: hani.amouri@sorbonne-universite.fr.*

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Abstract: The employment of *N*-heterocyclic carbenes (NHCs) to design luminescent metal compounds have been the focus of recent intense investigations because of their strong σ-donor properties, which bring stability to the whole system and tend to push the d-d dark states so high in energy that it renders them thermally inaccessible, thereby generating highly emissive complexes for useful applications such as organic light-emitting diodes (OLEDs), or featuring chiroptical properties, a field which is still in its infancy. Among the NHC-complexes, those containing organic chromophores such as naphthalimide, pyrene and carbazole exhibit rich emission behavior, and thus have attracted extensive interest in the past five years especially carbene coinage metal complexes with carbazolate ligands. In this review, the design strategies of NHC-based luminescent platinum and iridium complexes with large spin-orbit-coupling (SOC) are described first. Subsequent paragraphs illustrate the recent advances of luminescent coinage metal complexes with nucleophilic and electrophilic based carbenes, based on silver, gold and copper metal complexes which have the ability to display rich excited state emissions and in particular via Thermally Activated Delayed Fluorescence (TADF). The luminescence mechanism and excited state dynamics are also described. We then summarize the advance of NHC metal complexes in the aforementioned fields in recent years. Finally, we propose the development trend of this fast-growing field of luminescent NHC metal complexes.

1-Introduction, purpose and scope

In the past two decades, a great deal of interest has been devoted to the design of luminescent complexes containing *N*-heterocyclic carbene ligands.[1-4] These ligands are strong σ-donors and can stabilize metal complexes with high or low oxidation states, which make them universal ligands in organometallic and coordination chemistry as well as in material chemistry.[5-14] They tend to push the non-radiative metal-centered (MC) d-d transitions to higher energy, rendering the target metal-NHC complexes strongly luminescent (Figure 1).[15-18]

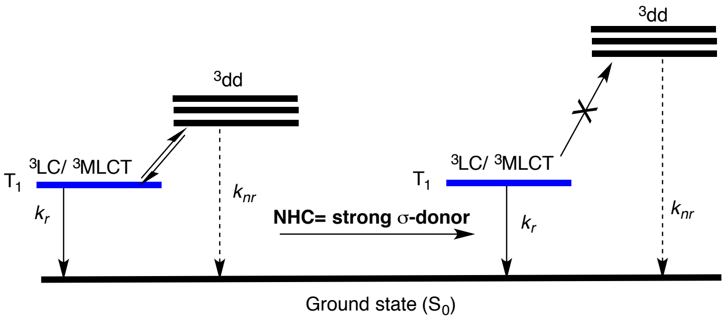


Figure 1. Simplified excited states diagram of metal-NHC complexes highlighting the effect of NHCs as strong σ-donor ligands on destabilizing of the ^{3}dd metal centered states.

Moreover they bring robustness to these compounds and thus may provide long-term functional materials. The great versatility of these ligands arises from their ease in modular synthesis and modifications.[19] For instance this can be achieved by functionalization of the imidazolium ring at the nitrogen center with different organic groups or the extension of the π-system in the backbone of the carbene structure, leading to a variety of NHC ligands with different forms and geometries.[20-21] Traditionally NHC ligands are employed in organometallic chemistry and catalysis, and there are several reports devoted to their synthesis, electronic properties, and applications in these fields.[22-26] In contrast only a few reviews were reported where such ligands were used to construct luminescent compounds.[1,4] The aim of this review is to cover the recent developments since 2015 in this fast growing area to demonstrate the thrust, richness and broadness of the field of luminescent complexes with NHC ligands. For instance, the choice of the NHC ligand and the geometry of the metal are important to design the target luminescent complex and to tailor the emission energy which eventually justifies the kind of applications for instance for biological applications where complexes emitting in the NIR region are required. We will also highlight the chiroptical properties of recent examples of luminescent chiral NHC complexes. This field is still in its infancy but is expected to expand greatly in the near future. Moreover we wish to highlight the importance of luminescent carbene complexes in the field of OLEDs. The quantum efficiency of an OLED device depends on the formation of electron-hole pairs known as excitons, which upon relaxation release energy in the form of light. However, electrically generated excitons can be either singlets or triplets, created in a 1:3 statistical ratio. While the use of fluorescent materials has limited efficiency because only 25% of the generated excitons can be used for light emission, the use of phosphorescent materials, mainly those based on transition-metal complexes that enable the access to triplet excited states due to the spin-orbit coupling of the metal luminophore, allows instead the potential use of all generated excitons, which quadruples the internal quantum efficiencies compared to fluorescent emitters.[27] Moreover one would expect that carbene ligands stabilize luminescent complexes, which make them more amenable as long-lived emitters for optical devices.[28]

Furthermore we wish to feature the research activities involving luminescent NHC-metals containing an organic chromophore such as naphthalimide,[29-34] pyrene[35-42] and carbazole[43-47] in their chemical structures. A special treatment will be given to this type of compound because they have been neglected in previous reviews. In fact, the presence of an organic chromophore in close proximity to an inorganic chromophore with NHC-ligand brings additional properties by promoting rich excited states in this class of compounds. For instance, in the past five years carbene-coinage metal complexes with carbazolate ligands have attracted much attention due to their remarkable luminescent properties.[48-49]A comparative presentation between those with *N*-heterocylic-carbenes and those with electrophilic carbenes (CAAC, MAC and DAC) will be presented, highlighting the need of a timely review to underscore this recent class of luminescent carbene complexes.

Indeed carbene-luminescent complexes displaying an organic chromophore in proximity to a heavy metal ion with large spin-orbit coupling (SOC) should facilitate intersystem crossing (ISC) to the triplet manifold of the organic dyes.[50-52] In fact intersystem crossing is favored by spin-orbit coupling with an efficiency approximately proportional to Z^4 (where Z is the atomic number).[51] As a consequence this type of compound will promote novel excited state properties, which make them ideal molecules for displaying dual emissions for useful potential applications.[53-54]

Thus in this review, we will first present recent advances in the preparation of luminescent NHC-platinum and -iridium complexes with $5d^8$ and $5d^6$ electronic configuration which possess planar and octahedral coordination geometries and display large spin orbit coupling. They also display very large ligand field splitting due to the good metal-ligand overlap. Eventually these carbene metal compounds tend to emit via ^{3}MLCT/^{3}LLCT excited states. In addition the planar platinum complexes at high concentration tend to aggregate via π-π or M···M interactions, which generate low energy emissions (vide infra). In complexes involving predominantly MLCT transitions, photoexcitation changes the d-electron configuration, leading to Jahn-Teller-type distortions in the excited state, which can enhance non-radiative decay. In others, operating by LLCT mechanisms, geometric distortion in the excited state can still play a role but there is no change in d-electron count and the metal center is much less involved.

The subsequent paragraph describes those with coinage metals (Cu, Ag, Au), which display linear two-coordinate, three coordinate and four coordinate geometries. Coinage metal complexes display closed-shell d^{10} ground state configuration. As a consequence the deactivation via MC dark states is absent however other non-radiative mechanisms involving excited state distortion occurs, for instance tetrahedral complexes rearrange towards a more planar geometry. In fact this explains why certain complexes can be luminescent in solid state or in films and why in solution the same complex is not luminescent. The flattening of the excited states renders the coinage ions accessible for coordination to solvent molecules or counter ions and as a consequence the formed excited complexes are non-luminescent.[55] Moreover the abundant copper complexes display a small energy gap ΔE (^{1}MLCT-^{3}MLCT) less than 1000 cm^{-1} which enable them to emit via prompt fluorescence or thermally activated delayed fluorescence (TADF) at room temperature. Therefore copper in particular and other coinage metal complexes are capable of harvesting singlet and triplet excitons for OLEDs applications.[56-57]Finally, we propose the development trend of NHC metal complexes, which presents attractive research prospects in the aforementioned fields.

2-Luminescent platinum(II) complexes with *N*-heterocyclic carbene ligands

2.1 Platinum (II) complexes with phosphines

Cyclometalated platinum(II) complexes containing NHC are currently considered as important class of compounds for multiple reasons.[1,58] For instance they show rich optical properties with high quantum yields and long lifetimes.[59-62] Moreover these compounds display stable square-planar geometry with a d^8 electronic configuration, as a consequence this allow them to form metal-metal and π–π interactions at the supramolecular level, which impact profoundly the properties of their electronic excited states (Figure 2).[63-74]

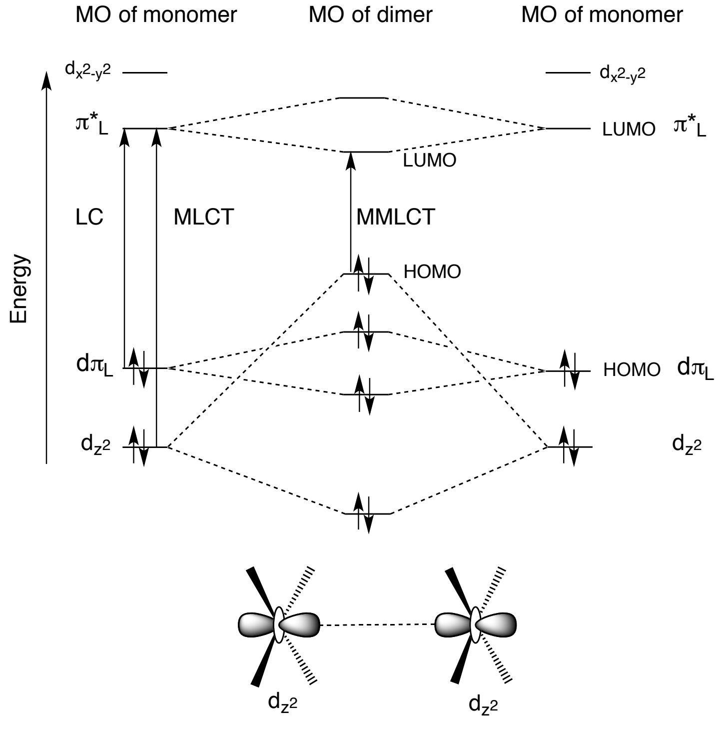


Figure 2. Simplified molecular orbital diagram for square planar platinum complexes involving monomer and dimer, showing the relative electronic transitions

On the other hand, upon modification of the substituents whether on the aryl unit of the cylometalated ligand or at the carbene units or even replacing the ancillary ligands induce dramatic changes in the excited state energy and as a consequence changes the color of these attractive complexes. As mentioned previously, cyclometalated platinum(II) complexes display strong phosphorescence with high quantum yields, which make them attractive molecules for variety of applications as optical devices and in OLEDs technology.[75]

To this end, Sicilia and coworkers described a family of blue phosphorescent platinum(II) emitters, (**1**-**5**) in PMMA films (PMMA = Poly(methylmethacrylate)). The authors designed a series of complexes where an NHC-unit is linked to either a naphthyl group (π-extended system) or a phenyl ring to which a variety of functional groups were attached (Figure 3).[76-77] They also varied the ancillary ligands in order to study their effect on the photophysical properties. In solution at room temperature the complexes were not emissive; however in a rigid matrix (CH_2Cl_2, 77K), these molecules show bright and long-lived luminescence. Compounds **1**-**5** acted as blue or greenish-blue emitters in PMMA films with high quantum yields varying from 68% (**1**) to 93% (**2**). As mentioned previously square planar Pt(II) complexes are known to aggregate via π-π or M···M interactions. Indeed, the authors demonstrated the complexes with π-extended system (**3**, **5**) in solid-state displayed yellowish-orange emission attributable to π-π* excited states formed by intermolecular π-π interactions. Electroluminescent devices were prepared from neat films of the compounds acting as emitting layers; for instance, complex **2** behaved as blue-light emitter while complex **3** displayed yellow orange emission. Interestingly a mixture of both compounds **2**-**3** behaved as white light emitters.

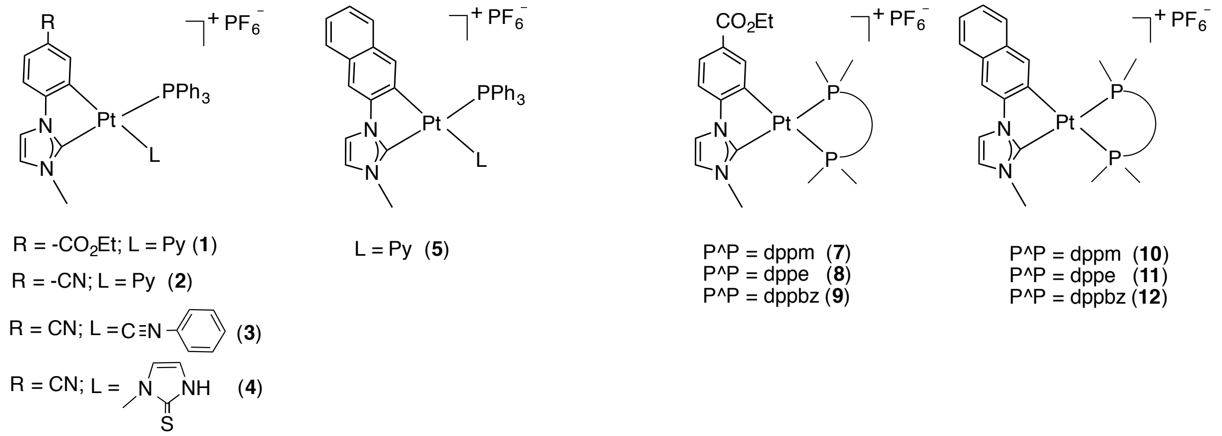


Figure 3. Cycloplatinated NHC complexes containing phosphine and diphosphine ligands.

In order to obtain warm white light emitting devices, the authors described the synthesis of cycloplatinated N-heterocyclic carbene compounds **7-12** by exchanging the ancillary ligands for chelating diphosphines (P^P).[78-79] The presence of two chelating ligands around the Pt(II) center confers robustness and thermal stability to these compounds. Complexes **7-9** displayed different optical properties when compared to those with a naphthyl group **10-12** (π-extended system), suggesting that emissions in these compounds arise from different kinds of excited states. For instance, in solution the emission of complexes **7-9** did not vary with concentration. In contrast complexes **10-12** at higher concentration displayed wavelength-dependent emissions. White light remote phosphor devices were achieved by combinations of platinum complexes **7** or **9** acting as blue emitters with the neutral compound [Pt(bzq)(CN)(CNXyl)] (bzq = benzoquinolate, Xyl = 2,6-dimethylphenyl) behaving as a red emitter using a 365nm LED as the pumping source. By changing the blue/red ratio, the authors were able to obtain a warm white light with optimal CRI and D_{uv} values and a great range of nominal CCT (4000-2000K).[78]

2.2 Platinum (II) complexes with bidentate acac ligands

Strassner and coworkers designed a family of neutral cycloplatinated N-heterocyclic carbene compounds containing β-diketone chelates as ancillary ligands (Figure 4).[1,80-82] Again the choice of a cyclometalation with a strong donating carbene unit (C^C*) is made in order to obtain phosphorescent blue emitters for use in organic-light emitting diodes (OLEDs). This type of compound was thoroughly investigated by the authors, where systematic changes were made to the substituents of the N-heterocyclic carbene unit as well as the functional groups on the chelating β-diketone moiety (Figure 4).

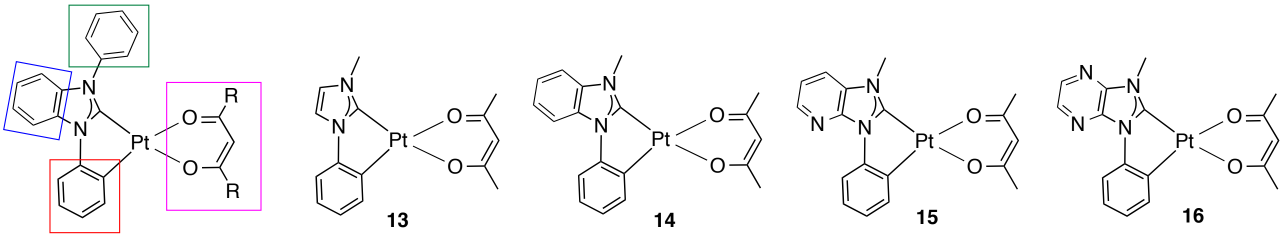


Figure 4. General motif of the cycloplatinated NHC complexes. Boxes indicate relevant modifications made on this type of complexes.

For instance the authors demonstrated that modification of the π-character of the NHC ligand improves the quantum yield of the Pt(II) complex. More interestingly a significant improvement of the quantum yield was achieved upon the introduction of a heteroatom in the backbone of N-heterocyclic carbene moiety. Indeed, while complex **14** displayed a 45% quantum yield, the platinum compound **15** with imidazopyridine showed 68% while complex **16** with imidazopyrazine provided 84% quantum yield.[83-84] This increase in quantum yield is accompanied by a decrease in the lifetime from 19.6 μs to 3.6 μs, which is appropriate for applications as OLED devices. The authors attribute the remarkably high quantum yield observed for the imidazopyrazine based complex to the fact that ^{3}MC dark states become less accessible than those compounds that lack a heteroatom in the backbone of the *N*-heterocyclic carbene.[83]

Moreover, attachment to the carbene unit of organic chromophores with extended π-systems such as dibenzofuran and dibenzothiophene was successfully achieved (Figure 5). Depending on the auxiliary ligand, these complexes displayed emissions in the deep blue or the orange-red part of the

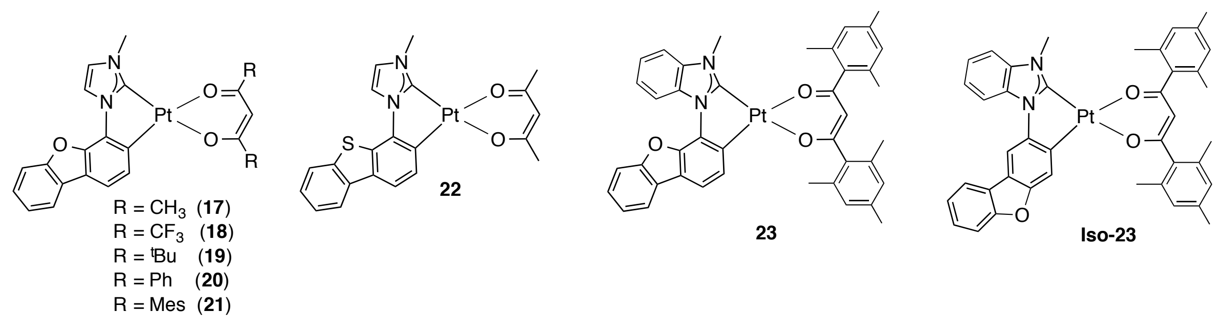


Figure 5. Cycloplatinated NHC (acac) containing π-extended organic chromophore.

visible spectrum. For instance, complex **17** in PMMA at 2 wt % displays vibronic emission bands at 463 nm, 497 nm with high quantum yield (90%) and a lifetime of 23μs. Replacement of the methyl group by a CF_3 affords complex **18**, which is non-emissive. Complexes **19** and **21** acted as blue emitters as well with high quantum yields (83%) and (91%) and lifetimes on the order of μs. As for complex **20** containing a phenyl group, a red-shifted structureless emission at 530 nm was observed. DFT calculations suggested that the phenyl ring rotates in the plane of the acac core (acac = acetylacetonate) in the triplet state and hence extending the π-conjugation. Complex **17** was used as a greenish-blue phosphor for OLED device. The electroluminescence spectra showed λ_{max} = 480 nm with structured emission bands. The maximum luminance depends on the doping concentration, for instance at 4900 cd m^{-2} (13V, 6% doping) to 6750 cd m^{-2} (13.2 V, 12% doping. The maximum EQE (6.2%) is achieved at the highest doping concentration of 12%.[85] The analogous cycloplatinated NHC-dibenzothiophene complex **22** showed lower performance when compared to the dibenzofuran congener **17**: the emission spectra recorded in thin film at 2 wt % emitter displayed vibronic bands at 474, 507 and 537 nm with a quantum yield of 63% and lifetime of 31 μs.[86] The authors attribute the high quantum yields observed in these complexes to the extended heterocyclic π-system due to the presence of the organic chromophores.

The cycloplatinated NHC-dibenzofuran containing mesityl-acac as auxiliary ligand was obtained as a mixture of two isomers complex **23** and **Iso-23** (NHC = benzimidazolin-2-ylidene).[87] The optical properties of the regio-isomeric complexes were found to be different. Both compounds displayed emissions in the blue region at 475 nm for **23** with vibronic progression, while **Iso-23** showed a broader band at 479 nm with comparable quantum yields of 84% for **23** and 80% for **Iso 23**. However their lifetimes showed marked differences, with a 10.8 μs lifetime for **Iso 23** which is 50% shorter than that obtained for complex **23** with τ = 22.4 μs.[87] Structure modifications made on substituted β-diketone ancillary ligands brought changes in the optical properties of the related platinum compounds. For instance, increasing the steric hindrance, upon moving from methyl group to larger substituents such as ^{t}Bu, phenyl, mesityl and tetramethyl-phenyl provoked an increase in the quantum yields and decrease in the lifetimes. Furthermore, while alkyl-substituted β-diketonates complexes displayed structured emission, those containing aromatic auxiliary ligands displayed a single structureless broad emission.

2.3 Platinum (II) complexes with alkynyl ligands

Venkatesan and coworkers designed another class of stable cycloplatinated NHC complexes containing dianionic biphenyls as auxiliary ligands (Figure 6).[88]

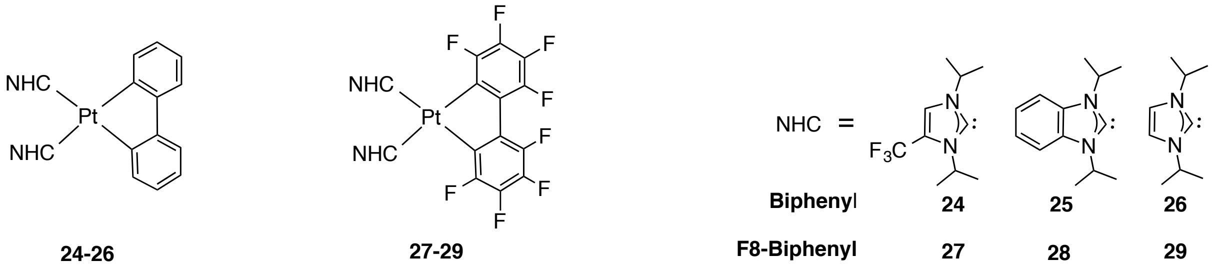
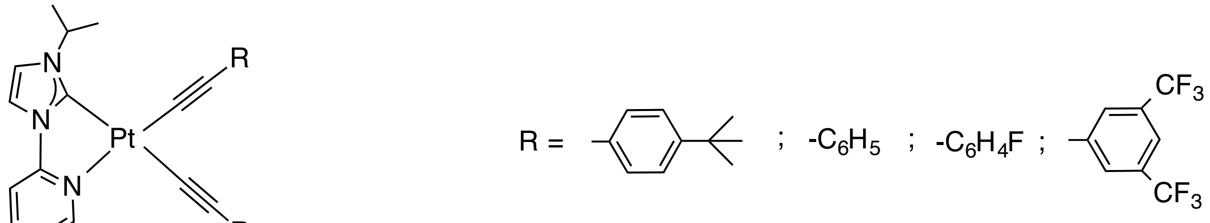


Figure 6. Cycloplatinated NHC containing biphenyl ligands.

Complexes **24-26** displayed high quantum yields up to 91% in thin films of PMMA at 3wt % emitter and showed vibronic emissions in the area 490-560 nm with lifetimes in the range 13.8 to 15.4 μs. The related compounds **27-29** containing the octafluorobiphenyl auxiliary ligand exhibited lower performance with quantum yields up to 46.1%. Moreover, the profile of the emission band is different, showing a broad band centered at 513 nm, which is hypsochromically shifted when compared to the nonfluorinated series. This difference is attributed to the electron deficient character of the F8-biphenyl ligand, which tends to stabilize the HOMO and eventually increases the HOMO-LUMO gap. TGA measurements carried out on compounds **26** and **29** to evaluate the thermal stability of these compounds revealed the onset of thermal degradation for **26** occurs at 309° C and for **29** at 374°C, highlighting their high robustness.

On the other hand the authors prepared a series of NHC-pyridine platinum complexes **30-33**, containing bis-acetylide ligands (Figure 7).[89] Such compounds behave as single component white light phosphorescent emitters. It should be mentioned that most of the other materials reported require multicomponent emitters that emit in the red, green and blue regions to cover the entire visible electromagnetic spectrum. However, disadvantages are that such white light emitting systems involve complicated mixing or doping processes and drawbacks related to device engineering.



30 **31** **32** **33**

Figure 7. Cycloplatinated NHC with bisacetylides

Complexes **30-33** displayed modulable high-energy triplet emission attributed to monomeric species in solution, however at higher concentration phosphorescence emission was observed assigned to excimer formation. As mentioned previously, square planar Pt(II) complexes tend to aggregate via π-π or M--M interactions. As a consequence, low energy excited states are generated and they are often concentration dependent. At room temperature in solution, the platinum compounds **30-33** were non-luminescent; however, at 1wt% in PMMA they exhibited structureless emission bands with λ_{max} in the range of 459-480 nm and emission quantum yields ϕ of 51-59%. Upon increasing the weight percentage of the complex in PMMA films, a low energy emission band at around 575-595 nm appeared. The maximum emission quantum yield was obtained at 20wt%; higher concentrations induced self-quenching. These compounds showed bright white photoluminescence covering the entire visible spectrum due to the presence of monomeric and excimeric emissions. For instance, complex **33** at a concentration of 20wt% in PMMA, emitted with CIE (Commission Internationale de l'Eclairage) color characteristic coordinates of x = 0.31 and y = 0.33, which are very close to the intended pure white light (x = 0.33, y = 0.33). Variation of the alkyne substituents allows fine-tuning of the emission leading to high quantum yields, thus rendering these compounds as promising candidates for single component triplet emitter based WOLEDs.

On the other hand Schanze and coworkers designed some luminescent square planar Pt(II) alkynyls displaying *trans* N-heterocyclic carbene ligands **34**-**44** (Figure 8).[75,90-91] Such compounds acted as blue phosphorescent emitters from triplet excited states ($^3\pi$-π*) centered mainly in the alkynyl-aryl moiety (-C≡C-Ar), with a minor contribution from ^{3}MLCT transitions. The platinum complexes display emissions at λ_{max} = 431-483 nm and lifetimes in the microsecond regime with quantum yields up to 45%. The authors demonstrated that variations of the N-heterocyclic carbene ligands, whether imidazole or benzimidazole, have little effect on the photophysical properties. Conversely, when the acetylide-aryl ligand was changed, dramatic variations in the emission energy, lifetime and phosphorescence were observed. It should be mentioned that the presence of strong σ-donating ability of the NHCs allows them to push the d-d states to higher energy and make these compounds luminescent, in contrast to their analogues containing phosphine ligands. However, the study on these compounds shows that, despite NHC ligands increasing the d-d state energy, yet it remains thermally accessible (ΔE = 1000 cm^{-1}) and therefore contributed significantly to the deactivation process at room temperature.

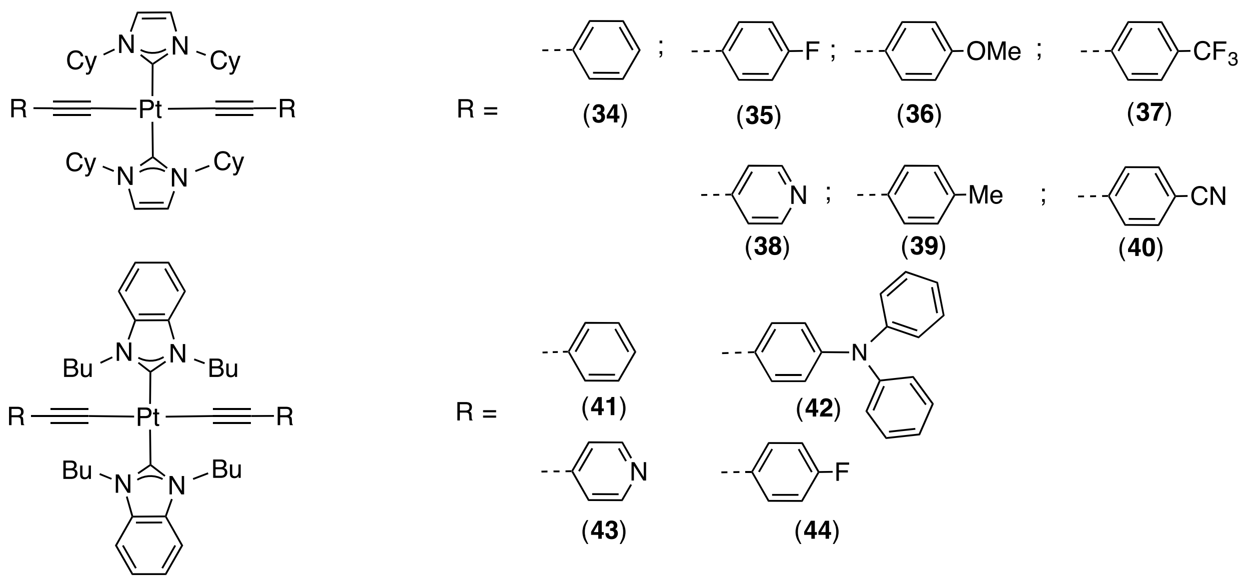


Figure 8. Pt(II)-bisacetylides containing *trans*-NHC-ligands.

