

Versatile Emissive Three-coordinated Gold(I) Systems. Properties and Perspectives

Adrián Alconchel, Olga Crespo* and M. Concepción Gimeno*

Abstract: Trigonal planar coordination at gold allows phosphorescent ^3MC transitions, not expected for luminescent mononuclear linear gold complexes. The careful selection and nature of the ancillary ligands bonded to gold, being fluorophore groups or not emissive ligands may cause a distortion of ideal trigonal planar coordination favoring different origins for the emissions. Consequently, intraligand (IL) or charge transfer (CT) transitions may be present and besides the expected phosphorescent MC transitions, fluorescence or thermally activated delayed fluorescence (TADF) may be the origin of the luminescence. In addition of the advantages of triplet population and deactivation via phosphorescent or delayed fluorescence processes, these systems are very versatile and may show interesting properties such as mechanochromism and vapochromism and, consequently, have revealed as promising candidates for optical applications. The objective of this review is to provide an overview of the reported luminescent three-coordinated gold systems and to get insight into their emissive properties.

1. Introduction

Gold was a metal already known in ancient civilizations and its chemistry has been widely studied and revised^[1-5]. However, it was not until 1970 that luminescence was observed in gold complexes and reported by Dori *et al.*^[6] Since then, many different gold emissive compounds have been reported and revised.^[7-16] The special properties of gold(I) compounds such as its tendency to linear coordination and the *au*ophilicity,^[17] which leads to aggregation of these linear unities into more complicated scaffolds, are well-known. The presence of $\text{Au}\cdots\text{Au}$ interactions may origin metal centered (MC) transitions responsible of the emissive behavior of many of these polynuclear aggregates. No metal centered luminescence is expected for mononuclear gold(I) linear species. Despite this trend to di-coordination a wide variety of gold(I) three- and four-coordinated compounds are known.^[18] Three-coordinated species may show emissions originated from metal centered transitions, in addition to those from charge

three-coordinated gold systems makes them attractive for the design of luminescent complexes.

The scope of this work is to resume the most representative examples of three-coordinated gold(I) luminescent complexes and the last studies which have led to highly emissive species and interesting properties. Except for comparative purposes, out of the scope of this review are three-coordinated complexes that exhibit additional weak *au*ophilic (or in general, metallophilic) interactions, or *pseudo* tetra-coordinated species in which a weak bond to a fourth donor atom is present (Figure 1).

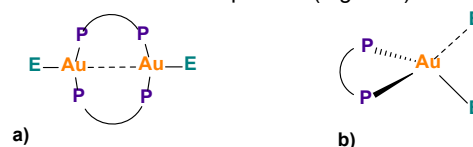


Figure 1. Dotted lines show auriphilic interactions in **a)** or short contact (or very weak bond) in **b)**. Both situations lead to deviation from the ideal three coordinated geometry

Complexes have been arranged based on the nature of the donor ligands surrounding the gold center. Phosphane ligands greatly stabilize these complexes and Figure 2 shows a selection of the diphosphanes used in the design of these complexes, whose photophysical properties are resumed in Table 1. At the beginning of each Section some general trends, based on the reported data are suggested, which further studies should confirm.

As discussed above, MC transitions are possible for three-coordinated complexes whose origin, accordingly to the diagram shown in Figure 3 for a $[\text{Au}(\text{PR}_3)_3]^+$ complex, has been claimed as MC $[\text{p}_z \rightarrow (\text{d}_{x^2-y^2}^2 \text{ d}_{xy})]$.^[19] In addition, Figure 4 shows that distortion of linearity, from 180° to 120° , leads to changes in the molecular orbital diagram, leading to a decrease of the HOMO-LUMO gap.^[20]

Two main structural changes upon excitation have been proposed as the origin of the luminescence in $[\text{AuL}_3]^+$ species displaying MC transitions: the shrinkage of the $[\text{AuL}_3]$ unit^[21] or the distortion from a triangle to a T-shaped structure.^[22,23]

Spin orbit coupling (SOC) is responsible for the presence of phosphorescent emissions, as triplet-singlet transitions are spin forbidden. SOC is favored by the presence of heavy atoms and thus, a phosphorescent nature is expected for the ^3MC gold transitions. Phosphorescence allows the use of the triplet states increasing the number of excitons useful for light emission and make complexes which emit through these mechanisms attractive for the design of light emitting devices.^[24]

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transfer (CT) or intraligand (IL) transitions. Thus, the versatility of

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