In THF, the quantum yield of platinum complex **34** with imidazolin-2-ylidene was found to be 0.029, which increases by 10-fold when doped into a PMMA matrix along with a longer triplet excited state lifetime ($\Phi_{PMMA} = 0.3$, $\tau_{solid} = 9.4$ μs). Varying the doping concentration over the values 1, 10, 20, 50, 90, 100% shows qualitatively the same emission, suggesting no indication of excimer formation. The authors suggest that lack of excimer formation is likely due to the large cyclohexyl groups oriented orthogonally to the plane of the Pt-ligand bonds. Complex **34** was used as a blue phosphor for OLED devices. The electroluminescence spectrum showed a maximum at $\lambda = 444$ nm. The CIE coordinates of the device emission are (0.2, 0.2) with a maximum EQE of 8%.

Moreover, the platinum complexes displaying N-heterocyclic carbene with benzimidazole backbones display better performance as blue emitters. For instance, the platinum complex **41** with benzimidazolin-2-ylidene in THF displays a quantum yield of 0.08. When doped in PMMA matrix, the quantum yield increases to ($\Phi_{PMMA} = 0.56$, $\tau_{solid} = 21$μs) much higher than that obtained for complex **34**. Given the efficient phosphorescence in the solid state, complex **41** was used as a blue emitter for OLED devices. The electroluminescence spectrum exhibits an emission maximum at $\lambda =$ 439 nm, with 14% EQE, the highest performance within this class of compounds. The CIE color coordinates of the device emission are (0.16, 0.13) which is close to that of the National Television System Committee CIE color coordinate for ideal blue (0.14, 0.08).

2.4 Platinum (II) complexes with pincer ligands

Gray and coworkers constructed another family of N-heterocyclic carbene Pt(II) complexes **45**-**53** displaying a BIMCA pincer ligand (BIMCA = bis-imidazolylcarbazolate) and isonitrile or acetylides as ancillary ligand (Figure 9). The BIMCA ligand contains an organic carbazole chromophore, to which are directly attached two NHC units, generating a rigid (C^N^C) pincer ligand around the Pt(II) center.[92-93] Owing to steric factors around the metal center, the X-ray structures of these complexes showed that the metal is tetra-coordinated displaying a distorted tetrahedral geometry instead of a square-planar structure.

Complexes **45**-**49** were weakly emissive in solution at 298 K; at 77K in CH_2Cl_2 they show emission maxima in the range of 460-475 nm. In the solid state they are moderately emissive displaying Φ_{PL} values up to 22%. Replacing the isonitrile by acetylide ligands, which are strong σ-donors, provided the related platinum alkynyls complexes **50**-**53**, displaying higher optical performance.

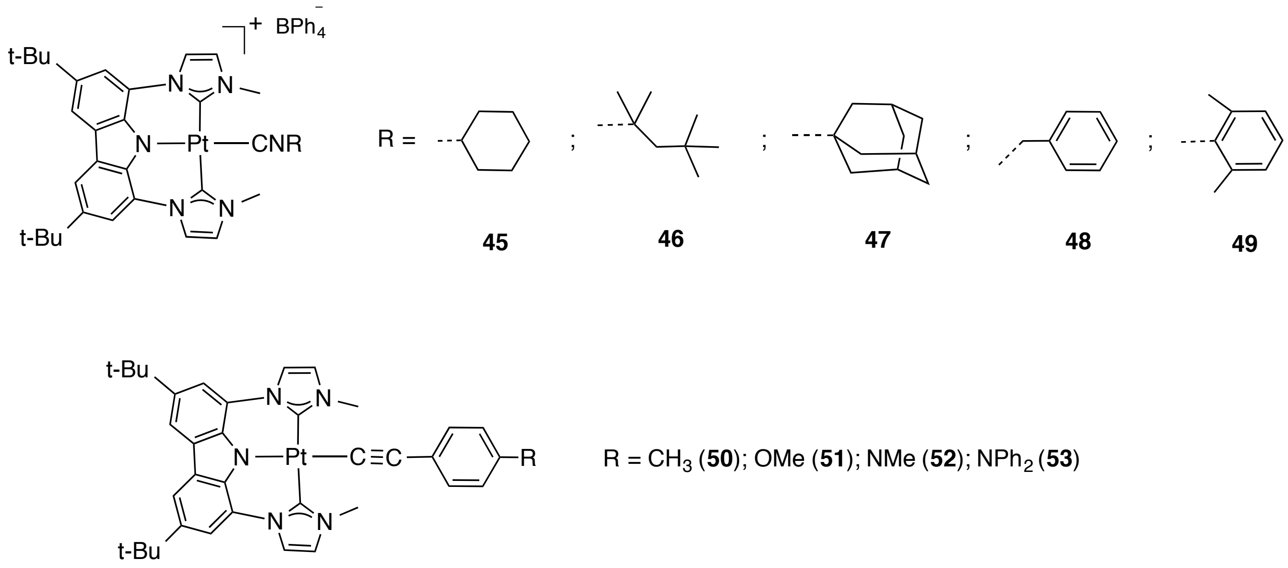
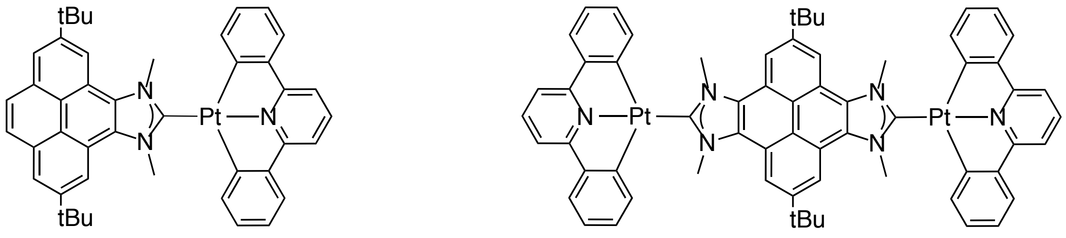


Figure 9. Cycloplatinated-NHC with (C^N^C) pincer ligand.

In the solid state, complexes **50-53** acted as blue/green emitters with λ_{em} = 496-523 nm. As for complex **51**, an intense green emission was observed with CIE 1931-coordinates (0.29, 0.65) and Φ= 93% with τ = 11ms. TD-DFT calculations were performed to rationalize the optical properties of this kind of compound, suggesting that the origin of the excited states is ^{3}(MLCT/LL) with high contribution from the ^{tBu}BIMCA pincer ligand in the HOMO and the LUMO as well.

On the other hand, Peris and Poyatos described the synthesis of some cyclometalated Pt(II) complexes **54-55** containing (C^N^C) pincer ligand, (C^N^C = 2,6-diphenylpyridine) supported by pyrene-based mono- or bis –NHC-ligands.[94] The authors intended to prepare a novel class of emissive complexes by combining the benefits of an organic chromophore and that of an inorganic Pt(C^N^C) luminophore within the frame of stable complexes provided by the NHC ligands (Figure 10).



54

55

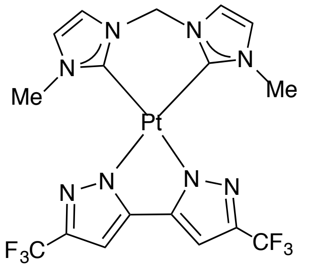
Figure 10. Cyclometalated Pt(II) complexes **54-55** supported by pyrene-based NHC-ligands.

The UV-vis spectra of the mono-NHC-Pt(II) and bis –NHC-Pt(II) complexes **54** and **55** recorded in CH_2Cl_2, showed intense absorption bands between 246-255 nm and 236-262 nm respectively. Additional less intense bands are visible up to 352 nm for **54** and 394 nm for **55**. The related pyrene-azolium salts (free ligands) displayed intense vibronic–structured bands at 310-340 nm with bands spacing of 1488 and 1443 cm^{-1}. These absorption bands are attributed to pyrene-centered π-π^* transitons.

At room temperature, complexes **54** and **55** were emissive in CH_3CN. Both complexes displayed similar emissions pattern in the range of 372-437 nm with short biexponential decays featuring a long component 70.9 ns and short contribution 6.5 ns lifetimes for **54** and 42.6 ns and 3.2 ns for **55** with comparable quantum yields Φ = 3.5% and 3.1% respectively. It should be mentioned that the mono- and bis-pyrene-azolium salts displayed similar emissions form but displayed higher quantum yields Φ = 32% and 42% respectively with short lifetime in the nanosecond regime for mono-azolium (78.8 ns) and bis-azolium (43.1 ns) suggesting the fluorescence character of the observed emissions. This data suggests a minor contribution from the Pt(II) center on the pyrene-based excited states in the above complexes.

2.5 Platinum (II) complexes with bis carbene (NHC) chelating ligands

Chi, Chen and Hung described the synthesis of some square planar Pt(II) complexes of general formula [Pt(C^C)(X^X)] (**56**-**63**) displaying bis-carbene chelating ligand (C^C) associated to three functional dianionic azolate chelates (X^X = 5,5'-di(trifluormethyl-3-3'-bypyrazolate (**56**-**58**); X^X = 5,5'-di(trifluormethyl-3-3'-bi-1,2-4triazolate (**59-60**); X^X = 3-trifluormethyl-5-(4-(trifluoromethyl)phenyl-pyrazolate (**61**-**63**) (Figure 11).[95]



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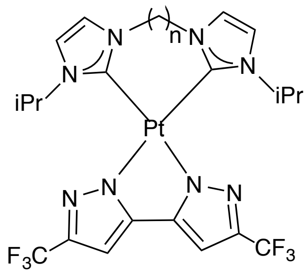
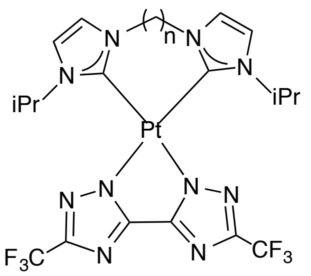
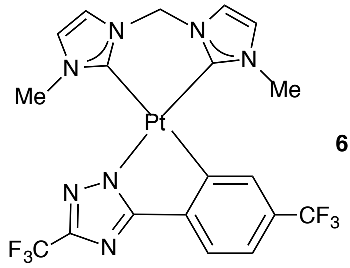


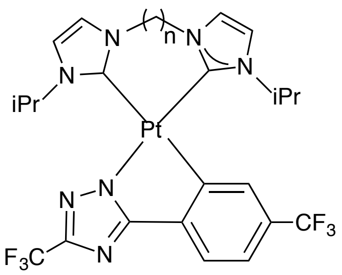
n = 1; (**57**)
n = 3; (**58**)



n = 1; (**59**)
n = 3; (**60**)



61



n = 1; (**62**)
n = 3; (**63**)

Figure 11. Cycloplatinated complexes with bis-NHC chelating ligands.

Complexes **56-63** were found to be non-emissive in solution at room temperature, in contrast in powder form they exhibited strong emission varying from purple to sky-blue emission with high quantum yields approaching unitary for complexes **56-57** with lifetimes of 29-33 μs respectively. The authors also noticed that the size of the linkage between the two carbene units affects the emission properties of these compounds. For instance the biscarbene complexes **58** and **60** with propylene linkage are weakly emissive with quantum yields of 6% and 2% respectively. The authors explain this behavior to be a consequence of the propylene spacer which forces the dicarbene chelate to display a perpendicular orientation to the square-planar Pt(II) architecture resulting in destabilization of the emitting excited state and hence quenching the emission. TD-DFT calculations were employed and showed that these compounds display a combination of ^{3}LLCT/^{3}LMCT/^{3}IL emission excited states, unlike related square planar Pt(II) compounds which usually emit from a combination of ^{3}MLCT and ^{3}IL π-π* electronic transition states. Compounds **61-62** were found to be amenable to prepare OLED devices. In particular complex **61** showed better performance, displaying high efficiency (8.9%, 19.4 cd.A^{-1}, 22.5lm.W^{-1}) with a sky blue emission and CIE$_{x,y}$ coordinates of (0.18, 0.32).

On the other hand *Che and coworkers* designed another class of square planar Pt(II) complexes (**64-69**) supported by bis-carbene chelates and a combination of bidentate terphenyldiacetylide ligands (Figure 12).[96] It is believed that such a type of chelating ligands should bring rigidity to the system, in addition the nature of strongly σ-donor ligands tend to enhance their photophysical properties.[61]

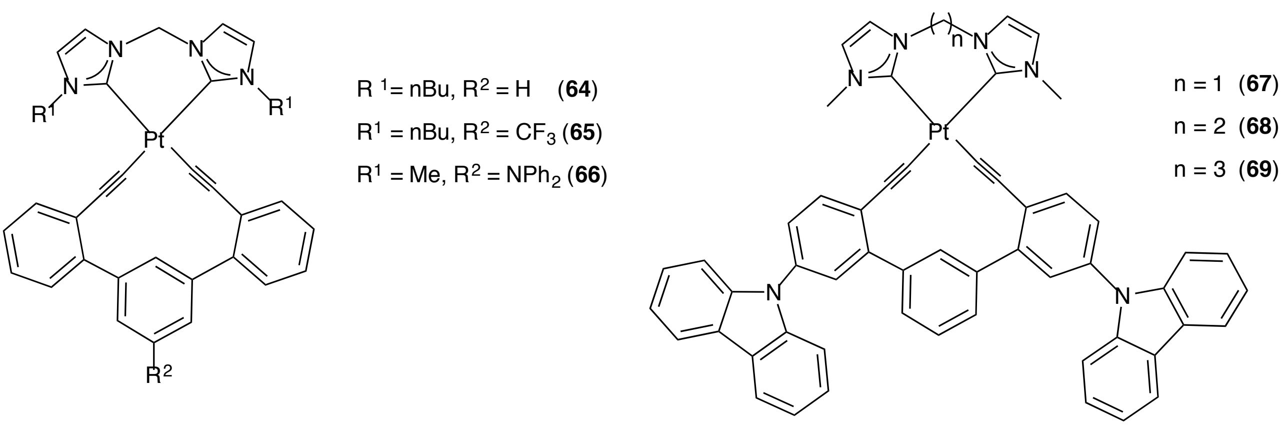


Figure 12. Pt(II)-bisacetylides with bis-NHC chelating ligands

Compounds **64-69** were found to be emissive in CH_2Cl_2 solution at room temperature. For instance those containing carbazole substituents at the terphenyldiacetylide **67-69** are more emissive (Φ = 23-27%) with lifetimes (τ = 28-42.6 μs) than the non-substituted compounds **64-66** (Φ = 3.4-5.4%) and displaying shorter lifetimes (2.7-4.1 μs). Moreover all complexes displayed vibronically structured emissions profile and were assigned to originate primarily from metal-perturbed ^{3}IL (π-alkynyl-π*alkynyl excited states. Within the same series **67-69**, the authors note a minor variation in emission quantum yields (23-27%), when the spacer length (-CH$_2$-)n of the biscarbene ligands is varied (n= 1 to 3). Furthermore in solid state at 298 K, these compounds were also emissive displaying again structured emission bands ranging from blue-green to yellow emission with λ_{max} = 470-533 nm, and at 77K they display emission bands at λ_{max} = 470-530 nm. In glassy media at 77K, complex **65** displays a structureless emission band at λ = 477 nm with full width at half maximum, (FWHM) of 75 nm. In contrast complexes **64**, **66**-**69** exhibited structured emission at λ max = 448-497 nm. The vibrational progressive spacing for complex **67** was estimated to be 1470 cm^{-1}, which indicates the skeletal vibration is assigned to the diacetylide ligand.

The upcoming paragraph will present recent advances on luminescent iridium complexes containing N-heterocyclic carbenes.

3-Luminescent iridium(III) complexes with *N*-heterocyclic carbene ligands

3.1 Homoleptic cyclometalated iridium complexes facial versus meridional regioisomers

Octahedral cyclometalated Ir(III) complexes possess a range of important properties such as rigid configurational stability, high emissive quantum yield (ϕ), microsecond-regime phosphorescence lifetime (τ) and high electrochemical stability.[4,97-105] Moreover they act as high efficiency emitters in OLED devices.[50,106-112] This field of study has attracted much attention and continues to be highly investigated; thus we intend to present the most recent work in this area. As mentioned previously, the presence of NHCs, which act as strong σ-donor ligands, can serve as a tool to push the metal-centered d-d transitions to higher energy in order to make them thermally inaccessible.[4,113-115]

The first cyclometalated iridium complexes **70**-**71** containing NHC ligands were reported in 1982 by Lappert and coworkers (Figure 13).[116] Forrest, Thompson and coworkers investigated thoroughly this type of compound in order to construct blue emitters. The choice of NHCs in the coordination sphere of cyclometalated iridium complexes is crucial, because they tend to emit from high-energy triplet states.[117-121]

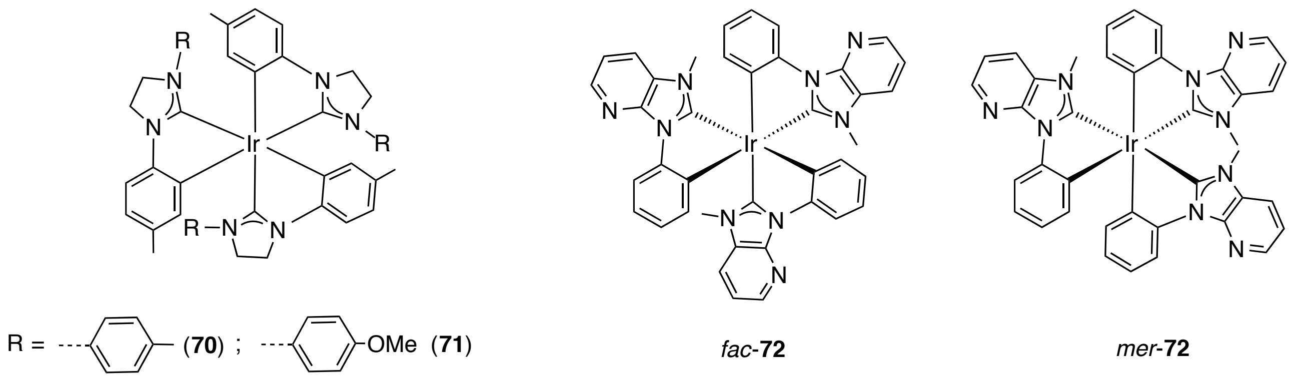
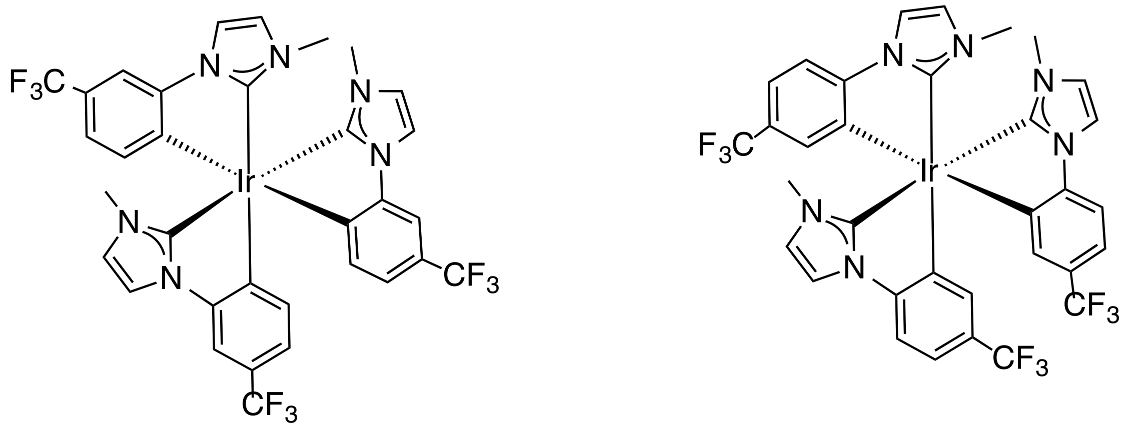


Figure 13. Homoleptic cycloiridated NHC complexes displaying facial and meridional regioisomers.

More recently the group designed a luminescent cyclometalated NHC iridium complex in which the backbone of the imidazole ring contains a fused pyridine moiety. The two geometrical isomers *fac*-**72** and *mer*-**72** were isolated and characterized (Figure 13).[107] The electrochemical properties were investigated for both compounds and allowed to estimate the HOMO-LUMO gaps, for instance the *mer*-**72** isomer displayed the smaller gap. At room temperature in CH_2Cl_2 both complexes are highly emissive in the blue region at λ = 418 nm, (Φ = 76%, τ = 1.2μs) for *fac*-**70** and at λ = 465 nm, (Φ = 78%, τ = 0.8μs) for *mer*-**72**. This result indicates that the emission of complex *mer*-**72** is red-shifted compared to the other geometrical isomer, in line with the electrochemical properties. The study also shows a more dominant ligand-centered ^{3}LC transitions relative to a ^{3}MLCT excited states in *fac*-**72**, while the emission in complex *mer*-**72** stems more from the ^{3}MLCT emission rather than the ligand-centered ^{3}LC excited state. Due to their high optical performance in solution and solid state, both compounds were employed as blue emitters for OLED devices. The electroluminescence spectra of *fac*-**72** and *mer*-**72,** measured at a current density of J = 10 mA cm^{-2}, displayed emission in the deep blue with CIE coordinates of (0.16, 0.09) and (0.16, 0.15) with maximum external quantum efficiencies EQE = 10.1 and 14.4 respectively.

Zysman-Colman, Samuel and coworkers, prepared the homoleptic meridional cyclometalated iridium complexes **73** and **74** containing NHC ligands (Figure 14).[122] To enlarge the HOMO-LUMO gap, the electron-withdrawing group CF_3- was attached to the phenyl-rings in the *para*- and *meta* positions relative to the carbene-unit, which permits sufficient stabilization of the HOMO energy of the emissive triplet state.



mer-**73** *mer*-**74**

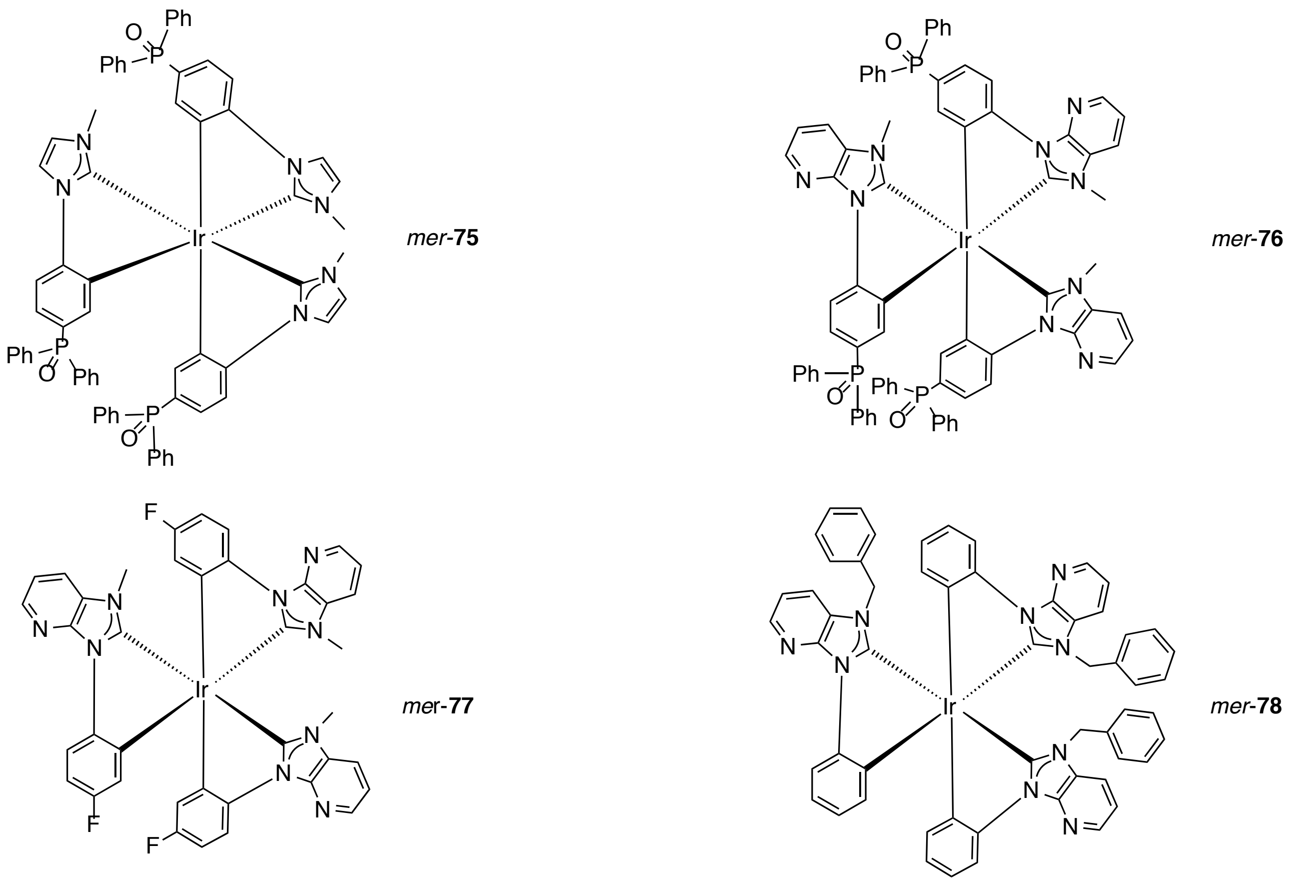
Figure 14. Homoleptic cycloiridated (NHC-trifluoromethyl-phenyl) complexes displaying meridional regioisomers.

Both complexes act as blue emitters in CH_2Cl_2 solution and in PMMA film at 10% emitter. At 298K in solution, complex **73** displayed structured emission at λ = 414 nm with moderate quantum yield Φ = 25%, complex **74** behaved similarly (λ = 412 nm) but showed higher quantum yield Φ = 72%. Both complexes exhibited biexponential decay lifetimes τ with longer τ at 77K in de-aerated 2-MeTHF, when compared to those at 298 K in degassed CH_2Cl_2. Due to their interesting optical properties, complexes **73** and **74** were used as blue emitters for OLED devices. The optimal device consisted in using complex **74** as the emitter and complex **73** as an efficient exciton/electron blocker, and the device provided blue emission with CIE coordinates (0.154, 0.052) with external quantum yield EQE of 13.4%; this value decreases slightly to 12.5% at 100 cd m^{-2}. This data fulfills the requirement for a deep blue OLED application. For instance, the television display criterion is of (0.14, 0.08) as specified by the European Broadcast Union (EBU). It should be mentioned that most cyclometalated iridium complexes do not meet the deep blue chromaticity requirements; they exhibit CIE_y coordinates greater than 0.1 because their triplet energies are not sufficiently high (≥ 2.8 eV).

The development of blue triplet emitters for OLED devices with high EQE continues to be a challenging objective. As mentioned previously, cyclometalated iridium complexes containing NHC ligands are among the most promising candidates. To this end, Jin and coworkers prepared a series of homoleptic cyclometalated iridium complexes **75**-**78**, and isolated the meridional kinetic isomers (Figure 15).[123] Complexes **75**-**77** were designed with different electron-withdrawing groups being introduced at the phenyl ring (-F, $O=PPh_2$) in order to obtain pure blue phosphoresce by elevating the T_1 energy of these emitters. As a consequence, complex **77** with a pyridyl-carbene ligand exhibits pure blue phosphorescence with high quantum yield (95%), and short lifetime (τ = 0.116μs), the electroluminescence (EL) spectrum of **77** displays emission band with λ = 430 nm with the CIE color emission (0.16, 0.08) where the CIEy perfectly matches the NTSC standard blue. However, complex **77** shows slightly a lower maximum EQE (7.1%) than that of **75** {EQE = 8.6%, CIE (0.16, 0.12)}, but higher than that displayed by complex **76** {EQE = 3.8%, CIE (0.17, 0.13)}. The authors attribute this downfall to the intermolecular interactions at higher doping concentration. To overcome this obstacle, the authors prepared the meridional kinetic isomer **78** in 65% yield in which a benzyl unit instead of a methyl was introduced to the pyridyl-carbene unit.

The presence of a benzyl unit suppresses intermolecular interactions and triplet-triplet annihilation (TTA) of the cyclometalated iridium complex **78** at high doping ratios, owing to the steric hindrance. Moreover placement of a benzyl group on the pyridylcarbene unit reduces concentration quenching of the *mer*-Ir complex **78**. The electrochemical and photophysical properties of complex **78** were investigated. At room temperature, complex **78** displays a blue emission at λ = 450 nm in 2-MeTHF. This emission band is sensitive to the solvent polarity in use; for instance in CH_2Cl_2, this band is red shifted to λ = 470 nm. When doped in diphenyl(4-

(triphenylsilyl)phenyl)phosphineoxide (TSPO1) film at 10vol% of complex, the emission band appears at λ = 442 nm with very high quantum yield at (Φ) = 95%.


mer-**75**

mer-**76**

mer-**77**

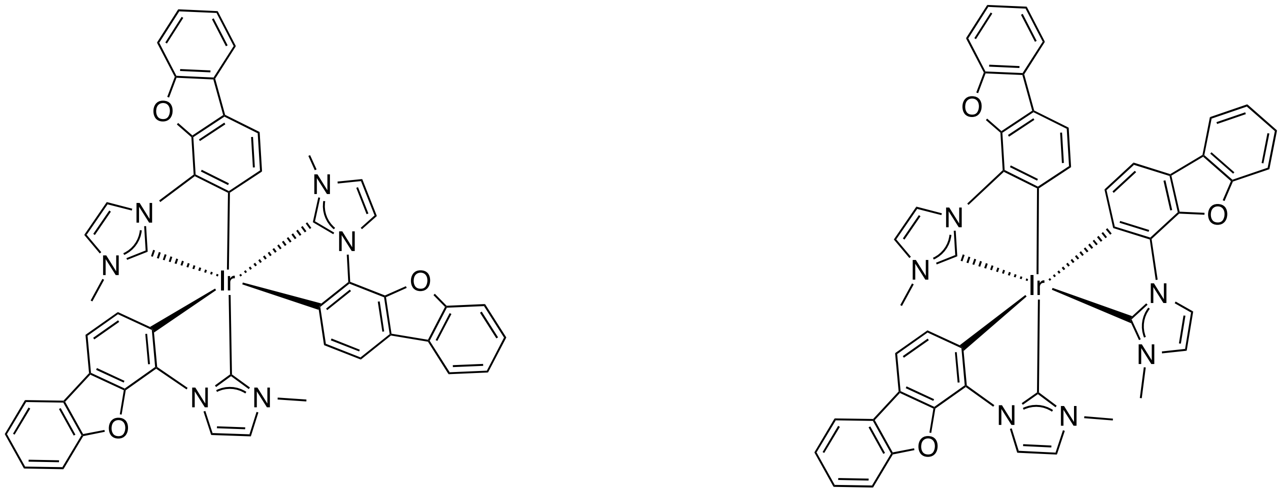
mer-**78**

Figure 15. Homoleptic cyloiridated NHC-complexes displaying meridional regioisomers

Due to its excellent optical properties, complex **78** was used as a blue emitter for OLED devices. The manufactured device with high dopant ratio (40 vol%) of complex **78** gives a deep blue emission with CIE coordinates (0.149, 0.085) and a very high EQE of 24.8%.[124] The authors suggest that these important results highlight the role of the N-benzyl substituted pyrimidazole carbene-based Ir(III) complex for the fabrication of high performance deep blue OLEDs.

The impact of the geometrical isomers whether meridional or facial on the optical properties of cyclometalated iridium complexes was investigated by Kang, Son and coworkers.[125] Thus the complexes *fac*-tris(*N*-dibenzofuranyl-*N*-methylimidazole)$_3$Ir(III) (*fac*-**79**) and *mer*-tris(*N*-

dibenzofuranyl-*N*-methylimidazole)$_3$Ir(III) (*mer*-**79**) were prepared and their photophysical properties were investigated and compared (Figure 16).[126]Compounds **79** were originally reported by Sasabe and Kido.[127] These compounds contain in their structure a dibenzofuranyl, which acts as an organic chromophore.



fac-**79**

mer-**79**

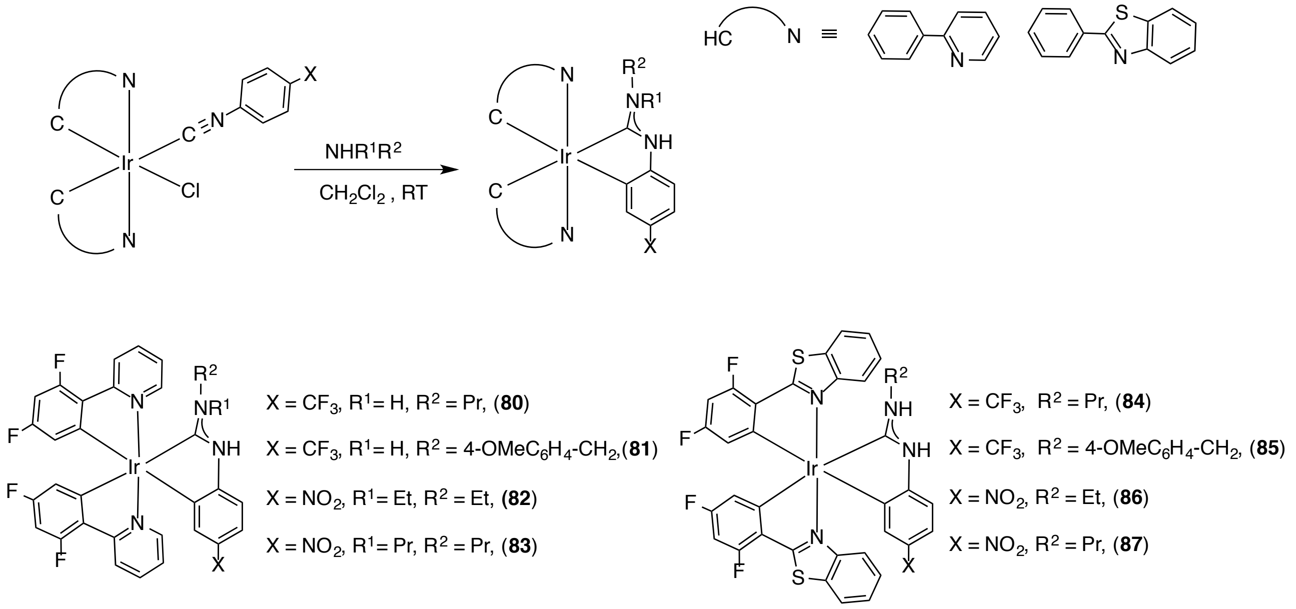
Figure 16. Homoleptic cyloiridated NHC complexes containing organic chromophore, displaying facial and meridional regioisomers

The electrochemical properties were first studied in CH_2Cl_2 solution. The cyclic voltammogram (CV) of *mer*-**79** shows a lower oxidation potential (E_{ox} = 0.17 V *vs*. Fc/Fc$^+$) than *fac*-**79** (E_{ox} = 0.26 V *vs*. Fc/Fc$^+$) while the reduction potentials of *fac*-**79** and *mer*-**79** are almost similar (E_{red} = 2.37 V and 2.64 V *vs*. Fc/Fc$^+$). This data indicates that *mer*-**79** has a smaller energy gap than *fac*-**79**, which eventually affects their relative photophysical properties. Indeed at 298 K the photoluminescence spectrum of *mer*-**79** showed a bathochromic shift with λ_{max} = 450nm when compared to the emission of *fac*-**79** (λ_{max} = 443 nm), with quantum yields Φ of 53% and 68% and lifetimes τ = 11.0 μs and τ = 11.2 μs respectively. Both isomers displayed structured emissions, suggesting that emissions originate not from pure ^{3}MLCT states but from the mixed ^{3}LC/^{3}MLCT transitions, although *mer*-**79** displayed a higher ^{3}MLCT contribution, as evidenced by solvent polarity dependence emission spectra and lifetime. Due to their high optical properties, these compounds were investigated as dopants for OLED devices. Both compounds act as blue emitters when doped in in diphenyl(4-(triphenylsilyl)phenyl)phosphineoxide (TSPO1) film at 10% of either complex. The electroluminescence spectra display blue emissions with the CIE chromaticity for *fac*-**79** device (0.14, 0.11) and EQE of 18.5% and for *mer*-**79** device (0.14, 0.14) and EQE of 18.2%.

3.2 Heteroleptic cyclometalated iridium complexes

3.2.1 Containing acyclic diamino carbenes (ADC) ancillary ligands

Teets and coworkers prepared some luminescent heteroleptic cyclometalated iridium complexes containing acyclic diaminocarbene (ADC) ancillary ligands (Figure 17). These compounds are formed via metal-mediated nucleophilic addition to a metal-coordinated isocyanide, with subsequent orthometalation of the ADC under mild conditions.[128-129]



X = CF_3, R^1= H, R^2 = Pr, (**80**)

X = CF_3, R^1= H, R^2 = 4-OMeC_6H_4-CH_2,(**81**)

X = NO_2, R^1= Et, R^2 = Et, (**82**)

X = NO_2, R^1= Pr, R^2 = Pr, (**83**)

X = CF_3, R^2 = Pr, (**84**)

X = CF_3, R^2 = 4-OMeC_6H_4-CH_2, (**85**)

X = NO_2, R^2 = Et, (**86**)

X = NO_2, R^2 = Pr, (**87**)

Figure 17. Cyclometalated iridium complexes containing acyclic diamino carbenes.

Two sets of complexes were prepared, those containing the cyclometalated ligand "F2ppy" (**80-87**) and those with 2-phenylbenzothiazole "bt" (**84-87**). Unlike those with NO_2-functionality (**82-83**; **86-87**) all other compounds were emissive in fluid solutions of de-aerated CH_2Cl_2 at room temperature. At low temperature when doped into PMMA films, these complexes become more luminescent. Complexes **80-81** with difluorophenylpyridine display blue emission in CH_2Cl_2 with

λ_{max} = 498 and 495 nm, and quantum yields (Φ) of 0.22 and 0.18 respectively. The related compounds **84-85** with bt "C^N" (bt = 2-phenylbenzothiazole) ligands exhibit yellow-orange broad emissions at λ_{max} = 588 and 585 nm respectively with significantly lower quantum yields (Φ) of 0.049 (**84**) and 0.047 (**85**). All complexes exhibit a biexponential decay lifetime τ with longer weighted average τ in the range of 0.90-1.1 μs for the F2ppy complexes **80-81** and smaller values of 0.50-0.60 μs for bt complexes **84-85**. The four CF_3-substituted emissive complexes (**80-81**; **84-85**) when doped into PMMA thin films (2 wt%) show dramatic increases in the quantum yields; for instance complexes **80-81** act as blue-green emitters with quantum yields of 79%, while compounds **84-85** display quantum yields of 30-38% and behave as orange emitters. It should be mentioned that the acyclic diaminocarbene (ADC) ancillary ligands are even better σ-donor than the usual NHCs as demonstrated by the electrochemical properties of these compounds, where the oxidation potentials are cathodically shifted when compared to related compounds with NHC ligand (NHC = Imidazolin-2- or benzimidazolin-2-ylidene). The authors have compared the X-ray solid-state structures of the acyclic diamino carbene complex **80** and the NHC cyclometalated iridium complex $[(F2ppy)_2Ir(C^\wedge C)]$ (C^C = 4-CF_3-C_6H_4-benzimidazolin-2-ylidene). The comparison revealed a notable difference between the carbene N-C-N angles, for instance in the NHC complex the N-C-N angle is 105.2(4)°, while in complex **80** this angle is wider (116.4(5)°). The authors suggest that ADC complexes display carbenes with higher donor ability because the widening of the carbene bond angle allows for greater $N \rightarrow C_{carbene}$ π-donation. As a consequence, the iridium-centered HOMO energies in complexes **80-81** are strongly destabilized due to the strong donation character of the ADC ligands. On the other hand, the group prepared other heteroleptic cyclometalated iridium complexes **88-90** with mixed carbene ligation, i.e. containing both NHC-derived cyclometalating ligands as well as the ADC ancillary ligands (Figure 18).[130]

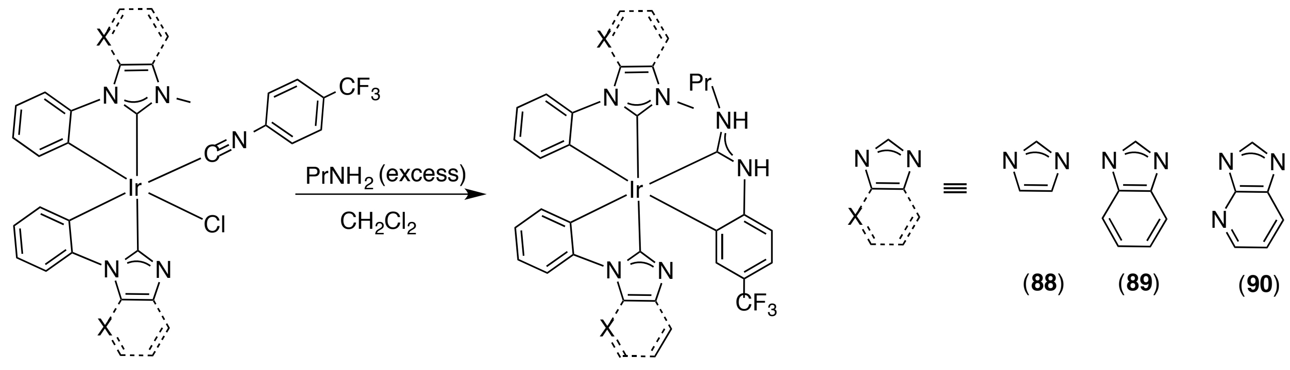


Figure 18. Cyclometalated-NHC iridium complexes containing acyclic amino carbenes.

The electrochemistry and the photophysical properties of **88-90** were investigated. In CH_2Cl_2 solution at room temperature, these compounds are weakly emissive with emissions observed at λ = 420 nm for **89**, and at λ = 511 nm for complex **90** while **88** is non-emissive. However, in PMMA films at 2wt%, they behave as blue emitters with higher quantum yields. For instance, complexes **88** and **89** display emissions at λ = 418 nm for both compounds but with different quantum yields (Φ) of 0.13 and 0.31 respectively. Complex **90** emit at λ = 459 nm, blue-shifted significantly in PMMA film with respect to CH_2Cl_2 and with a higher quantum yield of (Φ) = 0.48. Complex **90** gives sky blue coloration with the CIE coordinates of (0.16, 0.18), while complexes **88** and **89** display deep blue emissions with CIE coordinates of (0.16, 0.07) and (0.16, 0.10) respectively. The authors suggest that these mixed carbene complexes can be used as dopants for pure blue OLEDs.

3.2.2 Containing naphthalimide chromophore

Naphthalimide (NI) is a versatile organic chromophore and has been widely used in fluorescent molecular probes and as DNA targeting, anticancer and cellular imaging agents.[29-30,32,34] More recently efforts were devoted to prepare metal complexes containing this organic chromophore.[131-133] Amouri and coworkers prepared a series of phosphorescent heteroleptic cyclometalated Ir(III)-complexes displaying *N*-heterocyclic carbenes linked directly to a *naphthalimide fluorophore* (NI = naphthalimide).[134] Two sets of compounds were prepared containing NHC-derived naphthalimide ligands (NHC = Imidazolin-2-ylidene, (**91-93**); Benzimidazolin-2-ylidene, (**94-96**)) (Figure 19).[135]

These compounds are very stable in solution and in solid state, due to the presence of the NHC-NI (C^C) ligands.

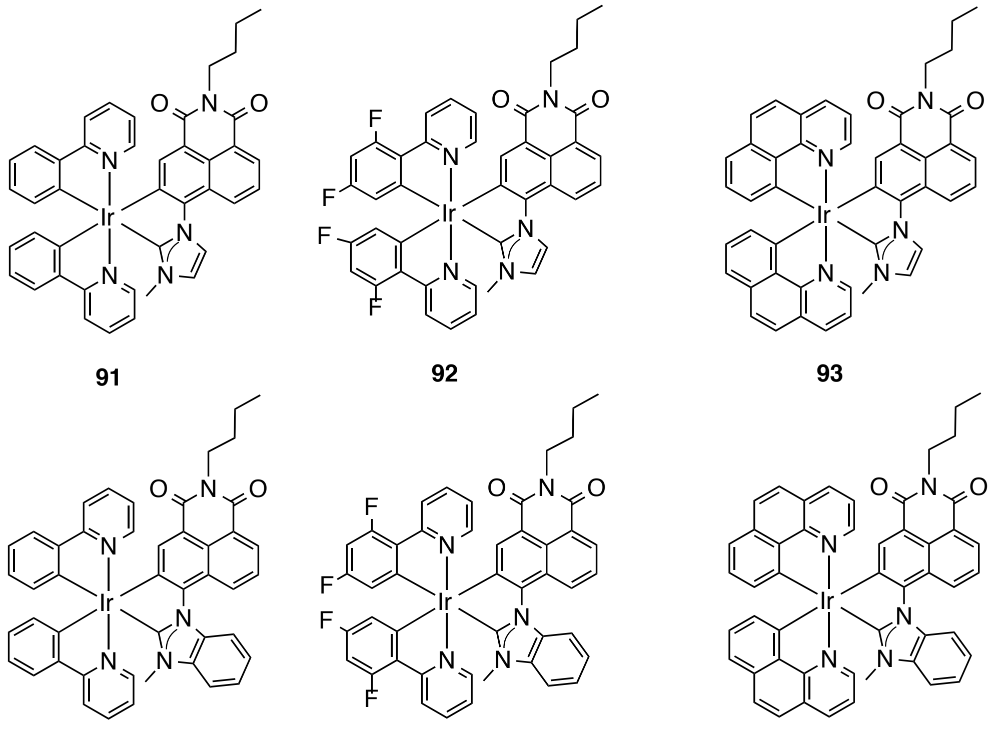


Figure 19. Cyclometalated-NHC iridium complexes containing naphthalimide chromophore.

All complexes act as deep red emitters CIE (0.71, 0.29) in fluid solution and solid state at room temperature and display long lifetimes in the microsecond regime with good quantum yields. In solution broad band emissions are visible which extend beyond 700 nm. It is well know that cyclometalated iridium of the type Ir(C^N)$_3$ without organic chromophores commonly emit from a ^{3}MLCT state. In the above compounds the art of linking directly the organic naphthalimide chromophore to the carbene unit, induce a dramatic change in the nature of the excited states from ^{3}MLCT to mostly naphthalimide-centered ^{3}LC, thanks to the iridium center with large spin-orbit coupling (SOC), which facilitates the intersystem crossing (ISC) to the triplet manifold of the organic dye.

Complexes **92** and **95** containing the cyclometalated ligand 2,4-difluorophenylpyridine (dfppy) provided a more vibrational band pattern structure. These emissions were hypsochromically shifted by 450–650 cm^{-1} relative to the other compounds. Moreover the radiative rate constant ($k_r = \phi / \tau$) was determined for all these compounds and was found to be in the order of 10^4 s^{-1} suggesting a predominantly ^{3}LC excited state. At room temperature in CH_2Cl_2 complexes **92** and **95** also have the highest quantum yields Φ (18% to 11% respectively) and the longest lifetimes (τ= 17.5 µs to 26.4 µs) of the series.

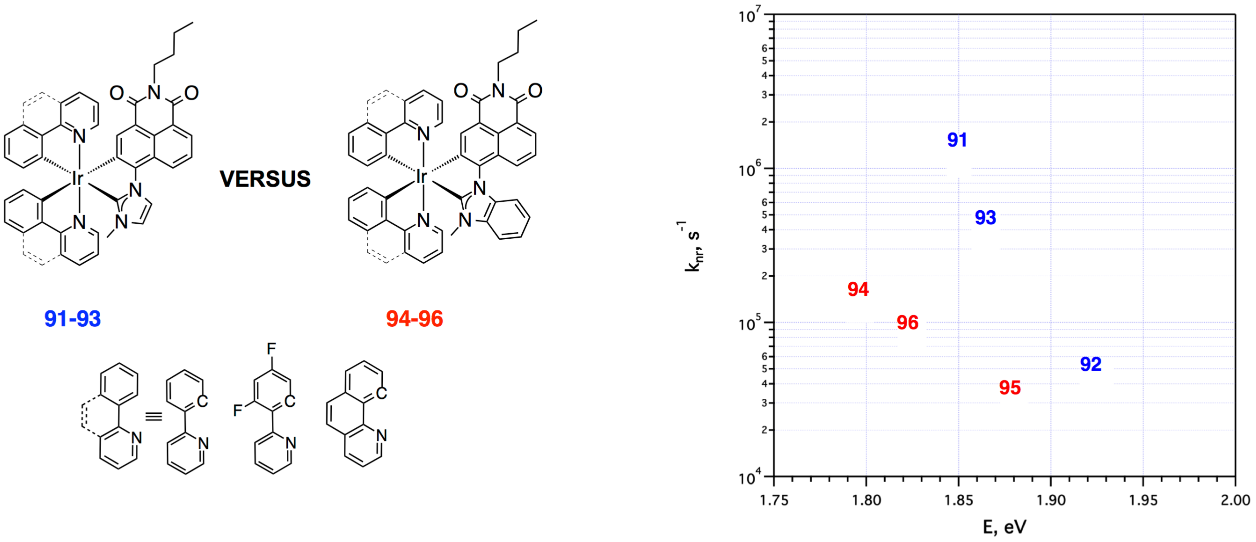


Figure 20. Plot of non-radiative rate constants, k_{nr}, as a function of the energy, E, of the emissive excited state of Ir(III)-NHC complexes (NHC = Imidazolin-2-ylidene, (**91-93**); Benzimidazolin-2-ylidene, (**94-96**) in CH_2Cl_2 at room temperature.

The influence of the NHC-derived naphthalimide ligand on the optical properties of these complexes was examined by plotting $k_{nr} = (1 - \phi) / \tau$, *vs*. the excited state energy E, measured at the maximum of the emission (Figure 20). The data obtained provided us with the following informations: (i) For both class of complexes whether with imidazolyl or benzimidazolyl carbenes, the k_{nr} constant increases linearly as the T_1–S_0 gap energy diminishes. This is line with the energy gap law. (ii) Moreover, these changes are faster in case of the complexes **91-93** with NHC = Imidazolin-2-ylidene (iii) The benzimidazolin-2-ylidene derivatives **94-96**, on the other hand, exhibits lower k_{nr} values relative to the analogous imidazolyl carbene complexes.[135] We feel that extending the π-conjugation at the backbone of the NHC-ligands should rigidify the system, which reduces the rate of non-radiative deactivations and eventually increases the quantum yield.

On the other hand *Amouri and coworkers* successfully prepared the related optically active compounds *Δ*-**91**$_{nBu}$, *Λ*-**91**$_{nBu}$ and *Δ*-**92**$_{nBu}$, *Λ*-**92**$_{nBu}$ by replacing the methyl group at the nitrogen of the carbene by an *n*-butyl chain to improve the solubility of these compounds (Figure 21). At room temperature they act as emitters in the far red and NIR regions. Their optical and chiroptical properties were investigated. Remarkably, the Vibrational Circular Dichroism (VCD) technique and TD-DFT allowed us to ascertain their stereochemistry.[136]

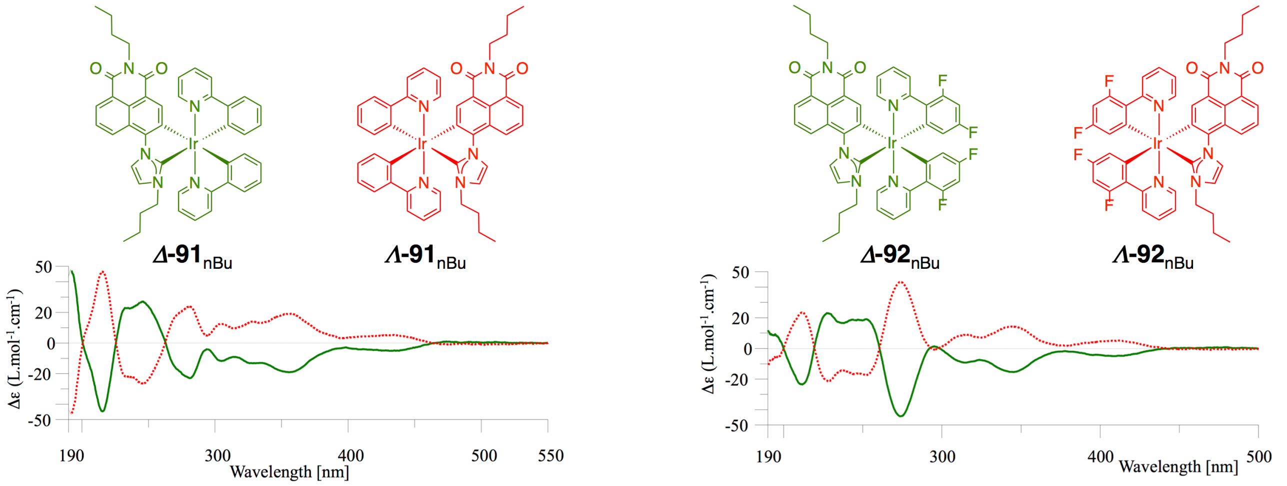


Figure 21. CD spectra of *Δ*-**91**$_{nBu}$ (green) and *Λ*-**91**$_{nBu}$ (red) and *Δ*-**92**$_{nBu}$ (green) and *Λ*-**92**$_{nBu}$ (red) recorded in CH_3CN at 0.19 mM and 0.2mM respectively.

3.2.3 Containing helicenes and chiroptical properties

Another important property displayed by cyclometalated NHC Ir(III) complexes containing three chelating ligands is chirality.[137-139] Thus efforts were devoted to merge chirality and luminescence in the hopes of establishing a novel class of compounds with dual properties.[136,140] For instance Crassous et al. designed a unique type of chiral meridional cyclometalated Ir^{III}-compounds containing NHC-helicene derived (C^C:) ligands (Figure 22).[141-142] These complexes were obtained in (70:30) yield as four diastereomers, *mer*-(*P*, *Λ*$_{Ir}$)-**97**/(*M*-*Δ*$_{Ir}$)-**97** and *mer*-(*P*, *Δ*$_{Ir}$)-**98**/(*M*-*Λ*$_{Ir}$)-**98**.

Each pair comprises two enantiomers, with the chirality arising from a combination of the stereochemistry at the iridium center (Δ, Λ) and the helicity of the NHC-helicene derived ligand (*P*, *M*). The X-ray molecular structure of the pure diastereomer **97** was obtained. The emission properties of complexes **97** and **98** were studied and showed light green phosphorescence. Structured vibrational bands are visible with λ_{max} at 525 nm, red-shifted relative to the model complex **99**, and quantum yields of 9-13%, suggesting that emissions originate from the mixed ^{3}LC/^{3}MLCT transitions and not from only ^{3}MLCT state as observed in the model complex **99** without a helicene moiety (Figure 22). Remarkably complexes **97** and **98** display long lifetimes τ of around 300μs, which are much longer than that observed for the model complex **99** τ = 3.1μs. These results also confirm the contribution of the ^{3}LC-centered transitions originated from the NHC-helicene derived ligand.[141]

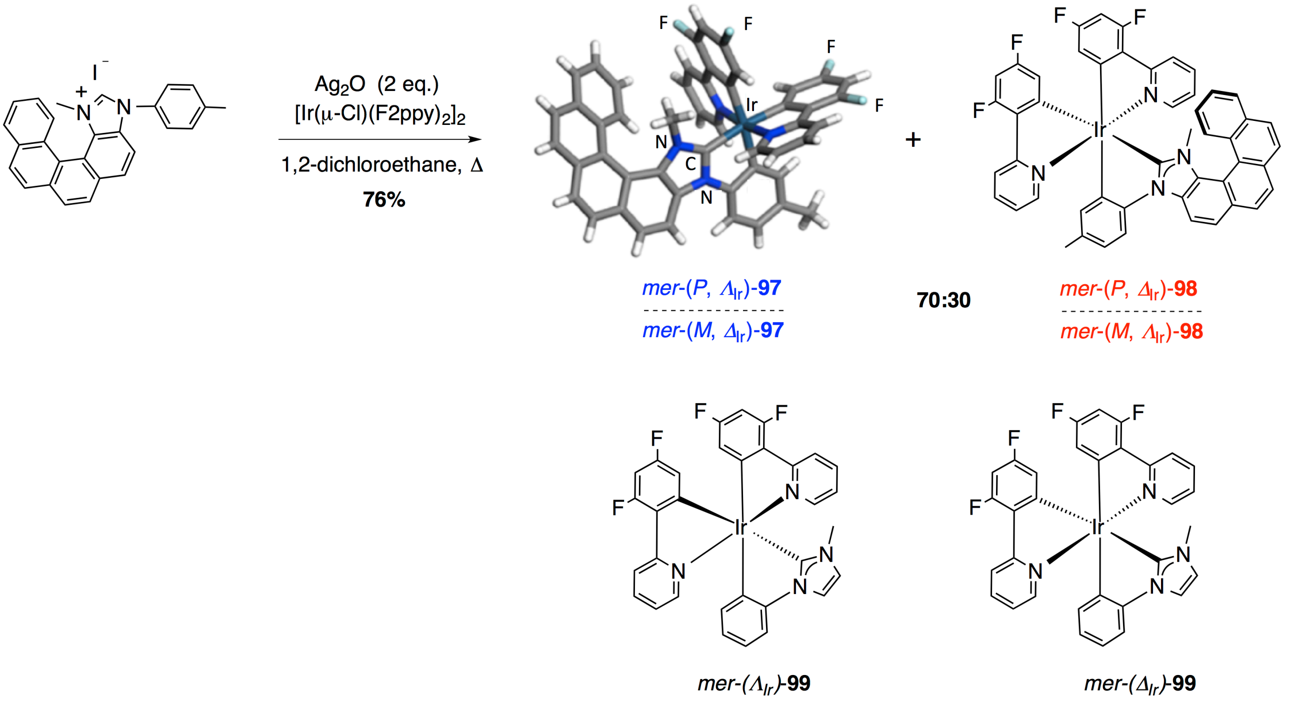


Figure 22. Cyclometalated Ir-NHC complexes with helicene ligands.

These complexes were successfully resolved using chiral column chromatography into their corresponding single enantiomers. It should be mentioned that the [5] helicenic carbene ligand displayed high configurational stability (inversion barrier > 125 kJ mol^{-1}), thus refluxing of the isolated pure samples in chloroform for several hours did not lead to any epimerization.

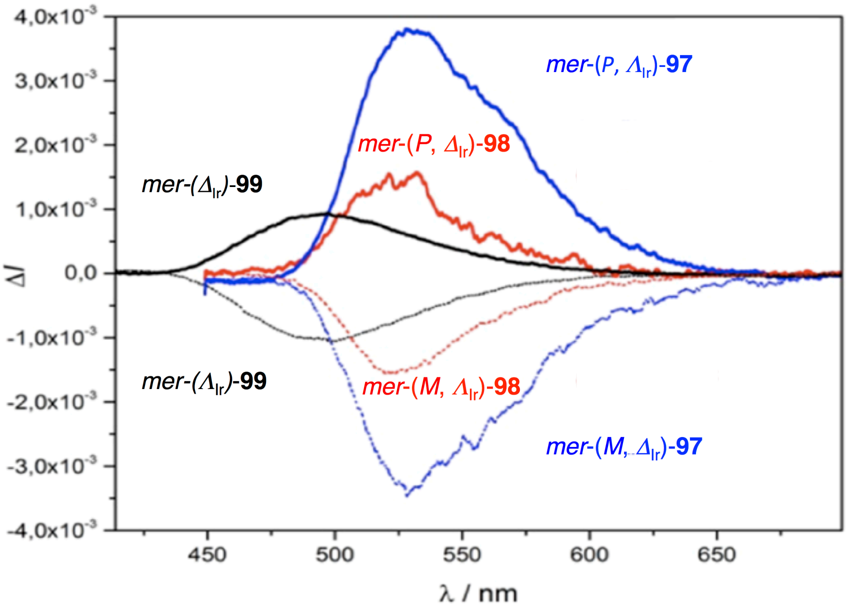
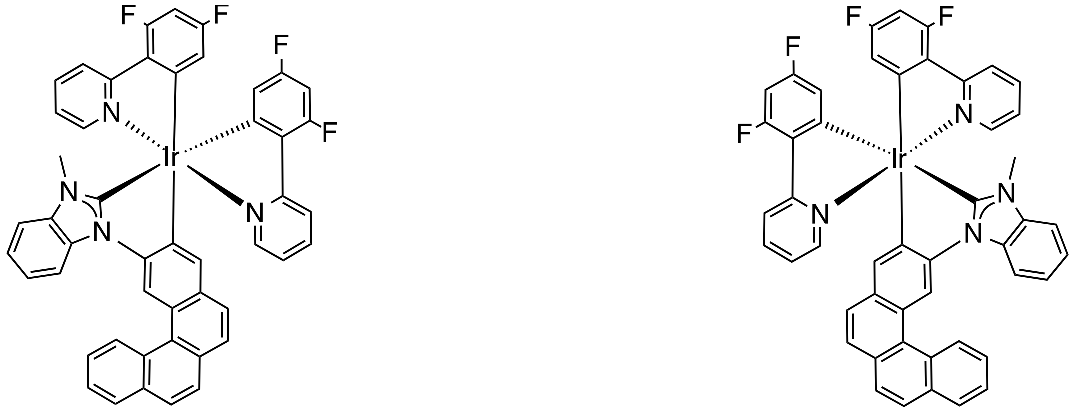


Figure 23. CPL traces of *mer*-(*P*, $\mathit{\Lambda}_{\mathrm{Ir}}$)-**97**/(*M*-$\mathit{\Delta}_{\mathrm{Ir}}$)-**97** and *mer*-(*P*, $\mathit{\Delta}_{\mathrm{Ir}}$)-**98**/(*M*-$\mathit{\Lambda}_{\mathrm{Ir}}$)-**98** containing NHC-helicene ligands and the model complexes *mer*-($\mathit{\Lambda}_{\mathrm{Ir}}$)-**99**/($\mathit{\Delta}_{\mathrm{Ir}}$)-**99**. Adapted with permission from ref [141]. Copyright 2017 Wiley.

The CPL (Circularly Polarized Luminescence) properties of the four enantiopure stereoisomers complexes *mer*-(*P*, $\mathit{\Lambda}_{\mathrm{Ir}}$)-**97**/(*M*-$\mathit{\Delta}_{\mathrm{Ir}}$)-**97** and *mer*-(*P*, $\mathit{\Delta}_{\mathrm{Ir}}$)-**98**/(*M*-$\mathit{\Lambda}_{\mathrm{Ir}}$)-**98** containing the NHC-helicene derived ligand and those of the model complexes *mer*-($\mathit{\Lambda}_{\mathrm{Ir}}$)-**99**/($\mathit{\Delta}_{\mathrm{Ir}}$)-**99** were investigated in deoxygenated CH_2Cl_2 (Figure 23). The authors demonstrate that the stereochemistry of the NHC-helicene ligand controls the sign of the CPL signal with a value of dissymmetry factor ($g_{\mathrm{lum}} = +3.7 \times 10^{-3}$) at 530 nm for (*P*, $\mathit{\Lambda}_{\mathrm{Ir}}$)-**97**, much higher than that obtained for (*P*, $\mathit{\Delta}_{\mathrm{Ir}}$)-**98** ($g_{\mathrm{lum}} = +1.5 \times 10^{-3}$). Moreover the presence of the NHC-helicene ligand amplifies the dissymmetry factor when compared with the model complex $\mathit{\Delta}_{\mathrm{Ir}}$-**99** ($g_{\mathrm{lum}} = +9 \times 10^{-4}$) at 493 nm.[141]

Moreover the authors prepared another type of chiral cyclometalated iridium compound containing NHC-derived helicene ligand (C^C:), which was resolved into its corresponding enantiomers *mer*-

(Λ_{Ir})-**100** and *mer*-(Δ_{Ir})-**100**. In this type of complex the [4]-helicene moiety is not fused to the NHC unit as in the preceding example but attached to the nitrogen center and cyclometalated to the iridium (III) (Figure 24).[143]



mer–Λ_{Ir}-**100**   *mer*–Δ_{Ir}-**100**

Figure 24. Cyclometalated iridium-NHC complexes containing [4]-helicenes.

Again, the π-extended helicene ligand changes the photophysical properties of complex **100** when compared to the model cyclometalated NHC compound **99** without the helicene moiety. In CH_2Cl_2 solution at room temperature, complex **100** displays structured emission bands with λ at 510, 549, 660 and 690 nm and quantum yield Φ = 5% with a very long lifetime of 140 μs. The emission of **100** is red-shifted relative to complex **99** which shows a broad band at λ = 483 nm with much shorter lifetime τ = 1.8 μs. The authors suggest that the excited state in **100** is highly centered on the π-system ^{3}IL with some participation from ^{3}MLCT, which is in accord with the long luminescence lifetime 140 μs observed for **100**. While in complex **99** the short luminescence lifetime as well as the different form of the mission bands is in accord with a strong contribution from the ^{3}MLCT state.[143]

At this stage a comment is required on the effect of NHC-derived organic ligand (C^C:, helicene, naphthalimide, etc.) on the photophysical properties of these cyclometalated iridium complexes. As mentioned previously, cyclometalated iridium complexes commonly emit from a ^{3}MLCT state. The presence of the organic chromophore or π-extended system directly linked to the NHC dramatically modifies the nature of the excited states from ^{3}MLCT to mostly ^{3}LC, triplet manifold centered on the organic dye.

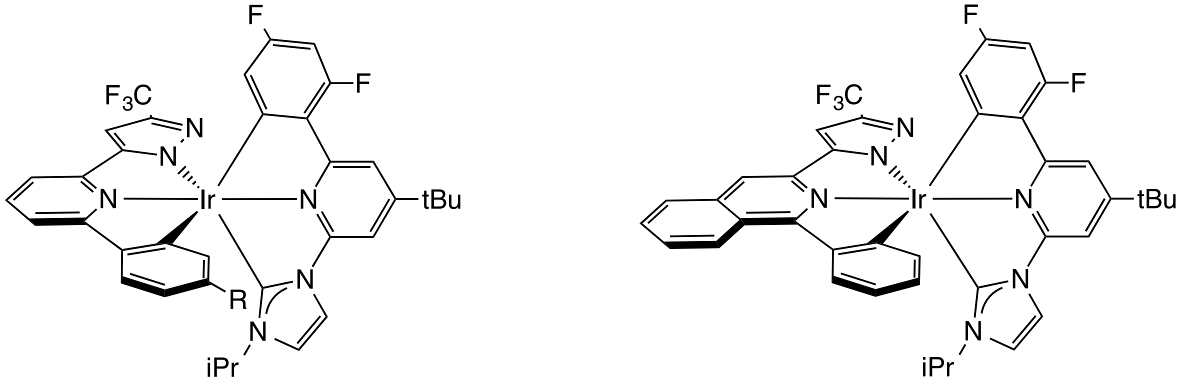
On the other hand the authors investigated the CPL properties of the enantiopure complexes-(Λ_{Ir})-**100** and *mer*-(Δ_{Ir})-**100** relative to the enantiomers of the model complex **99**. The CPL activity was found to be similar in both types of compounds. It should be mentioned that [4]helicene moiety in these complexes is configurationally unstable in solution and therefore do not impact their CPL properties as observed for compounds **97** and **98** described previously.

3.3 Cyclometalated iridium complexes with tridentate ligands

Throughout the previous section we have presented several examples of octahedral cyclometalated NHC iridium complexes with a variety of appealing structures, properties and useful applications. However all of these examples displayed tris-bidentate [2+2+2] chelating ligands coordinated to the Ir(III) center. More recently efforts were devoted to another class of octahedral cyclometalated NHC iridium complexes, which display bis-tridentate [3+3] chelating ligands instead. These investigations are motivated by the fact that only one isomer could be isolated, when compared to the previous iridium tris–bidentate family where at least two geometrical isomers are expected to form. Moreover, tridentate chelating ligands tend to strongly chelate the iridium center and hence deliver highly stable complexes for device applications. However due to the nature of the coordination mode of the bis-tridentate ligands around the iridium center, a strong distortion of the ideal octahedral geometry is expected when compared to those containing tris(bidentate) ligands. As a consequence this tends to stabilize the MC dd excited state and reduces the HOMO-LUMO energy gap. Again the use of ancillary NHC ligands destabilizes the MC centred excited states and provides entry to highly emissive compounds.

Williams and coworkers described a synthetic approach to obtain cyclometalated iridium complexes displaying the (N^C^N) tridentate chelate. The authors chose 1,3-di(2-pyridyl)-4,6-dimethyl benzene (dpyxH), to react with $IrCl_3.3H_2O$, for which two methyl substituents are attached to the central phenyl ring in order to direct the cyclometalation at the C2-position of the central phenyl ring to afford the dimer [Ir(dpyx-N^C^N)(μ-Cl)Cl]$_2$.[144] This dimer reagent and analogous compounds served as key-intermediates to prepare neutral cyclometalated bis(tridentate)iridium complexes by coupling monoanionic (N^C^N), whether (C^N^C) or (C^C^C) and dianionic tridentate chelating ligands.[59,145]

For instance Chi, Chou and coworkers combined the monoanionic (C^N^C) containing NHC ligand with the dianionic chromophoric tridentate pyrazolyl based ligand around the coordination sphere of the Ir(III) center in order to obtain the neutral bis tridentate [3+3] coordinated iridium complexes **101**-**103**.[146] Their emission properties ranged from cyan **101**, green **102** and to orange-red **103** respectively (Figure 25).



R = F, (**101**); R = CF$_3$, (**102**)

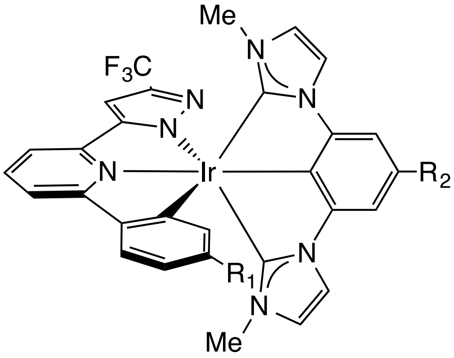
(**103**)

Figure 25. [3+3]-Iridium-NHC complexes displaying bis–tridentate ligands.

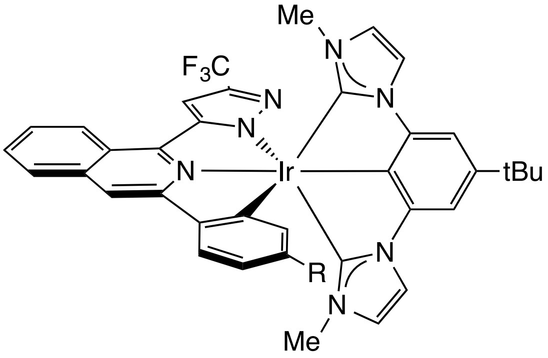
The authors demonstrated using TD-DFT calculations that the observed emissions largely originate from the ^{3}MLCT processes (L represents the dianionic chromophoric chelate) with contributions from ligand-centered $\pi-\pi^*$ transitions. The emission color is also influenced by the dianionic chromophoric chelate pyrazolyl ligand, ranging from 473 to 608 nm. These compounds were later used as OLED devices. For instance, green OLEDs using complex **102** give a peak external quantum efficiency of 18.8%, a luminance efficiency of 58.5 cd/A and a power efficiency of 57.4

lm/W. As for complex **103** the designed OLED device exhibits saturated red emission with maximum efficiencies of 12.5%, 10.4 cd/A and 9.0 lm/W.

On the other hand, the authors prepared another series of complexes by replacing the monoanionic (C^N^C) ligand with the tridentate (C^C^C) ligand bearing an NHC pincer ancillary.[108,147-148] The modification is inspired by the belief that a greater Ir-C bond strength of the NHC fragment (versus an Ir-N dative bond) would exert the strongest destabilization of the MC dd and hence enhance the luminescent properties of the target complexes **104-107** (Figure 26).



R_1 = F, R_2 = CF_3 (**104**)
R_1 = CF_3, R_2 = CF_3 (**105**)
R_1 = CF_3, R_2 = t-Bu (**106**)

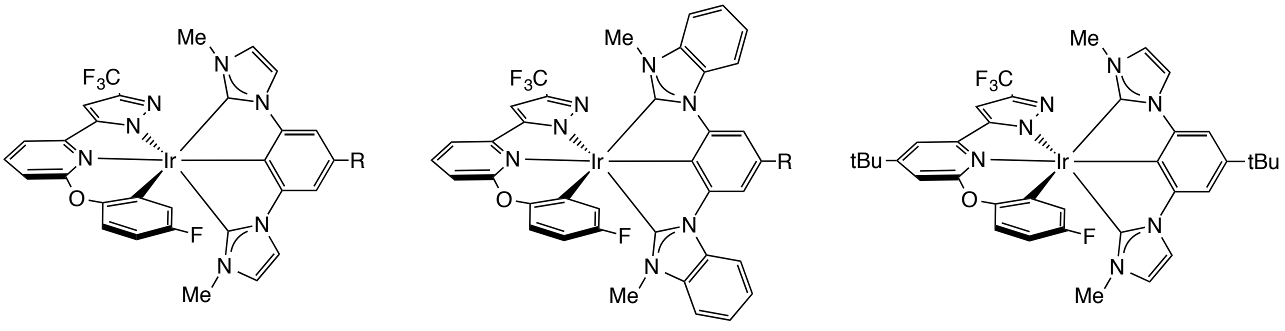


(**107**)

Figure 26. [3+3]-Iridium- bis(NHC) complexes featuring bis-tridentate (C^N^N)/C^C^C) ligands.

Complexes **104-107** were strongly luminescent in CH_2Cl_2 solution and also in thin films of 9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole-3-carbonitrile (mCPCN) and exhibited nearly 100% high quantum yields, which confirm the elimination of the non-radiative decay due to the greater skeletal rigidity. As mentioned in the previous paragraph, the emission properties of these compounds follow a similar trend, ranging from blue (**104**), cyan (**105**), green (**106**) and red (**107**), and displaying π-conjugation at the central isoquinolinyl moiety. These compounds were also used to design OLED devices. For instance, a blue OLED based on **104** was obtained with EL (electroluminescence) EQE efficiency up to 27% and (69.5 cd/A, 68.2 lm/W), while a cyan OLED based on **105** exhibited 30% efficiency with (100 cd/A, 92 lm/W), and a green OLED based on **106**, had an efficiency of 31.4% with (110.8cd/A, 108.7 lm/W), and finally a red OLED based on **107** with 27.4% (36.9 cd/A, 36.2 lm/W) was obtained. The authors consider that these Ir(III) phosphors display among the highest EL efficiencies.

Moreover Chi, Fox and Wu designed other bis-tridentate [3+3] coordinated Ir(III) phosphors **108-112** in order to obtain deep-blue OLED devices (Figure 27).[149-150] In order to achieve their objectives, the designed molecules displayed larger HOMO-LUMO gaps compared to those described previously. The synthetic approach follows that described previously, combining a monoanionic tridentate (C^C^C) ligand bearing two NHC units and the chromophoric dianionic ligand 6-pyrazolyl-2-phenoxy pyridine around the Ir(III) center. A major difference relative to the preceding complexes however resides in supressing the π-conjugation between the F-phenyl group and central pyridine unit by placing an oxygen atom between them.



R = CF_3 (**108**)
R = t-Bu (**109**)

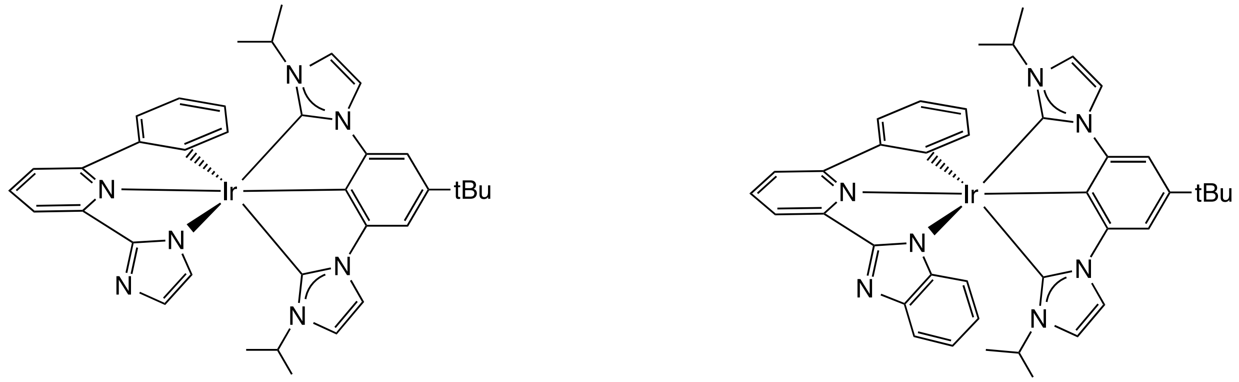
R = CF_3 (**110**)
R = t-Bu (**111**)

112

Figure 27. [3+3]-Iridium- bis(NHC) complexes with bis-tridentate (C^N^N)/C^C^C) ligands and lack of π-conjugation between F-phenyl group and central pyridine unit .

All complexes were luminescent in solution and in thin films and displayed high quantum yields. For instance in CH_2Cl_2, complexes **108-112** displayed structured blue bands with $\lambda_{max} \approx 472$ nm. Compound **109**, displayed a different behavior. For instance a broader emission band which is bathochromic shifted to $\lambda_{max} = 478$ nm is observed. In this series of compounds all emissions were blue-shifted relative to complex **104** described in the previous paragraph. Due to their high-performance optical properties (Φ = 82-91%; short lifetime τ = 4.4 μs and 8.7μs) and high stability, complexes **109** and **112** were used to prepare deep blue OLEDs. The electroluminescence spectra displayed blue emissions with the CIE chromaticity for a complex **109** device (0.15, 0.24) and EQE of 19.7%, 33.5 cd/A, 26.3lm/W and for a complex **112** device (0.15, 0.17) and EQE of 20.7%, 28.8 cd/A, 22. 6 lm/W.

Esteruelas and coworkers also investigated the optical properties of bis-tridentate metal complexes. Their approach consists of preparing the NHC pincer tridentate (C^C^C) ligand, isolated as an iridium dimer complex $[IrI(\mu\text{-}I)(C^\wedge C^\wedge C)]_2$. The latter represents the key molecule necessary to attain the target bis-tridentate [3+3] coordinated iridium complexes. Subsequent treatment with the dianionic tridentate ligands based on imidazolyl-phenyl pyridine and benzimidazolyl-phenyl pyridine provides the neutral bis-tridentate iridium complexes **113** and **114** (Figure 28).[151]



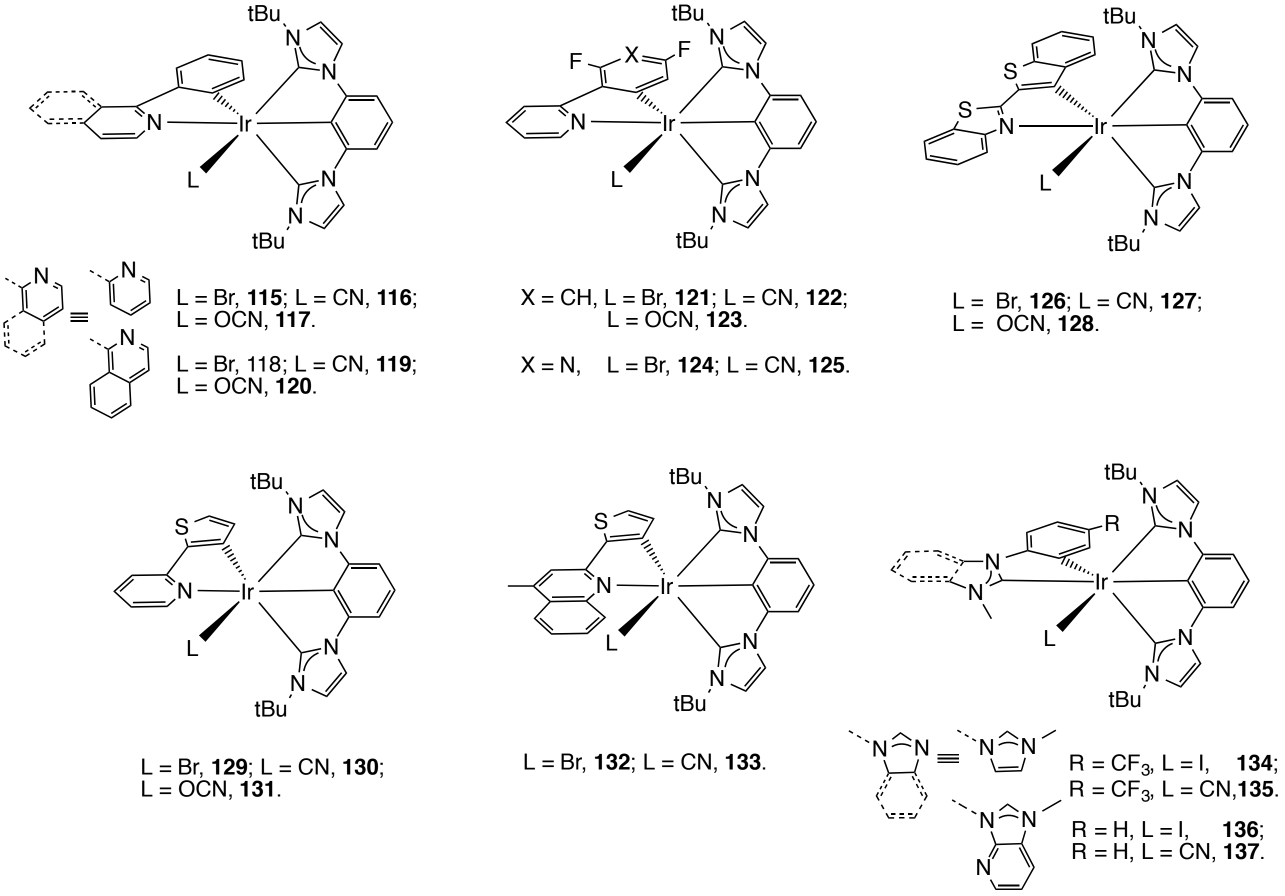
113 **114**

Figure 28. [3+3]-Iridium- bis(NHC) complexes featuring imidazolyl-phenyl pyridine and benzimidazolyl-phenyl pyridine ligands.

Complexes **113** and **114** acted as green and greenish yellow emitters upon photoexcitation in PMMA film and MeTHF solution and exhibited quantum yields between 0.73 to 0.49. These compounds were later used as iridium phosphors to prepare OLED devices. For instance, the electroluminescence spectra displayed emission at λ_{max} = 552 nm with the CIE chromaticity for complex **114** device (0.458, 0.530) and EQE of 12.0%.

On the other hand Yang, Cheng and Wei reported a novel series of phosphorescent iridium complexes (**115**-**137**) by combining the advantage of tridentate bis(NHC) ligands, bidentate cyclometalated (C^N) ligands and monodentate anionic ligands (L = Br, I, OCN and CN). These [3+2+1] coordinated iridium complexes are strong emitters and depending on the nature of the (C^N) bidentate ligand a fine control of the emission properties was established along the UV and visible light spectral range.[152] Thus, all Ir(III) complexes displayed structured phosphorescent emission profiles assigned primarily to ^{3}LC/^{3}LLCT transitions and in the range of 386-609 nm.

The X-ray molecular structures of complexes **123**, **128** and **129**, were determined and showed that the nitrogen center in cyclometalated ligands is displayed *trans* to the carbon in the benzene ring of the tridentate bis(NHC) ligands, while the carbon center in cyclometalated ligands adopt a *trans* configuration to the monodentate ligand L (Figure 29).



L = Br, **115**; L = CN, **116**; L = OCN, **117**.

L = Br, 118; L = CN, **119**; L = OCN, **120**.

X = CH, L = Br, **121**; L = CN, **122**; L = OCN, **123**.

X = N, L = Br, **124**; L = CN, **125**.

L = Br, **126**; L = CN, **127**; L = OCN, **128**.

L = Br, **129**; L = CN, **130**; L = OCN, **131**.

L = Br, **132**; L = CN, **133**.

R = CF_3, L = I, **134**; R = CF_3, L = CN,**135**.

R = H, L = I, **136**; R = H, L = CN, **137**.

Figure 29. A wide range of [3+2+1] Ir^{III} compounds displaying tridentate bis carbene ligands, bidentate cyclometalated (C^N or C^C) ligands and monodentate anionic ligands.

For instance (Ir(III)-CN)-complexes (**135**, **137**) containing (C^C) with strong ligand field of the NHC increases the energy gap by pushing higher the LUMO levels, and hence display ultraviolet to deep blue emissions (λ = 385 nm and λ = 410 nm) respectively with quantum yields (Φ = 14-20%; short lifetime τ = 1.73 μs and 0.72μs). The presence of electron-withdrawing groups (F, -CF_3) on the C-chelating (C^N) ligands lowers the HOMO levels. For instance the emission peak is blue shifted from 454 nm in **116**, to 440 nm in **122**. Furthermore replacing the phenyl ring with a fluorinated pyridine ring contributes to a more blue shift emission in **125** to 436 nm.

In contrast, Ir^{III}-cyanide complexes with (C^N) ligands containing extended π-conjugation or electron-donating thiophene ligands, displayed bathochromic shifts in their emissions toward the red region for instance complexes **129**, **130** and **133** emit at λ = 568 nm, 517 nm and 545 nm respectively. It should be mentioned that complex Ir(III)-CN (**127)** exhibited the lower red emission at λ = 591 nm. The related Ir(III)-OCN (**128**) emitted even further in the red region at λ = 609 nm. The authors also demonstrated that the Ir(III)-CN complexes shown in figure 28 displayed blue-shifted emissions when compared to related iridium compounds with [2+2+2] coordination mode containing the same cyclometalated (C^N) bidentate ligands. For instance the *fac*-$Ir(F2ppy)_3$, display emission at λ = 468 nm, with Φ = 0.43 while complex [Ir(F2ppy)(C^C^C)(CN)] (**122)** emits at λ = 441 nm, with Φ = 0.67), highlighting the importance of their synthetic strategy to prepare blue emissive [3+2+1] coordinated iridium complexes. Furthermore due to its high emission performance, complex **122** was used as an emitter in the design of blue OLED with maximum external quantum efficiency of 22.94% and CIE coordinates of (0.14, 0.24). Moreover the related Ir(III)-OCN complex [Ir(F2ppy)(C^C^C)(OCN)] (**123**) acted as a sky-blue OLED device at 20wt% in 4,4',4"-tris(carbazol-9-yl)triphenylamine (TCTA) used as host material and showed comparable performance relative to the well studied [2+2+2] sky-blue iridium complex [$Ir(F2ppy)_2$(picolinate)] (**FIrpic**) [153-156] OLED device under similar experimental conditions. But, at a high luminance of 1000 cd m^{-2}, complex **123** displayed improved efficiency roll-offs.

3.4 Cyclometalated iridium complexes with bis carbene (NHC) chelating ligands

Cyclometalated NHC iridium complexes emitting in the deep-red and NIR region were also developed by the group of Mao for their anticancer properties. For instance the authors designed the heteroleptic cationic cyclometalated Ir(III) complexes [(C^N)$_2$Ir(C^C)][Cl] (**138-139**) containing a bis-NHC ligand and two dibenzo[a,c]phenazine (dbpz) ancillary ligands (Figure 30).[157]

138 **139**

Figure 30. Bis(NHC) cyclometalated iridium complexes containing dbpz ancillary ligands

At room temperature in CH_2Cl_2 complexes **138-139** exhibited red emission bands at λ_{max} around 650 nm, while in phosphate-buffered saline (PBS) they behaved as NIR emitters with emissions at λ_{max} = 765 nm and λ_{max} = 812 nm. These complexes displayed lifetimes τ in the nanosecond regime, which also varied from 273ns to 674ns upon moving from PBS buffer medium to CH_2Cl_2 and CH_3CN. Under similar conditions the quantum yields Φ also varied from 0.95% to 14.3%, and was found to be dependent on the solvents polarity. These compounds show interesting mitochondria-targeting anticancer properties and potential use as photodynamic agents. The authors indicate that complexes **138-139** show higher cytotoxicity against cancer cells when compared to the benchmark cisplatin and they also display higher photocytotoxicity under 450nm and 630nm LED light.

Che and coworkers designed a novel class of cationic phosphorescent iridium complexes (**140-148**) supported by bis(NHC) ligands containing a variety of cyclometalated (C^N) ligands for a multiple useful applications spanning from photocataysis driven by radical cyclization, to CO_2 reduction and also for cellular imaging (Figure 31).[100] Again as mentioned previously in this document, it is the kind of emission energies and lifetime durations that justify the kind of applications.

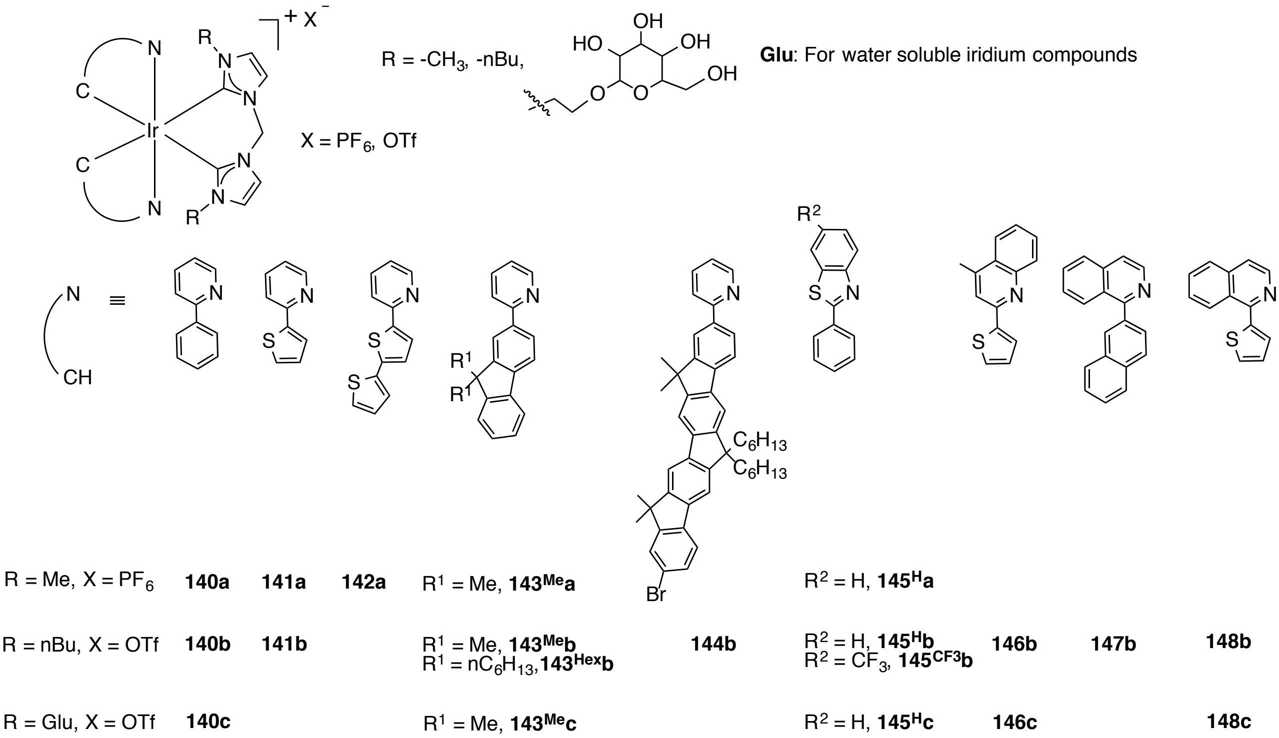


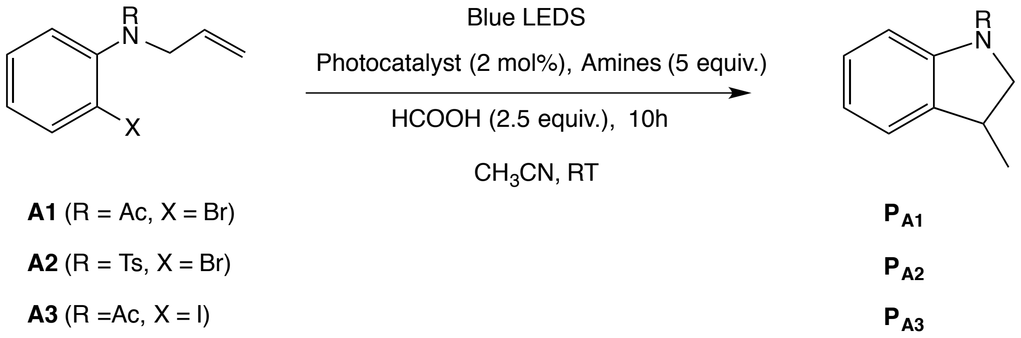
Figure 31. An exhaustive range of luminescent bis(NHC)Ir(III)-complexes containing a variety of cyclometalated (C^N) ligands for useful applications.

The bis(NHC) ligands bring a great stability to these molecules, and variation of the R-group on the nitrogen atom of the carbene ligands (R = Me, nBu, Glu: Glucose) affects the solubility of these compounds and make them soluble in water (R = Glu). On the other hand the nature of the (C^N) ligands impacts their photophysical properties and the nature of the excited states whether ^{3}MLCT, ^{3}LC/^{3}LLCT and eventually the duration of the lifetimes of the excited states.[100]

The authors investigated first the photostability of these compounds in solution. Thus upon irradiation of a representative complexes of the above family mainly **143^{Me}b** and 1**45^{H}b** in degassed CD_3CN for five days using blue light (12 W blue LEDs) and monitoring their ^{1}H-NMR spectra, only 5% of decomposition was observed, suggesting the high photostability of these compounds, is due to the bis-carbene ligands chelating ligands. For comparison purposes the related complexes [Ru(bpy)$_3$][Cl]$_2$, *fac*-Ir(ppy)$_3$, and [(dFCF$_3$ppy)$_2$Ir(dtbbpy)$_3$][PF$_6$] (dFCF$_3$ppy = 3,5-difluoro-2-[5-trifluoromethyl)-2-pyridinyl]phenyl; dtbbpy = 4,4'-bis(1,1-dimethylethyl)-2,2'-bipyridine), under similar conditions were found to decompose after only 10h of irradiation as demonstrated by their ^{1}H-NMR spectra.

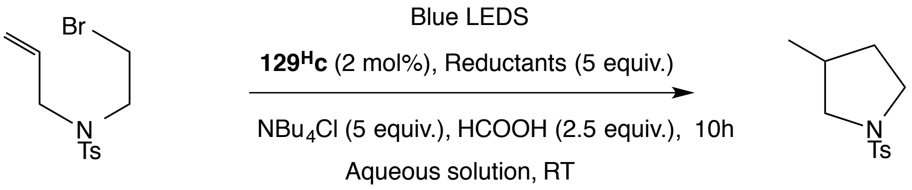
Owing to their high photostability, and good quantum yields and long lifetimes in the microsecond regime, complexes **140b** (Φ= 89%, τ = 2.1 μs), **143^{Me}b** (Φ = 75%, τ = 28.2 μs), and **145^{H}b** (Φ = 78%, τ = 6.4 μs) were used as photocatalysts for the formation of pyrrolidine derivatives via visible-light induced radical cyclization of arylbromides and aryliodides (Scheme 1). Using substrate A1, with DIPEA (diisopropylethylamine) the photocatalyst **143^{Me}b** showed excellent (97%) substrate conversion and 64% product yield. This yield increased to 72% when DBU was used as an amine. Complexes **140b** and **145^{H}b** when used as photocatalysts afforded the desired product with 67% and 64% yields respectively. For comparison purposes, under similar conditions the ruthenium complex [Ru(bpy)$_3$][Cl]$_2$ provided no product formation, while the iridium compound *fac*-Ir(ppy)$_3$ led to only a 16% yield of product.[100]

Scheme 1. Visible light induced radical cyclization at room temperature in CH_3CN.



It is noteworthy that such chemical transformation was also performed in aqueous media (H_2O/MeOH; 3/1) using complex **145^{H}c** (Φ = 66%, τ = 5μs), which is soluble in water thanks to the glucose substituents on the bis-carbene ligands (see Scheme 2). The target product was formed in 87% yield with 99% substrate conversion.

Scheme 2. Visible light induced radical cyclization at ambient temperature in aqueous media.



Moreover the authors also investigated the catalytic properties of complex **143$^{\mathrm{Me}}$b** in the presence of a cobalt catalyst [(Co(TPA)Cl][Cl] (TPA = tris(2-pyridylmethylamine) for CO_2 reduction, and obtained excellent turnover numbers (TON > 2400) with selectivity (CO/H_2 in gas phase > 95%). The performance of **143$^{\mathrm{Me}}$b** again exceeded that of the well known photocatalyst *fac*-Ir(ppy)$_3$ which under similar experimental conditions led to only (TON>900) (CO) and a selectivity of 85%.

Finally the authors also demonstrated that such bis-carbene cyclometalated iridium complexes with a variety of (C^N) ligands can be used as luminescent probes for bioimaging applications and display high cytotoxicity against Hela cancer cells with *N*-butyl bis-carbene ligands when compared with the related compounds with Me and glucose functional groups.[100]

The next section deals with recent advances in luminescent coinage metals containing *N*-heterocyclic carbenes.[158]

4-Luminescent coinage metals with *N*-heterocyclic carbene ligands

4.1 Coinage metal complexes with alkynyl ligands

Coinage metal complexes display low-dimensional coordination geometries. As a consequence they tend to form non-covalent metal-metal interactions, the best known are complexes containing Au(I) metal centers.[159-160] These kinds of interactions, which impact the photophysical properties[161-169] of the desired compounds, have been coined as aurophilicity by Schmidbaur [170-171] and were investigated in theoretical studies performed by Pyykkö.[172-173] Unlike luminescent complexes with iridium and platinum, which depend on strong spin-orbit coupling (SOC) to generate triplet metal to ligand charge transfer ^{3}MLCT emission, the two-coordinated coinage metal complexes emit via prompt fluorescence or thermally activated delayed fluorescence

(TADF).[174] Their fast radiative lifetimes are mainly related to two factors: (1) the small energy gap between their lowest singlet and triplet excited states (ΔE_{ST}) and (2) spin-orbit coupling displayed by the metal center. These particular properties enable them to be important phosphors to act as optical devices and for a wide range of applications.[175-176]

Poyatos and coworkers designed some gold alkynyl complexes **149-152** attached to a central pyrene organic chromophore (Figure 32).[177] Complexes **149-151** were found to be luminescent in solution at room temperature. In particular compounds **149 and 150** display high luminescent quantum yield Φ = 90%-92% and lifetime in the nanosecond regime while complex **151** exhibits a lower quantum yield of 38% and τ = 1ns. For comparison purposes, the monometallic gold complex **152** was also prepared and was found to be nonluminescent. The emission spectra of NHC gold complexes **150-151** recorded in degassed CH_2Cl_2 display pyrene-centered vibronic bands at λ = 481, 507, 543 nm and λ = 481, 508, 546 respectively.

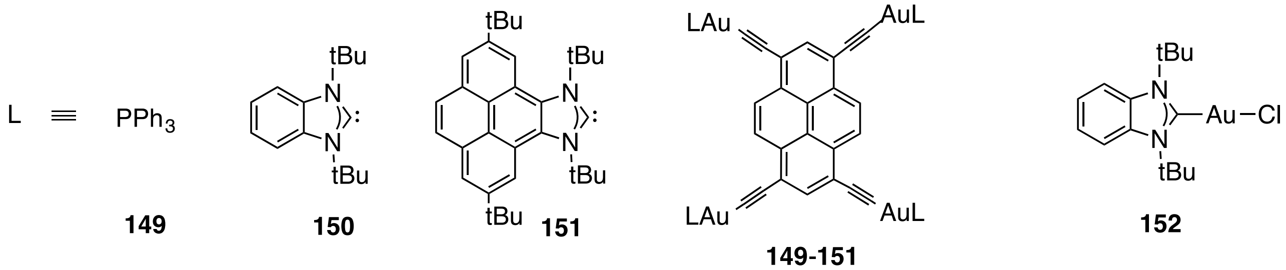


Figure 32. Gold-NHC complexes **150-151** supported by pyrene-based tetra-acetylide-ligands.

Complexes **150-151** displayed broad band emissions at λ_{max} = 585 nm , (Φ = 2.2%) and at λ_{max} = 541 (Φ < 1%) respectively in the solid state at room temperature. This kind of emissions was assigned to the formation of pyrene-excimers. The authors attribute this behavior to π-π stacking interactions occurring in the solid state, which is responsible for the aggregation quenching of the emission. At low temperature (T = 77K), the emission color of complex **150** switches from blue to yellow, which also might originate from formation of aggregates of **150**. The ^{1}H-NMR spectra of **150** recorded at variable concentration (0.1-20mM) shows that the aromatic protons of the pyrene moiety are shifted downfield upon decreasing the concentration of the complex. The authors suggested that aggregation through π-π stacking is occurring at high concentration. The association constant $K = 48$ M^{-1} was determined.

Due to its high optical properties, complex **150** was tested as a bioimaging probe in healthy cheek cells. After 30 min, intense luminescence was observed in the nucleus, proving the efficient uptake of **150** into the cell interior.

Gray and coworkers described the synthesis and photophysical properties of several mononuclear Au(I) complexes (**153-155**) attached through a Au-C σ-bond to a benzothiazole-fluorenyl chromophore and displaying either a phosphine or NHC as ancillary ligand (Figure 33). For comparison purposes they also prepared the related alkynyl Au complexes (**156-158**), in which the organic chromophore is now attached to the acetylide unit, acting as a linkage between the organic chromophore and the gold center.[178-179]

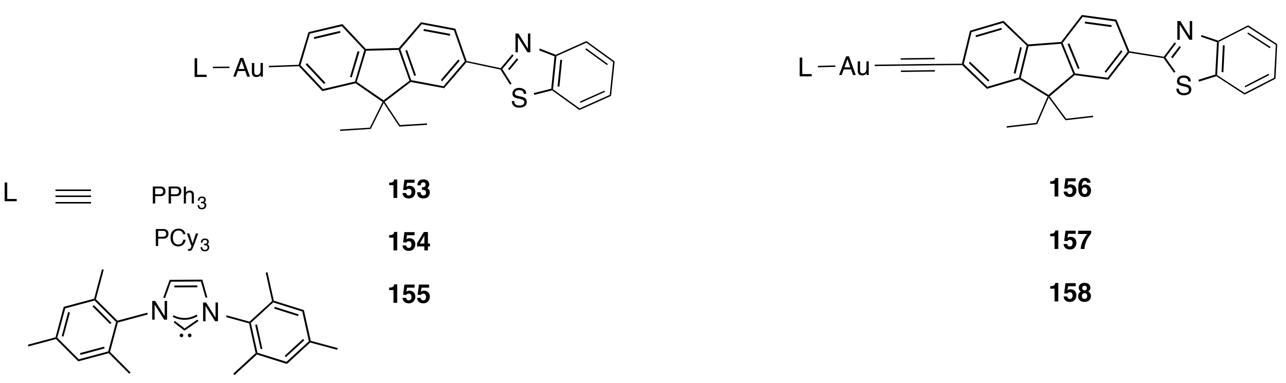


Figure 33. Gold NHC-acetylide complexes containing fluorenyl organic chromophores.

Compounds **153-155** exhibit dual emissions at room temperature, i.e. both fluorescence and phosphorescence. The corresponding ancillary ligand (NHC, organophosphine) affects the excited state dynamics of the complexes. For instance, in toluene at room temperature, complexes **153-154** behaved similarly and displayed fluorescence emissions at $\lambda_{fl} = 388$ nm with ($\tau = 79.3$ ps, $\Phi_{fl} = 0.08$) and at $\lambda_{fl} = 389$ nm with ($\tau = 89.4$ ps, $\Phi_{fl} = 0.09$) respectively. The phosphorescence emissions for both complexes appeared at $\lambda_{PHOS} = 538$ nm with ($\tau = 810$ μs, $\Phi_{PHOS} = 0.09$) and (τ =

766 μs, Φ_{PHOS} = 0.07) respectively. In both compounds the fluorescence and phosphorescence quantum yields are similar; as a consequence, the resulting dual emission provides white light. The gold carbene complex **155** behaves differently, displaying a longer fluorescence lifetime of 229 ps, with (λ_{fl} = 397 nm, Φ_{fl} = 0.22), while the phosphorescence emission appeared at λ_{PHOS} = 541nm with (τ = 872 ms, Φ_{PHOS} = 0.11). Complex **155**, displayed a phosphorescence quantum yield, which is one half that of the fluorescence as a consequence a violet emission is observed. The alkynyl gold complexes **156-158** also display dual emissions, with fluorescence lifetime in the ps regime, with emission bands in the range λ_{fl} = 366-371 nm and quantum yields Φ_{fl} in the range of 0.23-0.44, higher than those observed for the previous complexes **153-155**. The phosphorescence emissions occur in the range λ_{PHOS} = 555-560 nm with lifetimes in the microsecond regime but with lower quantum yields 0.02-0.04 compared to the previous complexes. DFT and TD-DFT calculations carried out on these complexes revealed that intersystem crossing occurs faster with σ-bonded Au(I)-aryl complexes when compared to those containing alkynyl linkage which is in line with the experimental photophysical data. Moreover, the HOMO and LUMO of the complexes are localized on the aryl–chromophore for **153-155** and on the alkynyl chromophore for **156-158** with small contribution from the gold.

As mentioned in the beginning of this section, two-dimensional coinage metal complexes form non-covalent metal-metal interactions,[180-182] thus *Lu, Chen, Che and coworkers* took advantage of this property and constructed several phosphorescent supramolecular 1D coordination polymers containing bis-carbene gold (I) cations $[Au(NHC)_2]^+$ associated to anionic $[MX_2]$ complexes (M = Au(I) , Cu(I) X = arylacetylides, cyanide or halides) and displaying metallophilic backbones (Figure 34).[183] Depending on the nature of the cation complex and the anion species, multi-color emissions spanning the entire visible region and extending into the NIR were obtained. For instance the assembly [**160**][A1] shown in (Figure 34) displayed a red emission at λ = 630 nm, with lifetime τ = 0.2 μs and quantum yield of 19%. The $[Au(NHC)_2][CuCl_2]$ double salts displaying Au···Au metallophic interactions showed the highest quantum yields close to unity. For instance [**159**][A11] displayed a blue emission at λ = 488nm, with τ = 4.2 μs and Φ = 99%.

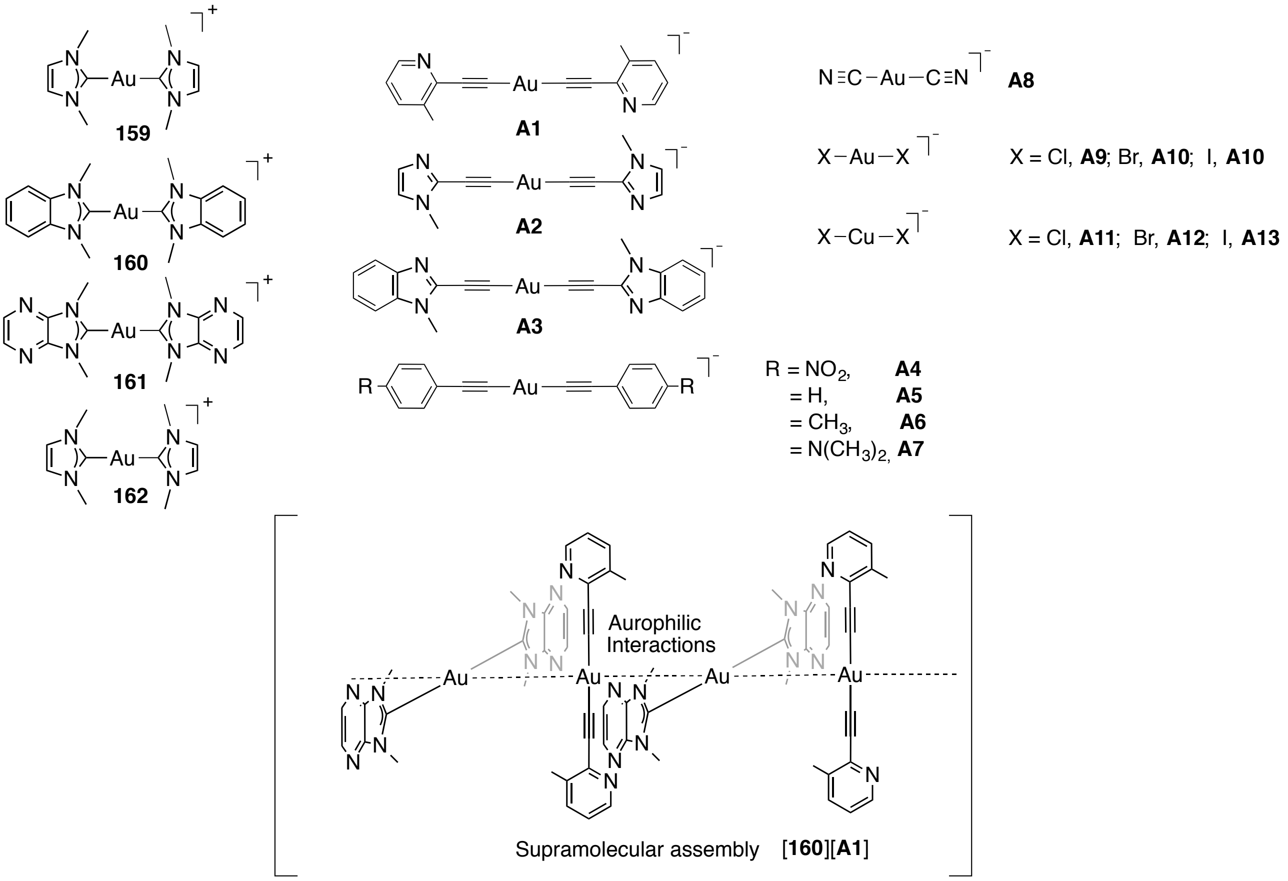


Figure 34. Supramolecular 1D coordination polymers containing bis-carbene Au(I) cations [Au(NHC)$_2$]$^+$ associated to bis-acetylides Au (I) anions and displaying aurophilic interactions.

TD-DFT calculations were carried out on [**160**][**A8**], allowed the rationalization of the nature of the excited state transitions involved in these phosphorescent compounds. For instance, the HOMO is localized on the dicyanoaurate anions with contribution from the dσ* orbital of the Au···Au displaying aurophilic interaction. The LUMO is localized on the bis-carbene Au(NHC)$_2^+$ species. Thus, low lying electronic transitions can be ascribed to admixture of L(anion)L'(cation)CT and MMCT (dσ* -Pσ) Au···Au interactions. Remarkably, the authors were able to generate multi-emissive species by judiciously combining two anions and one Au(NHC)$_2^+$ species. For instance the cocrystalization of **160**:**A8**:**A10** with molar ratio 2:1:1, provided the triple salt **160-A8/A10**. Single crystals of the latter displayed dual emission bands at λ = 586nm and λ = 652nm. Upon changing the ratio of both anions in the assembly, the luminescent properties of the resulting triple salt were altered for instance at a ratio of (**160-A8/A10**: 200:198:2), white light-emitting species with CIE coordinates (0.37, 0.31) and a quantum yield of 73% were obtained. These results highlight the importance of the aurophilic interactions on the luminescent properties of the coordination assemblies of coinage metals. Indeed the authors have used this approach to construct chiral gold complexes featuring aurophilic interactions, which enable them to act as smart luminescent materials. The work is mentioned on section 4.3 of this review.

Tunik and coworkers designed some luminescent gold alkynyl complexes supported by NHC ligands and displaying aurophilic interactions (Figure 35).[184]

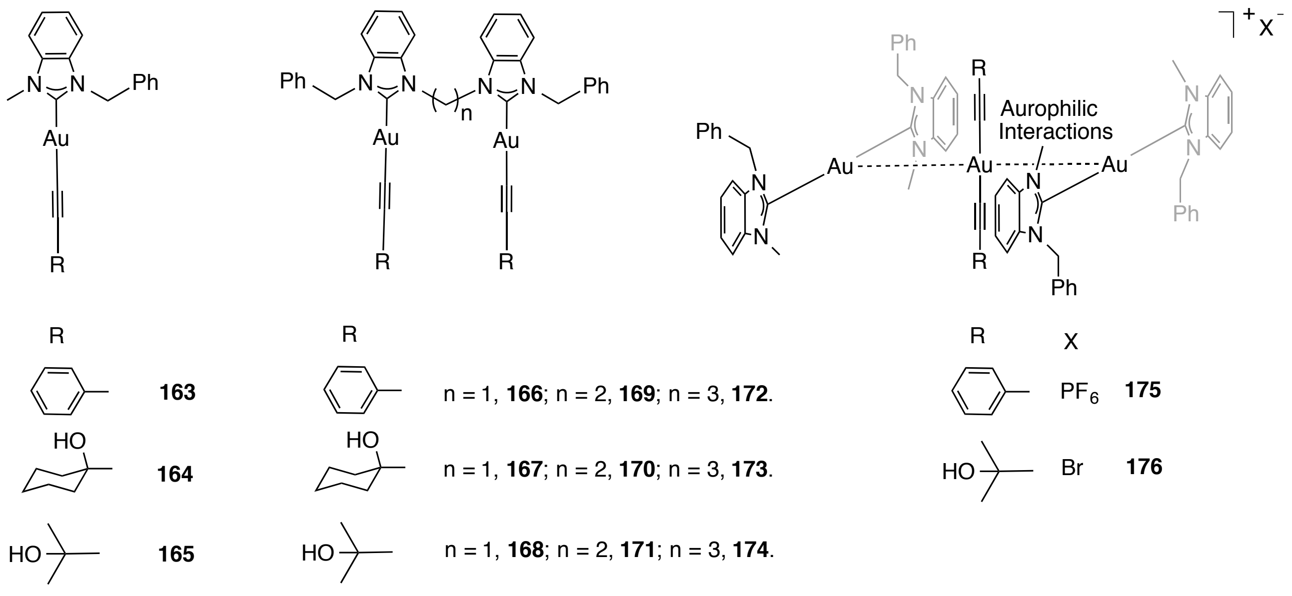


Figure 35. Monomeric and dimeric Au(I) alkynyl complexes supported by NHC ligands. B) Supramolecular cationic trinuclear Au(I) complexes showing aurophilic interactions.

The authors obtained these compounds starting from the NHC-gold halogenated precursors followed by treatment with the appropriate alkyl- or aryl-acetylene in the presence of a base. The dinuclear gold complexes **166-174** were obtained in a short period of time, however the mononuclear species required 5 hours to obtain pure mononuclear gold species **163-165**. When the reaction was left to proceed for only 1 hour followed by crystallization a rare class of cationic trinuclear species **175-176** was isolated in which the anionic $[Au(RC_2)_2]^{-1}$ acetylide complex is sandwiched by two cationic bis-carbene $[(NHC)_2Au]^{+1}$ species displaying aurophilic Au···Au backbones. The crystal structure of **175** shows short Au···Au interactions of 2.9375 (7) similar to those reported in the previous section. Perhaps due to steric hindrance around the gold centers discrete cationic species were obtained instead of a 1D supramolecular coordination polymers displaying alternate anionic/cationic motif.

The luminescent properties of these compounds were investigated in fluid media and solid state. In general the NHC-Au-alkylalkynyl complexes whether mononuclear or binuclear were non-emissive in solution, unlike the related phenyl-alkynyl complexes. In solid state, the mononuclear alkylalkynyl complexes **164-165** were also non-emissive, while their dinuclear congeners **167-168**, **170-171**, **173-174** were luminescent, however in the absence of crystal structures no correlation between their structural organization and emission properties was made. The mononuclear complex phenylalkynyl **163** was isolated in three different polymorph forms and a pseudopolymorph and their crystal structures were determined: a blue emissive polymorph $\mathbf{163}^{\mathbf{blue}}$, with no aurophilic or π-stacking interactions, two green emissive species denoted as $\mathbf{163}^{\mathbf{green}}$ and $\mathbf{163}^{\mathbf{greenDCM}}$ displaying similar aurophilic interactions (Au···Au = 3.3603(4) Å and Au···Au = 3.4190(3) Å respectively). The only difference between two crystals is the presence of 0. $38CH_2Cl_2$ molecule per formula unit in $\mathbf{163}^{\mathbf{greenDCM}}$. The third yellow-emitting polymorph $\mathbf{163}^{\mathbf{yellow}}$, showed a long aurophilic interaction distance of 3.6164(3) Å. Furthermore, the molecules are disposed in head-tail fashion with π-staking between two adjacent NHC ligands with distance of 3.350Å. The room temperature emission spectra of complex $\mathbf{163}^{\mathbf{blue}}$ in solution and solid state were similar and displayed well-resolved vibronic structure with spacing of 1100, 1600 and 2100 cm^{-1} ascribed to phenyl and acetylide –C≡C- stretching modes. Thus the observed emissions is thus assigned to a gold-perturbed $^3[\pi \rightarrow \pi](C{\equiv}CPh)$ state, the phosphorescence character is confirmed by the lifetime $\tau = 3.9$ μs. Unlike complex $\mathbf{163}^{\mathbf{blue}}$, the emission band forms of $\mathbf{163}^{\mathbf{green}}$, $\mathbf{163}^{\mathbf{greenDCM}}$, and $\mathbf{163}^{\mathbf{yellow}}$ were broad structureless suggesting that the excited state may be localized on the Au···Au aurophic interactions and not on the phenylalkynyl moiety. It should be mentioned that the complex exhibiting longer Au···Au interaction (**163**$^{\mathbf{yellow}}$$d_{Au-Au}$ = 3.6164(3) Å) displayed the lower emission energy at λ_{max} = 573 nm, relative to the green polymorphs **163**$^{\mathbf{green}}$, **163**$^{\mathbf{greenDCM}}$ possessing shorter Au···Au interactions with λ_{max} = 524 nm and λ_{max} = 527 nm. In general, it is expected that complexes displaying shorter Au···Au aurophilic interactions usually display lower energy emission bands.[160,166,185-190] The authors ascribed their counterintuitive structure-luminescence behavior to the different extents of distortion of the Au···Au interactions triplet in the excited states. Anomalous structure-luminescence behavior has been reported.[191-193] Similar behavior was observed for the dinuclear gold phenyl alkynyl complex **172** and also to the cations trinuclear complex **175** as well.

4.2 Coinage metal complexes containing naphthalimide chromophores

Amouri et al. set up a novel synthetic approach to obtain coinage metal carbene complexes in which an organic chromophore (naphthalimide) is attached to a carbene unit (Figure 36). Two families of compounds were prepared, one class featuring direct linkage to the NHC-unit [(L^1)-M-Cl], M = Cu (**177**), M = Ag, (**178**) and M = Au (**179**) while in the second class the naphthalimide fluorophore is distal from the metal center by an alkynyl-arene bridge [(L^2)-M-Cl], M = Cu (**180**), M = Au, (**181**).[194] The purpose of this study is to probe the effect of the chromophore on the optical properties of this kind of compounds.

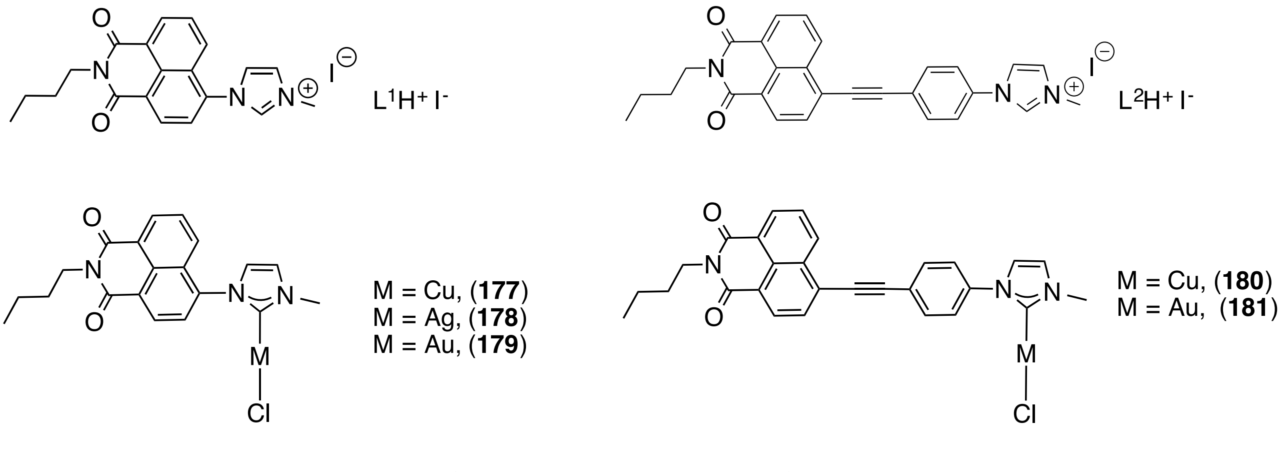
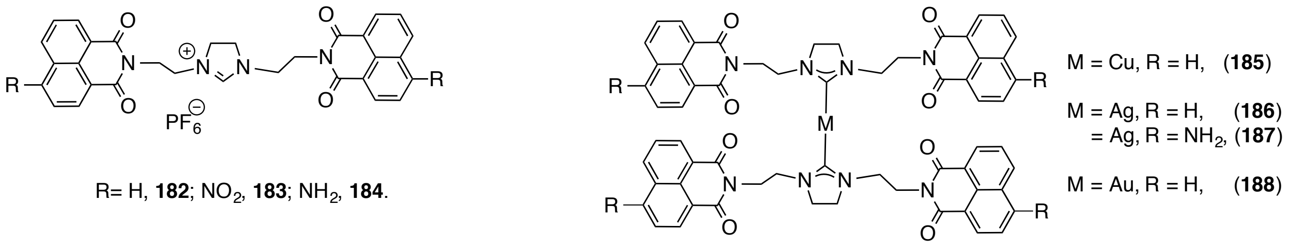


Figure 36. Two classes of metal carbene compounds displaying naphthalimide fluorophore

The solid-state molecular structure of **179** determined by single crystal X-ray diffraction revealed the presence of a weak Au$\cdots$Au contact at d = 3.407(1) Å. At room temperature complexes **177-179** and **180-181** displayed structureless broad bands in the blue region (420 to 451nm) when recorded in dichloromethane. It is noteworthy that the coinage carbene complexes [(L^1)-M-Cl], exhibited bathochromic shifts when compared to the starting material **L^1**-H$^+$I$^-$ (Figure 36). Those with extended π-system [(L^2)-M-Cl] (**180**, **181**) displayed a similar behavior. Furthermore, they were found to be more emissive, with Φ = (0.01-0.07) for complexes **179**, **177** and Φ = (0.21-0.29) for compounds **180-181** respectively.

Jamali and coworkers described the synthesis of some coinage metals containing four naphathalimide units attached to NHC-ligand through an ethylene chain (Figure 37). [195]



R= H, **182**; NO$_2$, **183**; NH$_2$, **184**.

M = Cu, R = H, (**185**)
M = Ag, R = H, (**186**)
= Ag, R = NH$_2$, (**187**)
M = Au, R = H, (**188**)

Figure 37. Coinage metal complexes containing four naphthalimide chromophores

The X-ray molecular structures of complexes **185-186** and **188** were determined and showed the presence of intramolecular π-stackings between the two adjacent naphthalimide units. All attempts to obtain the crystal structure of the silver congener **187** containing an –NH$_2$ group at the naphthalimide units were unsuccessful. The emissive properties of the azolium salts **182** and **184** as well as the coinage metal complexes **185-188** were investigated in CH$_2$Cl$_2$ solution and in solid state. In general all compounds were emissive and their quantum yields greatly increased in solution. In particular, however complex **187** was non-emissive in solid state but showed high quantum yield of 91.9% in solution. Moreover their lifetimes were found to be in the nanosecond regime. These emissions are fluorescence from ligand-based local states and not connected to the metal or the NHC ligand. The emission spectrum of **182** shows a broad structured emission with λ_{max} = 385 nm, which the authors assigned to monomeric and excimeric emissions. While the azolium salt **184** with the amine functional group displayed a broad band at λ = 500 nm. The authors assigned this band to a mixture of excimeric and also to ICT (internal charge transfer from the amine to naphthalimide unit) emissions. To rationalize the observed emission properties, DFT and TD-DFT calculations were used to calculate the optimized geometries of the ground states **185-188**, as well as their singlet excited states. Two main parameters were found to have significant effects on the photophysical properties of these NHC-coinage metals **185-188** with naphthalimide chromophores. (i) The intramolecular distance *d* between the two adjacent naphthalimide rings to assure interchromophoric interaction which is enhanced in solution. (ii) The dihedral angle between the long axes of the two adjacent naphthalimide units. In solid state this interchromophoric dipole moment is at maximum for α angle of 38°. Moreover, these interchromophoric π-interactions increase from solid state to solution and also with metal ion radius on moving from Cu(I) to Ag(I) and Au(I). In solution complex **187** shows in addition strong intramolecular hydrogen bonding between the two amine substituents which bring rigidity to the system in light of the high quantum yield of 92% observed in solution.

4.3 Coinage metal complexes with chiral ligands and chiroptical properties

Chen and coworkers prepared some chiral gold (I) dimers [(*R*, *R*)-**189**][A] and [(*S*, *S*)-**189**][A], displaying a metallophilic interaction. The synthetic approach follows the one described in section 4.1, however in these examples the cationic carbene-Au complexes contain chiral functionalities tethered to the backbone of the NHC)-Au-unit (Figure 38).[196]

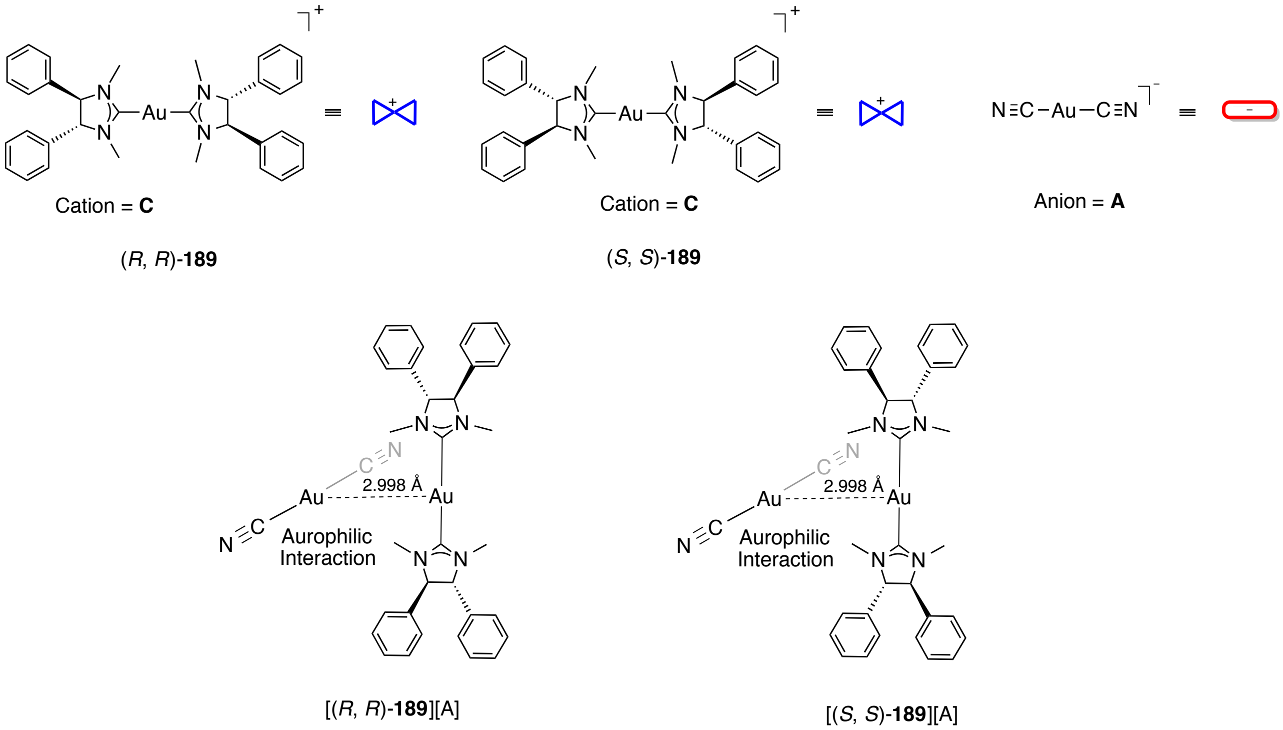


Figure. 38 Chiral Au(I) NHC complexes displaying short Aurophilic inteactions.

Due to the chiral bulky NHC-units, only dimer complexes were obtained. The crystal structure of [(*R*, *R*)-**189**][A] determined by X-ray diffraction study shows the presence of strong Au···Au interaction with $d_{(Au-Au)}$ of = 2.998 Å, suggesting strong aurophilic interactions.[160,197-198] Similar results were obtained for [(*S*, *S*)-**189**][A].

The optical properties of these complexes have been investigated in crystalline and amorphous forms and provided distinct behavior (Figure 39). For instance when crystals of [(*R*, *R*)-**189**][A] were excited at 365 nm, a vibrant greenish blue emission was observed (CIExy = 0.17, 0.36), the emission spectrum displayed a band at λ_{max} = 500 nm with τ = 1.29 μs, (Φ = 65%) and a shoulder at 450 nm with lifetime in the nanosecond regime. Thus the high energy emission can be ascribed to a fluorescence while the low energy emission with slow decay in the order of μs can be assigned to a phosphorescence emission. When the excitation wavelength was changed from 320 nm to 400 nm, the fluorescence and phosphorescence emission energies remain unchanged as can be expected following Kasha's rule.[199] In contrast, when a single crystal of [(*R*, *R*)-**189**][A] was mechanically ground, the photoluminescence properties were found to be dynamically dependent on the excitation wavelength. Interestingly the emission λ_{max} = 440 nm shifted to λ_{max} = 526 nm, upon changing the excitation wavelength from 300 nm to 400 nm. This interesting phenomenon is known as *excitation wavelength-dependent photoluminescence* (*Ex-De PL*) and might have important applications as anti-counterfeiting, in optoelectronics and also in the field of biomedical imaging.

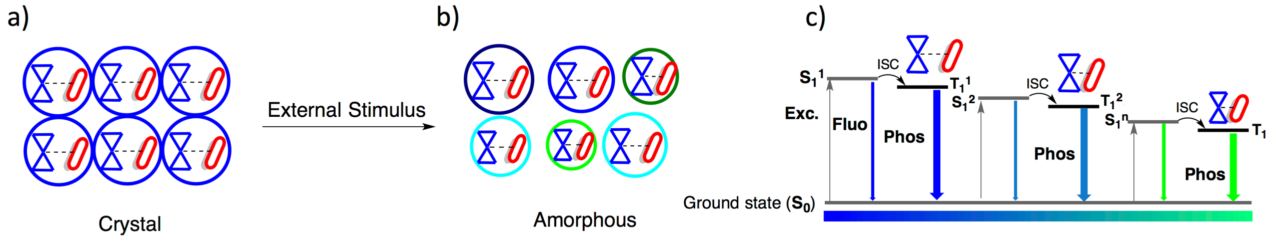


Figure 39. a) Uniform Au···Au interactions displayed in single crystal form of [(*R*, *R*)-**189**][A] or [(*S*, *S*)-**189**][A]. b) Mechanical stimulus generates dimers with different Au···Au interactions. c) Schematic drawing showing different emissions depending on the Au···Au contacts.

Similar behavior was obtained when the luminescent properties of [(*S*, *S*)-**189**][A] were studied in thin film of PMMA (poly(methyl methacrylate). The excitation spectra were red shifted with increasing emission wavelength suggesting the existence of different emission origins in the ground-state. Moreover the emission spectra remain unchanged when the concentration of the complex in PMMA was increased from 5% to 40%. These results preclude the presence of different oligomeric species whose composition is concentration dependent and support the presence of only dimeric species displaying different Au···Au aurophilic interactions in amorphous form. Experimental evidence was provided by the Raman spectra recorded for a single-crystal of [(*R*, *R*)-**189**][A] and the corresponding amorphous powder. In crystalline form the Raman spectrum shows a band at ν value of 88 cm-1, upon grinding the crystalline material to amorphous state, the spectra evolved and showed a broad band that spans from 70 to 91 cm^{-1} indicative of the presence of myriad Au···Au interactions. These various dimeric species are at the origin of the *excitation wavelength-dependent photoluminescence*. In contrast a uniform Au···Au bond distance is displayed in the single-crystal form (Figure 39).

The circularly polarized luminescence (CPL) spectra of [(*R*, *R*)-**189**][A] and [(*S*, *S*)-**189**][A] were investigated and were also excitation wavelength dependent (Figure 40).

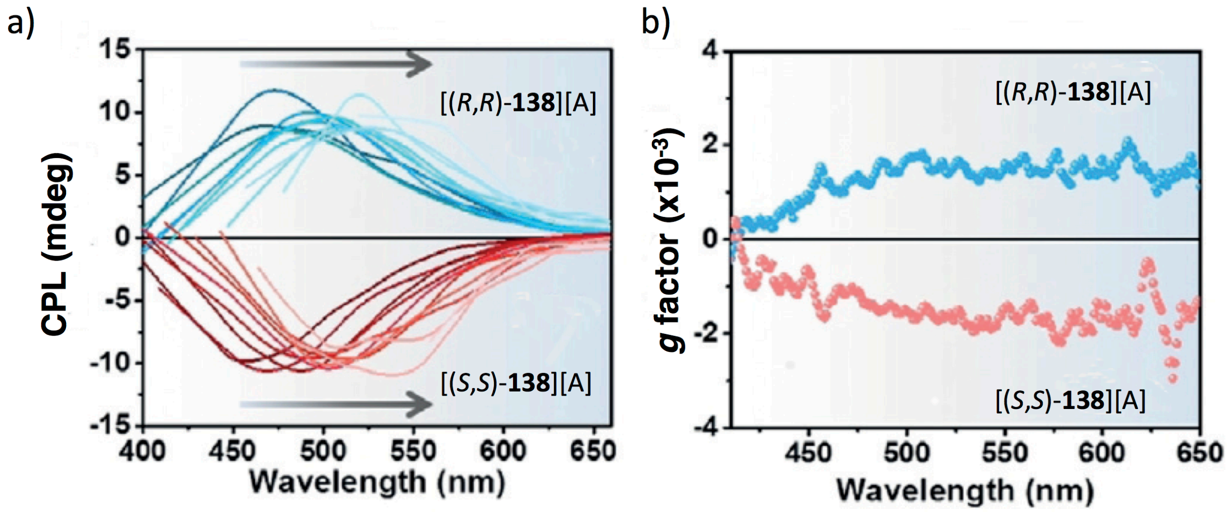


Figure 40. a) CPL spectra of [(*R*, *R*)-**189**][A] and [(*S*, *S*)-**189**][A] recorded in PMMA and varying the excitation wavelength from 300 to 400 nm through 10 nm increments. b) Dissymmetry *g*-factor versus wavelength curves. λ_{exc} = 340 nm. Adapted with permission from ref [196]. Copyright 2020 Wiley.

Upon changing the λ_{exc} from 300 to 400 nm, the CPL properties of [(*R*, *R*)-**189**][A] and [(*S*, *S*)-**189**][A] display mirror-image polarization emissions with λ_{max} shifting from 450 nm to 540 nm. The g-factor measured at the emission maxima of both compounds showed opposite mirror image curves with values up to 1.6×10^{-3} for [(*R*, *R*)-**189**][A] and -1.45×10^{-3} for [(*S*, *S*)-**189**][A].

Owing to its excitation dependent luminescent properties, ground powder of [(*R*, *R*)-**189**][A] was used as solid ink to reveal painted panda and TIPC images on a filter paper (Figure 41). The image color changed from blue to green in a dark room upon changing the excitation wavelength from λ = 245 nm to λ = 365 nm.

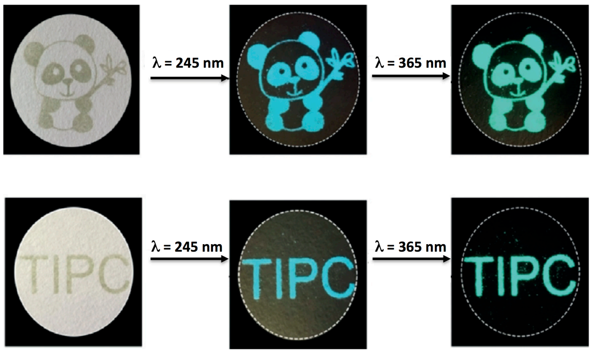
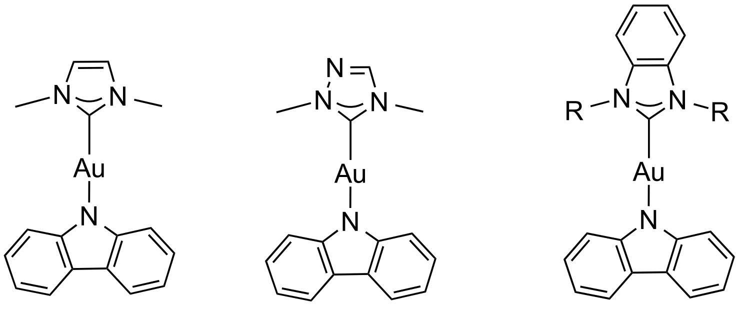


Figure 41. Photoluminescence images of screen printed panda and TIPC with [(*R*, *R*)-**189**][A] as solid ink, changing from blue to green upon varying the excitation wavelength from 245 to 365 nm. Adapted with permission from ref [196]. Copyright 2020 Wiley.

4.4 Coinage metal complexes containing carbazolate ligands

Carbazole derivatives are important organic chromophores: they display rigid planar structure, strong donor ability and rich photophysical and hole-transporting properties.[46,200] [43,45,201] Owing to these properties, extensive attention has been devoted to preparing fluorescent molecules based on carbazoles for variety of applications[202] including bioimaging probes.[44,47] In recent years efforts were devoted to construct novel class of luminescent metal complexes containing carbazolates and amides as ligands in which the anionic N-atom is bonded directly to the metal center.[203-206] As mentioned in this review, such molecules provide a platform where organic and inorganic chromophores are merged to generate novel excited states and hence it is expected to bring highly important electronic properties.

In 2005, *Lin and coworkers* prepared several carbazolate-Au(I)-NHC complexes (**190-193**) (Figure 42).[207] The crystal structure of **190** was reported and shows that the carbene and carbazolate ligands are coplanar with no Au···Au interaction ($d_{Au\cdots Au}$= 3.94Å) between two adjacent molecules; moreover the individual molecules form aggregates through π-π interactions of 3.42 Å between the carbene ring and the carbazolate ring and they display weak Au---H contacts.



190 **191** R = Me, (**192**); Et (**193**)

Figure 42. Au(I)-NHC complexes containing carbazolate chromophore

The UV-vis spectra of **190-193** performed in CH_2Cl_2 display absorptions in the range of 200-370 nm ascribed mainly to the carbazole ligand. DFT and TD-DFT calculations suggested that the HOMO and LUMO of the singlet ground state are predominately of ligands. The HOMO is localized on the Au and carbazolate ligand with 95% parentage of the latter, and the LUMO is situated on the carbene ligands. The solid state emission of these compounds displayed structured emission bands with HE (high energy) bands in the area of 404-438 nm and LE (low energy) bands in the range of 516-592 nm with lifetimes in the microsecond regime. The authors assigned these bands to the intraligand transition of the carbazolate ligand perturbed by the Au(I) center.

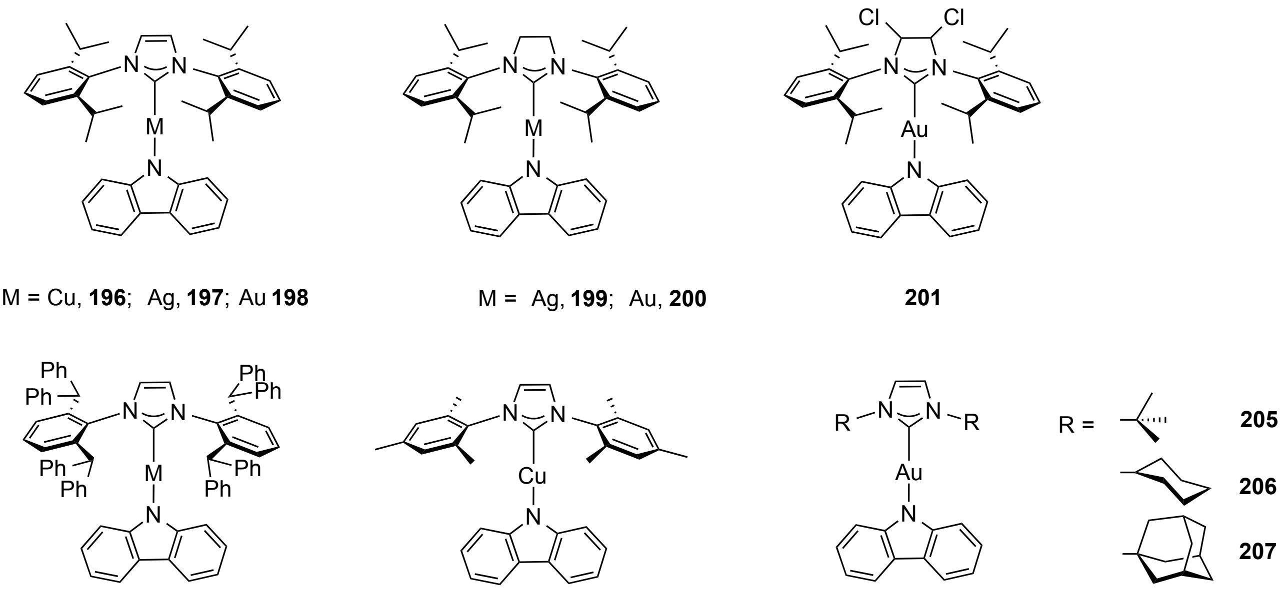
Liu and coworkers designed some copper complexes displaying a two coordinate structure around the metal center containing a carbazole ligand and N-heterocyclic carbenes **194-195** (Figure 43).[208]

194 **195**

Figure 43. Cu(I) NHC complexes containing carbazolate chromophore.

Compounds **194** and **195** were found to be luminescent and exhibit dual emission. For instance, at room temperature complex **194** exhibits structured emissive peaks at λ_{em} = 400-550 nm which are insensitive to O_2, with τ = (16, 24 ns) identified as fluorescence emission and a long-lived emission (τ = 55ms) with vibronic structure at λ = 550-750 nm denoted as phosphorescence. Similar behavior was obtained for complex **195**. The authors suggest that there exist singlet ^{1}LE and triplet ^{3}LE excited states localized at the carbazole ligand in the crystal. In order to highlight this behavior, the authors selectively deuterated the carbazole unit in complex **194**. The deuterated complex (IPr-Cu-dCbz) (**194**-deuterated) displayed longer lifetime for the room temperature phosphorescence (t = 140 ms) and enhancement of the phosphorescence PLQY = 22.8% compared to that of the (IPr-Cu-Cbz) (**194**) which is only 7.9%.

Nolan, Steffen and coworkers described a novel synthetic procedure to prepare a variety of NHC-coinage metals **196-207** containing carbazolate ligands (Figure 44).[209] The synthetic procedure involves the use of the weak base strategy (base = K_2CO_3, NEt_3) in acetone or ethanol under mild conditions for 24h.[210-211] It should be mentioned that K_2CO_3 provided better yields and is the base of choice for this reaction procedure. This synthetic approach was also used to obtain the halogenated precursors in good yields. The authors suggest based on DFT calculations that the reaction pathway to the target molecules involves a concerted metalation/deprotonation process.



M = Cu, **196**; Ag, **197**; Au **198**

M = Ag, **199**; Au, **200**

201

M = Ag, **202**; Au, **203**

204

Figure 44. Variety of coinage metal NHC-complexes containing carbazolate chromophore.

The X-ray molecular structures of the NHC-complexes of copper **196**, silver **197, 202** and gold **200**, **206-207** were determined.[209] As expected the coordination geometry around the metal is almost linear with angle θ values varying from 174.0 to 179.8°; moreover the carbazolates and the carbene ligands are coplanar.

The optical properties of these compounds were investigated in fluid and in solid state. In general the gold compounds displayed the higher stability in solution relative to the copper and silver congeners and due to their strong SOC (spin-orbit coupling) intersystem crossing (IST) $S_1 \rightarrow T_n$ occurs with higher efficiency. For instance, in THF solution the silver complex **197** showed dual emission; (i) a fluorescence emission between 380-440 nm assigned to metal perturbed ^{1}CBZ LC state and (ii) a weak phosphorescence emission from the ^{3}CBZ state at $\lambda = 437$ nm with significant longer life time $\tau = 1\text{-}10$ μs. The presence of a fluorescence band at $\lambda = 343$ ($\tau = 13.5$ ns) which is assigned to free carbazole as a photodecomposition product because the excitation emission does not correspond to the absorption of **197**. In contrast to copper and silver the gold compounds **198** and **200** in THF solution displayed only phosphorescence emissions from high ^{3}CBZ transition states at $\lambda = 430$ nm and ($\Phi = 0.32$) and life-times of $\tau = 332$ and 266 μs respectively. Due to the fast $k_{\mathrm{ISC}} > 10^{10}$ s^{-1} in the gold complexes, the fluorescence emission is quenched in favor of the phosphorescence. On the other hand, their low $k_{\mathrm{phos}} = 10^{-3}$ s^{-1} value allows them to act as good photo-catalysts because they possess long-lived triplet states. Thus their properties as photo-catalysts were explored in particular for complex **200** (vide infra).

The emission of the silver complexes **197-199** in the solid-state exhibited dual emissions; a fluorescence broad band from LC ^{1}CBZ at $\lambda_{\mathrm{flo}} = 390$ nm with nanosecond life-time regime and phosphorescence emission between $\lambda_{\mathrm{phos}} = 480$-$700$ nm ($\tau = 45\mu$s and 355μs for **197** and **199**). The triplet-state band is structured but broad and the excitation spectra in the range of 400 to 480 nm different from the absorption observed in solution, suggesting that aggregation in solid state affects their luminescent properties.

The gold compounds **198-200** display phosphorescence emissions similar to those observed in solution ($\lambda_{\mathrm{phos}} = 424$nm) but with shorter lifetimes $\tau = 74$ and 38 μs respectively. Interestingly a second lower energy phosphorescence structured emission is observed at $\lambda = 550$ nm with $\tau = 885$ μs and 347 μs respectively. The excitation spectra of the phosphorescence emissions of the gold complexes corroborate with their absorption in solution, however the longer phosphorescence excitation spectra show additional bands between 400-440 nm. These results suggest again that aggregation affects the luminescent properties in the solid state and the change in life-time suggest that aggregation exists already in the ground-state and not only the result of excimer formation in the solid state.

The Au-complex (**200**) displayed a long-lived triplet state in the blue-green range with the highest photostability, hence it was selected by the authors as a photo-catalyst for the [2+ 2] intramolecular cycloaddition of (E, E')-dicinnamyl ether to give the corresponding fused cyclobutane. Upon irradiation at $\lambda = 365$ nm with 18 W LED, at 5% catalyst loading, total conversion (> 99%) to the desired product was achieved after 4 hours (see Scheme 3 and Table 1).

These data suggest that complex **200** is highly efficient for the photocatalysis reaction and represent a proof-of-principle where two coordinate NHC-Au-carbazolate complexes with long-lived triplet state can be used as an efficient photocatalyst. [209]

Scheme 3. Photocatalysis of (E, E')-dicinnamyl ether and formation of fused cylobutane.

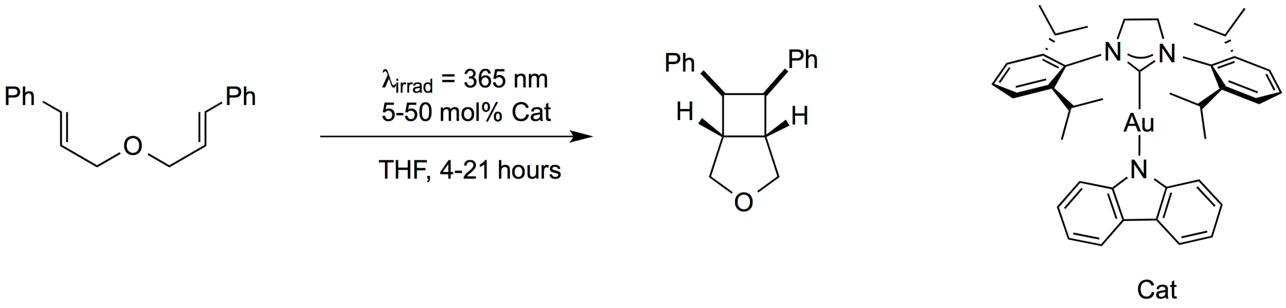


Table 1. i) Entry 1: catalyst amount was weighed. Entries 3 to 7, a stock solution in THF was employed. ii) Conversions were calculated using ^{1}H-NMR spectroscopy by determining the ratio of the product and reactant. iii) Control reaction carried out in the dark.

Entry	Catayst Load[i] [mol%]	Time [h]	Conversion[ii] [%]
1	50	21	>99%
2	10	21	>99%
3	5	21	>99%
4	10	4	>99%
5	**5**	**4**	**>99%**
6	none	21	12
7[iii]	10	21	0

As will be shown in section 5 the related compounds containing electrophilic carbenes (CAAC = cyclic (alkyl)(amino) carbene), (MAC = monoamido-amino carbenes), (DAC = *N*, *N*'-Diamidocarbene) display short triplet lifetimes which make them efficient emitters for OLED application.[212] We feel a review on luminescent carbene complexes will be incomplete without mentioning this novel class of highly emissive compounds. This work is presented in section 5.

4.5 Three- and four-coordinate coinage metal complexes.

Thompson and coworkers reported some phosphorescent three-coordinate carbene copper complexes **209-212** containing anionic non-conjugated (N^N) ligand, mainly di(2-pyridyl)dimethyl borate (**208**) (Figure 45).[213]Complexes **209-211** were found to be emissive in solid-state and provided sky-blue, yellow and orange emissions with quantum yields varying from 0.8, 0.7 and 0.16 respectively with life-times in the microsecond regime (11μs, 15 μs and 7.5 μs respectively).

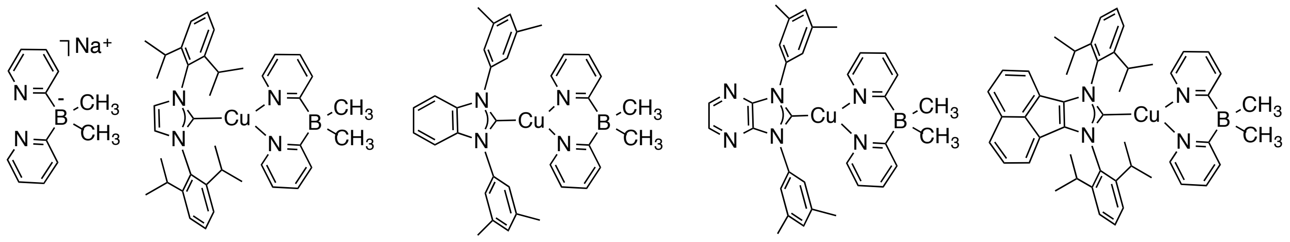

208 **209** **210** **211** **212**

Figure 45. Copper NHC-complexes containing di(2-pyridyl)dimethyl borate.

At low temperature (77K) complexes **209-211** displayed modest increases in the emission life-times (36μs, 17μs, 21μs respectively) suggesting that the observed emission at ambient temperature is phosphorescent in nature and not a Thermally Activated Delayed Fluorescence (TADF). TADF process occurs often with marked increase in emission life-times upon cooling of at least one order of magnitude.

TD-DFT calculations demonstrated that the HOMOs are mostly located on the anionic ligand **208** and on the metal center while the LUMOs are mostly located on the NHC ligand with substantial contribution from the carbene carbon $2p_z$ orbital. Thus functionalization of the backbone of the NHC ligand by π-extension or addition of heteroatoms lower the LUMO and hence reduces the HOMO-LUMO gap which explain the observed emissions from sky-blue to orange for complexes **209-211**. For comparative purposes complex **212** was designed by expanding the π-system of the NHC ligand backbone with a peri-naphthyl group. Unlike **209-211**, complex **212** was found to be non-emissive in solid-state at room temperature and at 77K. TD-DFT calculations carried out on **212** demonstrated that the HOMO levels are not changed relative to **209-211**: however the LUMO is now located on the aromatic system of the naphthyl group and has no electron density on the $2p_z$ orbital of the NHC carbon center. Thus the triplet spin density of **212** is located on the acenaphthyl moiety and in contrast to **209-211**, who display a node across C_{NHC}-Cu. As a consequence for **212** this reduces effectively the interaction with MLCT states responsible for promoting fast radiative decay.

Another class of three coordinate Cu(I) complexes (**213**-**217**) was reported by Cisnetti, Steffen and coworkers (Figure 46).[214] The dimer complexes were characterized by X-ray diffraction studies and showed short Cu---Cu interactions for instance; **213** with 2.5226(8)Å, **214** with 2.5638(4)Å, **215** 2.5668(8)Å, and **216** with 2.5744(9)Å.

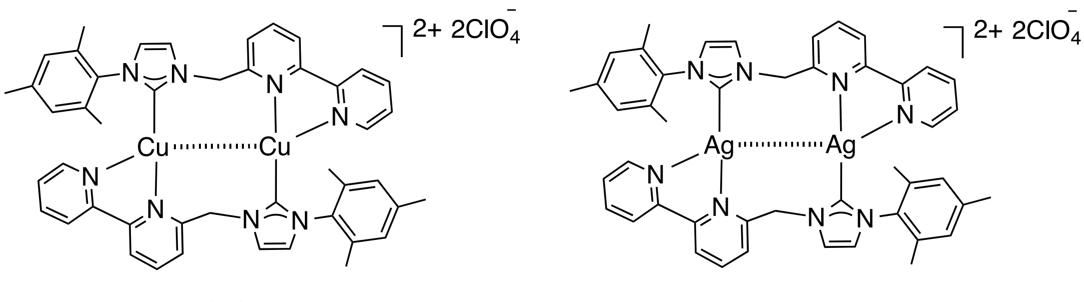
R = Cl, (**213**); H, (**214**); R = Me, (**215**); R = OMe, (**216**)

(**217**)

Figure 46. Cu(I) NHC-picolyl dimer complexes **213**-**216** and the related Cu(I) polymer **217**.

All complexes were luminescent in solid-state under argon and displayed greenish emissions. The dimer complexes **213**-**216** with cuprophilic interactions were more emissive than the polymeric compound **217**, which displays no Cu---Cu contacts. All complexes in solid-state and at ambient temperature exhibited broad bands in the range 520-550 nm with quantum yields ranging from $\Phi = 0.31$ to 0.59 and lifetimes in the microsecond regime. The temperature dependent emission lifetimes measurements of **213** and **214** provided sigmoidal curves with increase of lifetimes at 77 K by factor of 8 to 9 times suggesting a TADF process is occurring at room temperature. The resulting ΔE (S_1-T_1) was found to be only 710-740 cm^{-1}. On the other hand at low temperature complexes **216** ($\tau = 15.3 \mu s$; $\tau_{77K} = 18.7\ \mu s$) and **217** ($\tau = 14.6 \mu s$; $\tau_{77K} = 19.5\ \mu s$) showed minor increases in lifetimes, which favors that the emissions observed for **216** and **217** at room temperature are phosphorescent in nature. TD-DFT calculations suggest for the T_1 states involved in the TADF emitters **213** and **214** can be ascribed as ^{3}MLCT involving only one Cu(I) center. However the T_1 state of **216**, which is an efficient pure triplet emitter, can be attributed to the two Cu(I) centers as a ^{3}(Cu$_2$)LCT transition with τ_{77k} = 18.7 μs. Interestingly complex **215** displayed both behaviors a TADF and phosphorescence originating from two distinct triplet states mainly a ^{3}MLCT transition with a long lifetime (τ_{77K} = 113 μs) as observed for **213** and **214** and a ^{3}(Cu$_2$)LCT state with short lifetime (τ_{77K} = 23 μs) similar to **216**. As it might be expected, the strongest metallophilic contacts involved in the T_1 state should increase the SOC and hence decreases the T_1 lifetimes. The authors suggest that the presence of short cuprophilic contacts in the dimer complexes might serve as a synthetic approach to design highly efficient Cu(I)-based emitters. These metallophilic interactions can secure strong SOC for fast IST $T_1 \leftrightarrow S_1$ and $T_1 \rightarrow S_0$ transitions which provide fast radiative rate constants k_r either by TADF or by fast phosphorescence.

Roesky and coworkers described the synthesis of cationic bimetallic Cu(I) and Ag(I) carbene complexes **218-219** (Figure 47).[215]The mesityl-NHC is tethered to a bipyridyl ligand, which chelates the metal center generating three coordinate metal complexes. The rigidity of the tridentate ligand brings the two metal centers closer, generating a metal---metal interaction as confirmed by X-ray diffraction study, which provides a tetra coordinate geometry around each metal center.



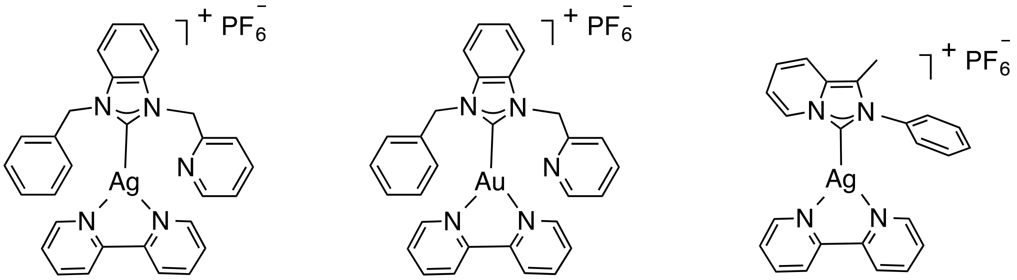
218

219

Figure 47. Bimetallic copper and silver carbene complexes supported by dipyridyl ligands.

Crystallization of the metal complexes provided red crystals for the copper **218** and colorless crystals for the silver compound **219**. The X-ray structures of **218** and **219** showed that the Cu----Cu contact is at 3.2168(9) Å and for Ag---Ag is at 3.1034(11). The copper complex displayed an absorption band at λ ~ 450 nm in acetonitrile, and exhibited a weak broad band emission in the NIR zone at λ ~ 800 nm. As for the silver compound the authors indicated that the photoluminescence behavior was complicated and unusual. For instance the life-time decay traces were temperature dependent and could be fit with at least three exponential components. At 16 K a long lifetime τ = 23 msec in the millisecond regime was measured which upon increasing the temperature shortens to the tens of microseconds at 295K. The authors suggest that a phosphorescence process is occurring which tentatively involves Ag-bpy groups and also the Ag---Ag argentophilic interaction. At room temperature the quantum yield for **218** was found to be Φ = 0.4%, and increases to 9% at 15 K. In the absence of TD-DFT calculations no details on the nature of the excited states involved were discussed.

Dinda and coworkers described some silver and gold carbene cationic complexes displaying trigonal geometry around the metal center (Figure 48).[216-217]



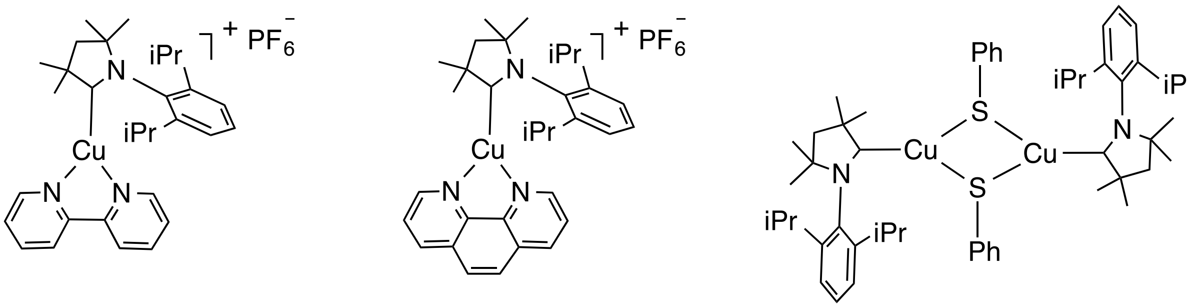
220 **221** **222**

Figure 48. Silver and Gold carbene complexes displaying trigonal geometry.

The X-ray molecular structure of complex **220** was determined and the crystal packing showed the individual molecules display a head to tail fashion with π-π and Ag-Ag (3.130 Å) interactions between two adjacent molecules. Compounds **220** and **221** were emissive in solution and in solid state at room temperature. The photoluminescence spectra recorded for **220** and **221** in CH_3CN

provided a broad band at λ_{em} = 430 nm and λ_{em} = 440 nm respectively. In solid state these bands are red shifted to λ_{em} = 540 nm and λ_{em} = 567 nm. The lifetimes and the quantum yields were not determined. DFT calculations suggested that the HOMOs are mostly located on the metal and the NHC ligand while the LUMOs are situated on the bipyridyl ligand. As for **222** the complex displayed absorption maxima in CH3CN, at 284-330 nm. Moreover the complex displayed strong emission in solution at ambient temperature with λ_{em} = 407 nm and Φ = 16.9% with short lifetime τ = 3.25 ns. DFT calculations suggested again that the HOMOs are mostly on the metal and carbene ligand while the LUMOs are on the bpy ligand. Despite the very short lifetime of the observed emission, the authors suggest that the emission might be due to MLCT and (IL) transitions.[217]

Steffen et al. prepared some phosphorescent tricoordinate Cu(I) diimine complexes containing cyclic(alkyl)amino carbene (CAAC) (Figure 49). CAAC ligands are stronger σ-donor and better π-acceptor than NHC-ligands (see next paragraph).[218]



223 **224** **225**

Figure 49. Three coordinate Cu(I) compounds displaying cyclic(alkyl)amino carbene ligands.

The trigonal diimine complexes **223**-**225** were emissive in the far red and near infra-red regions. Complex **223** displayed very weak emission at λ = 670 nm while complex **224** displayed a similar broad band at λ = 672 nm with low quantum yield Φ = 0.01 and biexponential decay lifetimes. In contrast the dimer complex **225** was found to be strongly emissive and displayed a phosphorescence emission at λ = 612 nm tailing into the NIR region with Φ = 0.39 and τ = 36 μs.

The authors also noted in comparison with related trigonal diimine compounds featuring NHC-ligand [Cu(phen)(IDipp)][OTf], complexes **223** and **224** displayed a red-shifted emission by 50 nm into the NIR region. This behavior is attributed to the stronger donor capacity of CAAC, which destabilizes the HOMO copper d orbitals while the LUMO remains unchanged and located on the diimine ligand.

Thompson and coworkers reported another class of three and four coordinate Cu(I) complexes containing CAAC and anionic trispyrazolborates (Tp) ligand (Figure 50). [219]

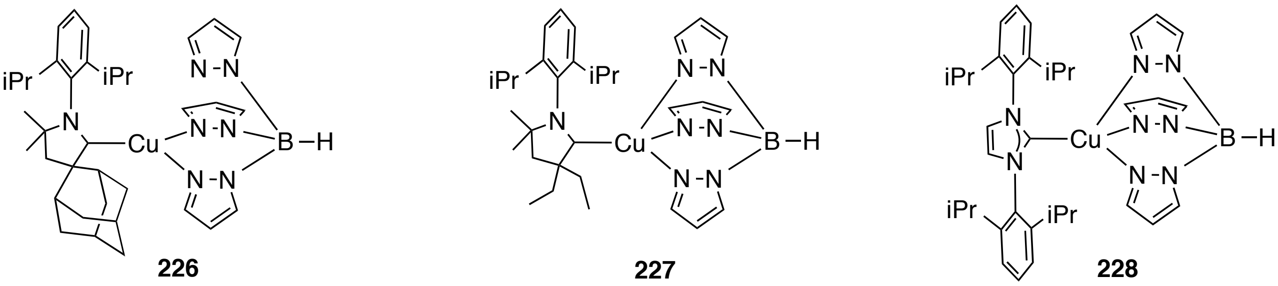


Figure 50. Tri- and tetra-coordinate carbene Cu(I) complexes containing trispyrazolylborates.

Complex **226** was obtained as a tricordinate species due to the steric hindrance of the bulky adamantyl substituent on the CAAC ligand which forces one pyrazolyl arm to remain uncoordinated. Complex **226** displayed a weakly orange emission (λ_{max} = 616nm, Φ = 0.02) with biexponential lifetime decay (τ_1 = 0.4μs, 40%; τ_2 = 1μs, 60%). At low temperature this complex displayed stronger emission with concomitant increase in its biexponential lifetimes.

Upon replacing the bulky adamantyl group with smaller ethyl groups the tetracoordinate Cu(I) complex **227** was obtained. Complex **227** provided bright yellow phosphorescence at λ_{max} = 550 nm with good quantum yield Φ = 0.46 and lifetime τ = 12μs. It is plausible to suggest that the free pyrazolyl ligand might contribute to deactivating the radiative decay in **226**, via a PET mechanism, which shows a dramatic decrease in the PLQY compared to **227**. DFT calculations carried out on these compounds suggested that the HOMOs are mostly Cu-based and the LUMOs are largely located on the carbene ligand.

For comparison purposes the tetracoordinate Cu(I) complex **228** was prepared in which the CAAC ligand was replaced by NHC ligand in order to probe the carbene effect on the luminescent properties of the related complexes. Compound **228** exhibited blue phosphorescence emission at λ_{max} = 462 nm, τ = 29μs and Φ = 0.25. DFT calculations performed on **228** demonstrated that E_{LUMO} = -0.37eV while for complex **227** with CAAC ligand, E_{LUMO} = -0.74eV which is highly stabilized providing a smaller HOMO-LUMO gap and eventually the expected yellow phosphorescence but with higher PLQY and lower lifetime when compared to **228**.

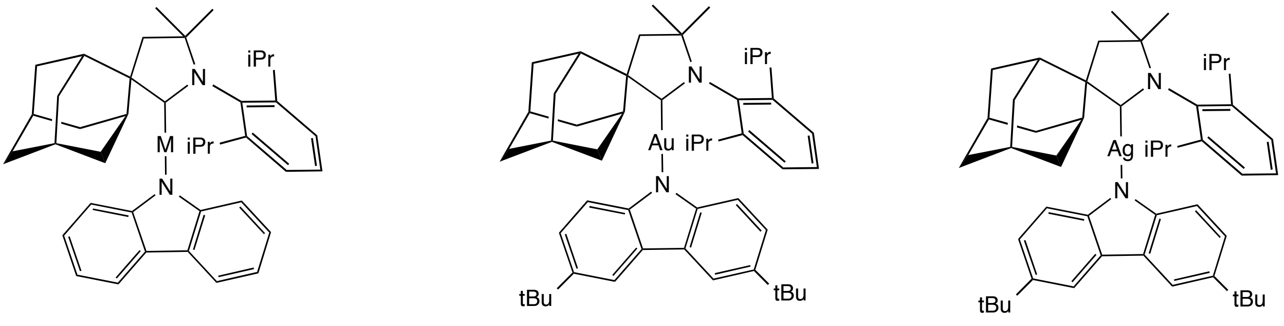
This example highlights the importance of CAAC ligands and their use in preparing efficient phosphorescent complexes. This type of complex is detailed in the next paragraph.

5-Luminescent coinage metals with CAAC, MAC and DAC carbene ligands

In the previous section we described a variety of luminescent complexes containing *N*-heterocyclic carbene (NHC) with appealing structures, and demonstrated their useful applications. It is noteworthy to mention that in the past five years there has been a great interest to investigate another class of metal carbene complexes due to their remarkable luminescent properties where the carbenes display more π-accepting character compared to the *N*-heterocyclic carbenes (NHCs). These carbenes are designated by Cyclic (alkyl) (amino) carbene (CAAC), *N*, *N*'-diamidocarbene (DAC) and monoamido-amino carbenes (MAC). For instance, the classical *N*-heterocyclic carbene contains two σ-electron-withdrawing and π-donor N-atoms, while in CAAC, a σ-donating carbon center is now visible instead of one N-atom. As a consequence, the CAAC displays only one σ-electron-withdrawing and π-donating N-atom, which generates a smaller HOMO-LUMO gap in CAAC when compared to the classical NHC. DFT calculations on CAAC revealed that the LUMO is lowered, concomitant with a rise in the HOMO relative to NHC.[220-221] This kind of carbene was coined by Bertrand and coworkers in 2005.[222]

Two other non-conventional carbenes are DAC and MAC which also show high electrophilicity, comparable to CAAC. They include amido groups in their chemical structure, which increase the electron-withdrawing properties of the carbene and consequently lower the energy level of the LUMO.[223-225]

Bochmann, Romanov, Linnolahti, and Credgington prepared and studied the photophysical properties of some luminescent coinage metal complexes containing carbenes as well as amide ligands and displaying linear two-coordinate geometry (Figure 51).[48,204-205,212,226-232] Unlike the preceding examples, in this new class of luminescent carbene-metal-amide (CMA) complexes **229-233** the anionic amide ligand is the σ-donor ligand and upon photo-excitation an electron from the π-system of the amide is promoted into the CAAC carbene-based LUMO.[222] These carbene-metal-amide complexes display high quantum yields (Φ_{PL} up to 98%) and very short excited state lifetimes (< 1μs). The authors highlight the importance of rotational flexibility along the C-M-N axis of the carbene-metal-amide complexes for photoemission efficiency. For instance, the S1-T1 energy gap converges to zero at high torsion angles, as a consequence this accelerates the intersystem crossing and provides luminescence with short lifetimes in the submicrosecond regime.



M = Cu (**229**) , Ag, (**230**) Au (**231**)

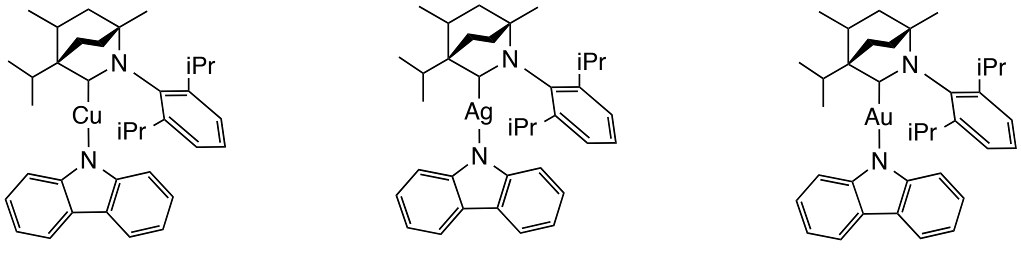
232

233

Figure 51. Coinage metal complexes with cyclic (alkyl)(amino) carbene (CAAC) ligands and featuring carbazolate chromophore

Due to their high optical properties, compounds **229-231** were used as green emitters to design efficient OLEDs. For instance, the Cu-carbene complex **229** and the Au carbene compounds **231-232**, dispersed in PVK host provide efficient green electroluminescence in OLEDs, with (EQE max) = 9.7%, 26.3% and 27.5% respectively. EQE performance was also measured at different brightness (100 cd m^{-2} / 1000cd m^{-} for **229** (8.9%/9.2%) and **231** (26.1%/ 25.2%) and **232** (26.6% / 24.5%).[212] Moreover, OLEDs based on Ag-carbene complexes **230**, **233** were also manufactured and displayed (EQE max) = 4.3% and 13.7% respectively. EQE values at low brightness 100 cd m^{-2} were also obtained for **230** (2.7%) and for **233** (12.9%).[228] At ambient temperature both complexes emit via TADF-type process with short lifetimes in the sub-microsecond regime (**230**, τ = 358 ns and **233**, τ = 368 ns in PVK matrix). The lower EQE observed for the silver complex **233** when compared with the gold complex **231** is consistent with PLQY of the silver complex which is around 74% compared to the PLQY of the gold compound which is around 98%.[232]

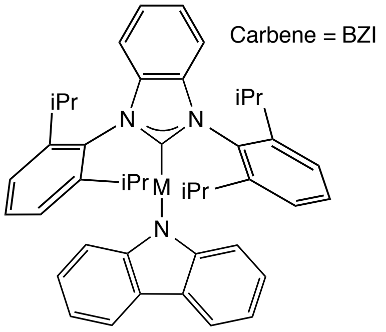
While these examples featured five-membered rings in the carbene ligands, the Bochmann group reported also several luminescent carbene-metal-amide (CMA) complexes (M = Cu, **234**; Ag, **235** ; Au, **236**) displaying six-membered rings in the cyclic (alkyl)(amino) carbene (Figure 52). Interestingly the related bicyclic carbene metal amide complexes displayed higher performance; this was attributed to an increase in the rigidity of the carbene ligand which minimizes the nonradiative deactivation processes, generating CMA complexes with 100% quantum yields and shorter excited state lifetimes on the order of 0.5μs.[48]



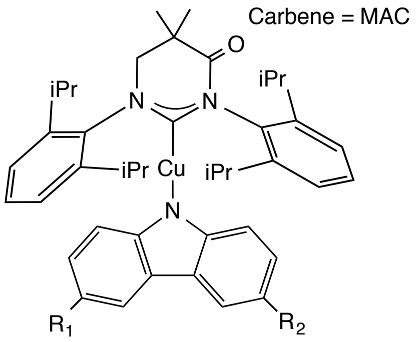
234 **235** **236**

Figure 52. Bicyclic carbene coinage metal amide complexes.

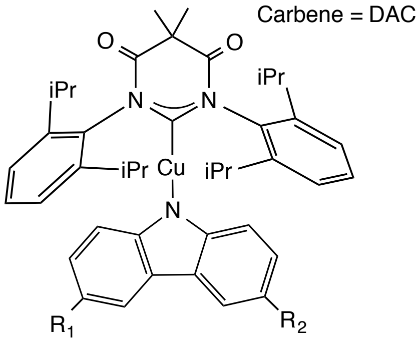
Thompson and coworkers also investigated the optical properties of luminescent coinage metal complexes displaying linear coordination geometries with only a two-coordinate arrangement around the metal center.[233-234] The authors took advantage of the steric hindrance displayed by the ligands to bring rigidity to the desired molecules and to avoid structural deformation in solution, which should eventually impact their photophysical properties. These compounds comprise sterically bulky benzimidazolyl carbene (BZI) (**237**-**239**), unconventional N-heterocyclic carbenes such as monoamido-amino carbenes (MAC) (**240**-**242**) and diamidocarbenes (DAC) (**243**-**245**) or cyclic (alkyl)(amino)carbenes (CAAC) (**246**-**248**) and carbazolate (Cbz) as the anionic ligand (Figure 53). [49,203,206,235] In these compounds, the authors highlight the electrophilic character of the carbenes.[224-225] Hence, as in the previous section, these (carbene)M(amide) compounds display intramolecular charge transfer "ICT" emission, with electron transfer occurring from an amide-N (Donor) to carbene-C (Acceptor). This transition is also known as ligand-to-ligand charge transfer "LLCT". The luminescence color of these complexes to be tuned from deep blue to deep red by changing the electrophilicity of the carbenes as well as the nucleophilic properties of the amides bound to the metal center. Moreover they are highly emissive with quantum yields ($\Phi_{PL} > 80\%$).



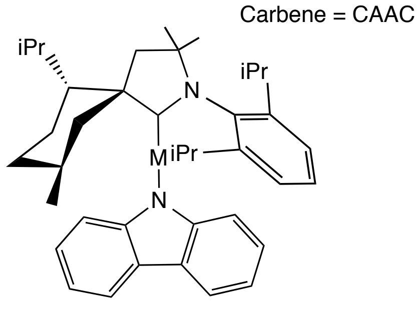
M = Cu (**237**); M = Ag (**238**); M = Au. (**239**)



R_1, R_2 = CN (**240**); R_1 = CN, R_2 = H (**241**); R_1, R_2 = H (**242**)



R_1, R_2 = CN (**243**); R_1 = CN, R_2 = H (**244**); R_1, R_2 = H (**245**)



M = Cu (**246**); M = Ag (**247**); M = Au. (**248**)

Figure 53. A variety of coinage metal complexes with NHC, MAC, DAC and CAAC carbenes and featuring carbazolate chromophore.

For instance, complexes with BZI carbenes showed similar behavior (structures, redox potentials, and photoluminescence quantum yields, Φ_{PL} = 80%-100%) to those with MAC carbenes, but displayed different excited state dynamics and are reported to have efficient blue photoluminescence and to give good efficiencies as dopants in OLEDs. For instance, the gold carbene **239** in 1,3-bis(triphenylsilyl)benzene host, was used as a dopant for OLED device and displayed an external quantum efficiency of 12% with narrow deep-blue emission with CIE (0.16, 0.06).[49]

The coinage metal complexes with MAC and DAC carbenes display narrower HOMO-LUMO gaps compared to the other series, because of the more electrophilic character of the carbene ligands which contain carbonyl functions in their cyclic structure that tend to lower the LUMO. For instance, the reduction potentials for the DAC complexes are more anodically shifted relative to the analogous MAC compounds. Hence emission in these derivatives **243**-**245** is bathochromically shifted to the lower energy of the light spectrum. However, substitution of the carbazole ligand with cyano groups tends to stabilize the HOMO and blue-shift the emission as observed for complexes **240** and **241**. In general, the absorption spectra of these compounds displays negative solvatochromism, while the emission spectra undergo red shift in polar solvents with decrease in quantum yields and lifetimes. For instance, complex **242** displays (Φ_{PL} = 0.90, τ = 1.55μs) in MeCy (methylcyclohexane) and (Φ_{PL} = 0.18, τ = 0.41μs) in CH_3CN. At ambient temperature in polystyrene thin film, the observed emission of complex **242** is attributed to thermally activated delayed fluorescence[236-238] (TADF), because of the large increase in emission lifetime upon cooling to 77K and to the small energy separation between the singlet ^{1}LLCT and triplet ^{3}LLCT transition states. The TADF process often occurs at room temperature with short emission lifetimes. This is due to spin-allowed emission from the S_1 state upon thermal rISC (reverse intersystem crossing) $T_1 \rightarrow S_1$. At lower temperatures however, the emission lifetime becomes much longer up to one or three orders of magnitude due to impediment of rISC and less efficient emission from the T_1 state, which leads to a sigmoidal lifetime curve typical of TADF.[57,239] Due to its high optical performance the copper complex (MAC)Cu(carbazole) (**242**) was doped at 40% into 3,3'-di(9H-crabazol-9-yl)-1,1'-biphenyl (*m*CBP) for green OLED devices and provided a maximum EQE = 19.4%.[235] On the other hand the copper complex (CAAC)Cu(carbazole) (**246**) was doped into 1,3 bis(triphenylsilyl)benzene (UGH3) at 20 volume % to generate an efficient blue OLED device with EQE = 9% and 16cd/A at 2mA/cm^2.[203] It should be mentioned that EQE and emission energies of OLEDs strongly depend on the structure of the OLED and the chosen host material. A critical assessment is only possible if these factors are taken into account.[240-241]

The importance of luminescent carbene-metal-amide (CMA) complexes has also stimulated theoretical chemists and physicists to perform computational studies in order to support the experimental observations and to rationalize the obtained results.[242-247] For instance, the Shuai group employed a hybrid quantum mechanics and molecular mechanics (QM/MM) approach to investigate the TADF pathways of two CMA complexes in solution and solid state. The authors demonstrated that intersystem crossing (ISC) and reverse intersystem crossing (rISC) are enhanced by two to four orders of magnitude upon aggregation i.e. by close proximity of individual molecules in solid state but without formation *M-M* contacts discussed earlier in this manuscript. The steric hindrance provided by the CAAC ligand employed does not permit close intermolecular contacts. As a consequence this aggregation leads to higher TADF efficiency in the solid state.[248] The Cui group used DFT/MRCI (Multireference Configuration Interaction) methods to investigate the TADF pathways of a CMA copper compound displaying a bicyclic six membered ring in the CAAC ligand (Figure 54). The authors suggest that a model with only three states (S_0, S_1 and T_1) is sufficient to describe the TADF mechanism, because the S2 and T2 states are located at higher energy, and thus play a negligible role. The calculated S1-T1 energy gap is only of 0.1ev which is small and due to spin-orbit couplings, this facilitates the reverse intersystem crossing from T1 to S1 at room temperature. The calculated constant k_{rISC} = 8.81x10^6

s^{-1} is more than three order of magnitude larger than the T_1 phosphorescence rate $k_{phos} = 1.11 \times 10^3$ s^{-1} consequently TADF pathway occurs. At 77K the rISC is very slow with $k_{rISC} = 6.42 \times 10^1$ s^{-1}, which is much slower than the T_1 phosphorescence rate and hence the rISC process, becomes thermodynamically unsupportive.[249]

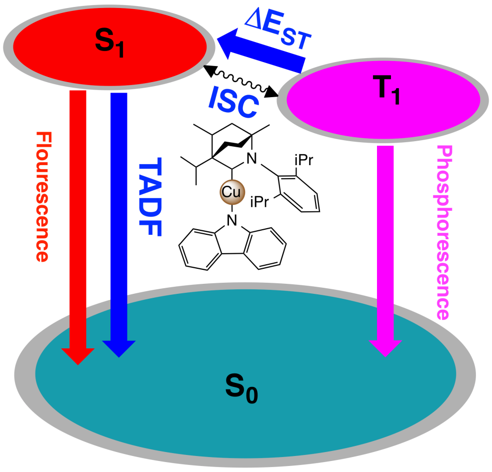


Figure 54. Proposed TADF pathways in CMA copper compound based on DFT/MRCI computational studies. Adapted with permission from ref [249]. Copyright 2022 American Chemical Society.

Steffen and coworkers prepared some copper complexes containing cyclic amino aryl carbene (CAArC) displaying different geometrical forms such as planar, linear and displaying half sandwich organometallic moieties **249-254** in order to obtain copper complexes exhibiting red emissions (Figure 55).[245]

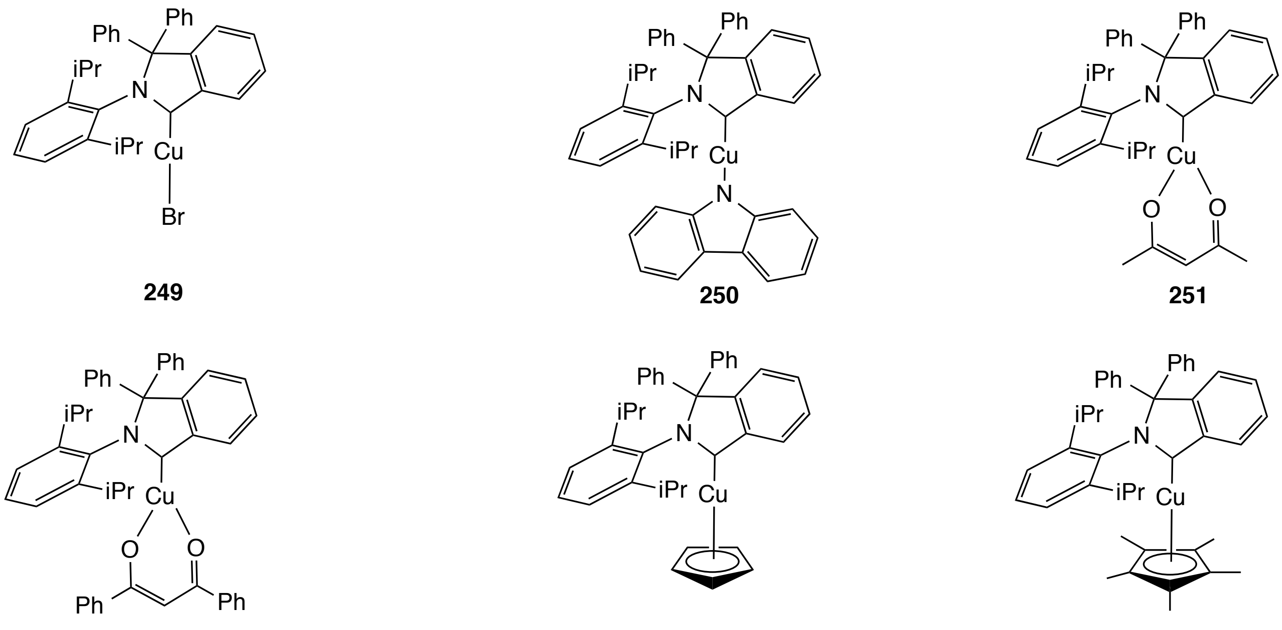


Figure 55. Cu(I) with cyclic(amino) (aryl) carbene (CAArC) ligands.

In these compounds the use of CAArC containing an organic π-fluorophore instead of CAAC promotes a red shift in the UV-vis spectra where absorption bands with strong extinction coefficient are displayed at lowest energy of the visible spectrum and mainly for complex **254**. At room temperature in THF solution only complex **250** was found to be emissive. The authors suggest that in polar THF solution the nonradiative decay is very efficient in these Cu(I) CAArC complexes. However, in solid state these complexes **249-250** are brightly emissive in the red region with λ_{em} = 621 nm (**249**) and 651 nm (**250**) with quantum yields up to 32%. The trigonal complexes **251**, **252** as well as the half-sandwich CpCu-complex **253** were emissive with displaying emissions at λ_{max} = 760nm, 772nm and 700 nm respectively. Complex **254** was not emissive. The (CAArC)Cu(carbzole) complex **250** was found be the most emissive in this class of compounds. On the basis of experimental studies involving VT luminescence, transient absorption, fluorescence upconversion, and theoretical calculations, the authors suggest that in the solid state a very efficient thermally activated delayed fluorescence (TADF) process involving singlet ^{1}LLCT and triplet ^{3}LLCT excited states is taking place in a similar fashion to that reported by Thompson and coworkers in the previous section.

Linnolahti and Bochmann and coworkers designed another class of two coordinate coinage metal complexes featuring a CAAC carbene and an anionic carbene ligand based on methylmalonate–derived NHC (*malo*NHC).[250] These complexes can be described as zwitterionic mixed carbene coinage compounds **255**-**257** (Figure 56). This type of anionic carbene ligand was first isolated by Cesar, Lavigne and coworkers, and demonstrated that such carbenes are strongly donor ligands and form stable metal complexes.[251]

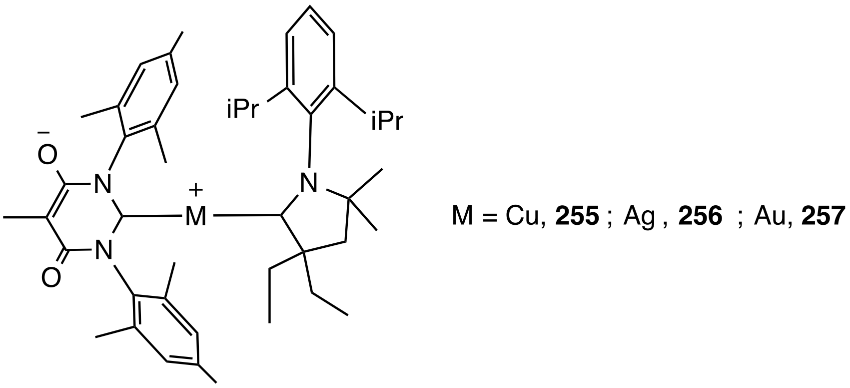


Figure 56. Mixed carbene coinage metal complexes

These compounds showed blue white-phosphorescence in the solid state with low quantum yields (**255**, Φ =1.7%; **256**, Φ = < 0.1%; **257**, Φ = 2.7) whereas in toluene they display very weak emissions. In the solid state the broadband emissions with large full-width-half-maximum (FWHM) are suggestive of multi-emissive processes as described by the authors. The excited state lifetimes show biexponential decay with short component assigned as charge transfer transition from CAAC to the metal (**255**, τ = 3.7 μs; **256**, τ = 4 μs; **257**, τ = 4.4 μs) while the long component involves transition from *malo*NHC to the metal (**255**, τ = 409 μs; **256**, τ = 353μs; **257**, τ = 49.9 μs). The decrease of the excited state lifetimes is in line with the increase of SOC of the metal center, suggesting the observed emissions are phosphorescence in nature.

In contrast to the carbene-metal-amide complexes described earlier, these complexes show low PLQY with long lifetimes (400 - 50 μs) highlighting the importance and the nature of the ligands bound to the coinage metal which impact the photophysical properties of the designed complex. In this case, it involves the replacement of a carbazolate ligand by anionic *malo*NHC.

On the other hand, Ung and coworkers prepared recently the chiral carbene Cu(I) complexes displaying CAAC ligands.[252] Starting with L-menthol as chiral auxiliary, the C_1-symmetrical Cu(I)-Cl complex $^{\mathrm{LMent}}$CAACCuCl (**258**) containing cyclic(alkyl)(amino)carbene was obtained following the synthetic procedure reported by Bertrand and coworkers.[253-255] The other unknown enantiomer $^{\mathrm{DMent}}$CAACCuCl (**258**) was obtained from D-menthol (Figure 57). The crystal structures of both enantiomers were obtained and confirmed the formation of the target compounds.

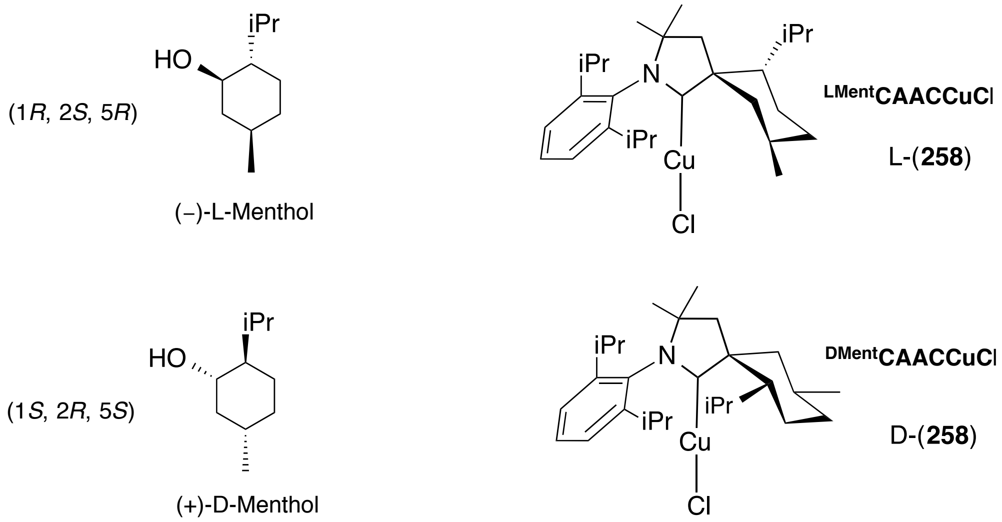


Figure 57. Chiral Cu(I)-Cl with cyclic (alkyl)(amino) carbene (CAAC) ligands and their chiral auxiliary precursors.

Both complexes acted as yellow emitters. For instance, upon excitation of $^{\mathrm{LMent}}$CAACCuCl (**258**) at $\lambda = 350$ nm in THF solution a broad emission band centered at $\lambda = 555$ nm was observed with quantum yield $\Phi = 1.8$ % was observed.

The circular dichroism spectra of both compounds were recorded and showed opposite image absorption bands, confirming the enantiomeric relationship (Figure 58) The circularly polarized luminescence (CPL) properties of ^{LMent}CAACCuCl (**258**) and ^{DMent}CAACCuCl (**258**) display opposite polarization emissions with dissymmetry factor (g_{lum} = +1.1 x 10^{-3}) at 555 nm for ^{LMent}CAACCuCl and (g_{lum} = −1.2 x 10^{-3}) for the other enantiomer ^{DMent}CAACCuCl (Figure 58).

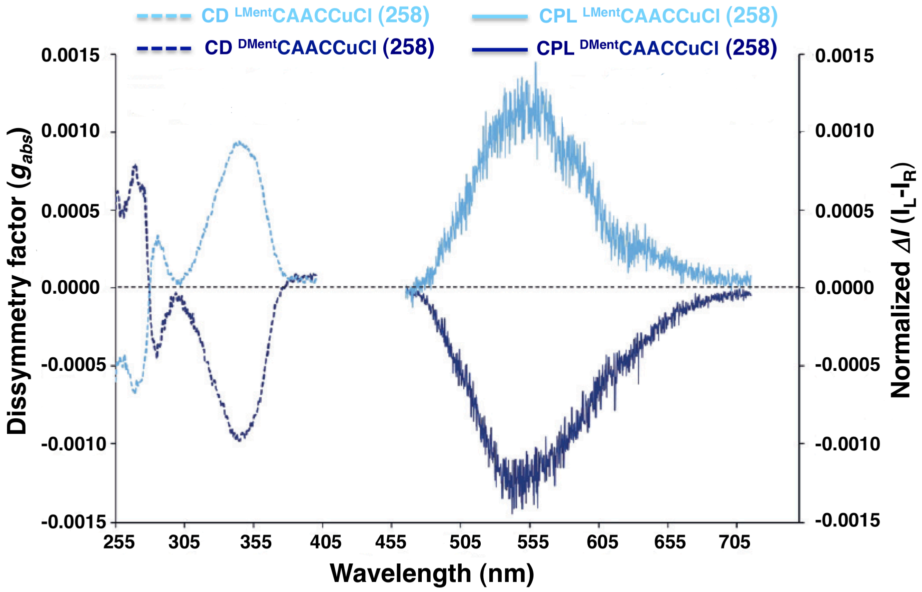


Figure 58. CD and CPL spectra of ^{LMent}CAACCuCl (**258**) and ^{DMent}CAACCuCl (**258**) complexes. Adapted with permission from ref[252]. Copyright 2020 Wiley.

It is worth mentioning that the ^{LMent}CAACCuCl (**258**) and ^{DMent}CAACCuCl (**258**) complexes displayed a significant circularly polarized emission despite the fact they lack the presence of a helical group or axial chirality; however the authors believe that such compounds display significant spin-orbit coupling which increases the rotary strength of the transition and eventually increases the chance of observing a circularly polarized emission signal.[252] Thus such compounds with chiral (CAAC) ligands pave the way to the preparation of a new class of enantiopure luminescent complexes displaying interesting CPL properties, in a field which is still in its infancy.

6- Summary, outlook and perspectives

Throughout this document, we have shown via many examples that NHC-based ligands are adequate tools to construct stable luminescent complexes. The fact that the structure of NHC-based ligands can be easily modified and functionalized brings important modifications to the photophysical properties of the final compounds. As mentioned throughout this review, their strong σ-donor properties tend to push the metal-centered d-d transitions to higher energy in order to make them thermally unattainable. Various luminescent carbene-metal complexes with different geometries based on platinum, iridium and coinage metals were included in this review. Moreover the luminescent properties of these compounds were discussed as well as the dynamic of the excited states, which impact their luminescent properties at the molecular and supramolecular level and hence determine the nature of potential applications. Moreover a special treatment was given to coinage complexes with carbazolate ligands; this field has been the focus of intense investigations in the past five years because of their remarkable luminescent properties. For instance coinage complexes with NHC-ligands tend to show long lifetimes and hence they are more appropriate to act as photoredox catalysts. On the other hand, the discovery by Bertrand and *coworkers* of CAACs--carbenes which display lower HOMO-LUMO gap compared to NHCs and are more electrophilic carbene ligands-- with more π-acceptor carbene ligands have enabled the construction of highly emissive compounds with PLQY > 99%. These electrophilic carbenes including DAC and MAC generate luminescent compounds with sub-microsecond lifetimes regime, which make them appropriate for OLED applications. Thus remarkable emitting OLED devices with EQE_{max} of 9.0% (blue) and 26.3%, (green) were achieved. It should be mentioned however, that blue emitting coinage-based OLEDs display lower efficiencies when compared to the yellow- or orange-emitting metal-based OLEDs (EQE >20). In this respect, a novel generation of coinage metal carbene compounds can be engineered to achieve higher EQE with blue emissions to reach the industrially competitive requirements.

We also demonstrated for the iridium complexes that the presence of organic chromophores (naphthalimide, pyrene) in the structure of the NHC-based ligand brings important modifications to the final optical properties of these compounds. For instance, while cyclometalated $Ir(C^N)_3$ generally emit from ^{3}MLCT excited states, the above compounds display emissions from ^{3}LC ($^3\pi$-π*) centered at the organic chromophore. In other examples dual emissions are observed and the designed complexes behave as white phosphors. Finally interesting examples of chiral luminescent complexes were also presented and displayed interesting CPL properties. This field is still in its infancy and is expected to grow rapidly in the future for variety of devices such as displays, sensing, for bioimaging and information storage.[140]

Moreover, the challenge in this area is to master the factors that control structure ↔ bonding ↔ property in order to engineer very stable and highly luminescent systems based on abundant and cheap metals such as copper[162,256-259], silver[260] and more challenging iron complexes.[261] The understanding of these factors will permit us to manipulate the rich and various excited-states energies, which proceed via different radiative decay mechanisms (fluorescence, phosphorescence, TADF mechanisms).

Apart from that goal, iridium, platinum and gold complexes will continue to be explored due to their intrinsic and high spin-orbit coupling that leads to highly luminescent complexes. Perhaps the coinage metal-based examples illustrate the importance of the carbene ligands to prepare efficient luminescent complexes with useful applications. This and many other results summarized in this review hold promise for future developments in the area of luminescent NHC-metal complexes.

All in all, one would expect that luminescent NHC-metal complexes will remain a very important field in which a large panel of functionalized carbene assembling ligands with structural diversity will be prepared and judiciously attached to variety of metal centers to generate novel class of luminescent complexes with intriguing properties to be discovered. However it should be kept in mind that such future compounds should present high stability and EQE efficiency to meet the standard industrial requirements.

AUTHOR INFORMATION

Corresponding Author: Hani Amouri, Sorbonne Université-Faculté des Sciences et Ingénerie Campus Pierre et Marie Curie, CNRS, IPCM (UMR 8232), 4 place Jussieu, 75252 Paris cedex 05, France. orcid.org/0000-0001-6955-8406. E-mail: hani.amouri@sorbonne-universite.fr.

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Notes

The author declares no competing financial interest.

Biography

Hani Haniel Amouri was born in Anapolis Goias (Brazil) and received his PhD degree from the Université Louis Pasteur (Strasbourg, France) under the guidance of Professor John A. Osborn in 1987. He was a postdoctoral fellow with Dr. Hugh Felkin In 1988 at ICSN (Gif-sur-Yvette, France). He was appointed a CNRS research fellow in 1989. Later on he obtained a CNRS-NSF fellowship (1992) for a postdoctotoral stay at University of California-Berkeley under the guidance of Professor K. Peter C. Vollhardt. He is currently a CNRS *Research Director* and is a group leader of "ARChitectures Moléculaires" (*coordination, chirality and luminescence*) at the Sorbonne Université, Campus Pierre et Marie Curie. His research activities span from chirality, organometallic chemistry to luminescent carbene coordination metal complexes. He has authored 143 publications, 4 patents and 149 plenary and communication abstracts at national and international meetings including several invited lectures. He coauthored the book "*Chirality in Transition Metal Chemistry*" published in 2008 by Wiley. He is a member of several advisory editorial boards.

Abbreviations

acac	acetylacetonate
bpy	2,2'-bipyridine
bt	2-phenylbenzothiazole
CAAC	cyclic (alkyl)(amino)carbene
CD	circular dichroism
CBZ	carbazolate
CIE	commission internationale de l'éclairage
CMA	carbene-metal amide
CPL	circularly polarized luminescence
DAC	diamidocarbenes
DFT	density functional theory
EQE	external quantum efficiency
fac	facial
F2ppy	2,4-difluorophenylpyridine
HOMO	highest occupied molecular orbital
IPr	1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene
IDipp	1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene.
IL	intraligand
ILCT	intraligand charge transfer
ISC	intersystem crossing
LC	ligand-centered
LED	light-emitting diode
LLCT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer

LUMO	lowest unoccupied molecular orbital
MAC	mono-amido-carbenes
mCPCN	9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole-3-carbonitrile
MeCy	methylcyclohexane
mer	meridional
MLCT	metal-to-ligand charge transfer
MMCT	metal–metal charge transfer
NHC	*N*-heterocyclic carbene
NI	naphthalimide
OLED	organic light-emitting device
PET	photoinduced electron transfer
pic	picolinate
PLQY	photoluminescence quantum yield
PMMA	poly(methyl methacrylate)
ppy	2-phenylpyridine
SIPr	1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
TADF	thermally activated delayed fluorescence
SOC	spin-orbit coupling
TD-DFT	time-dependent density functional theory
TGA	thermogravimetric analysis
THF	tetrahydrofuran
Tp	trispyrazolborates
UV–vis	ultraviolet–visible

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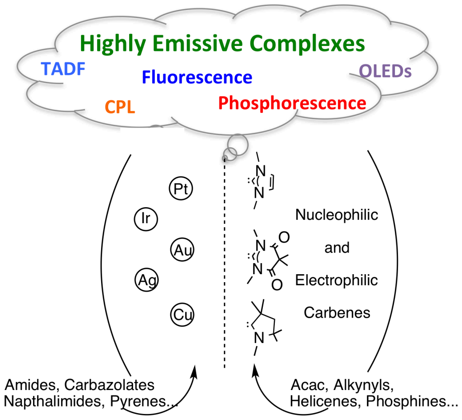
TOC graphic


Highly Emissive Complexes
TADF
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Ir
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Cu
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and
Electrophilic
Carbenes
Amides, Carbazolates
Napthalimides, Pyrenes...
Acac, Alkynyls,
Helicenes, Phosphines...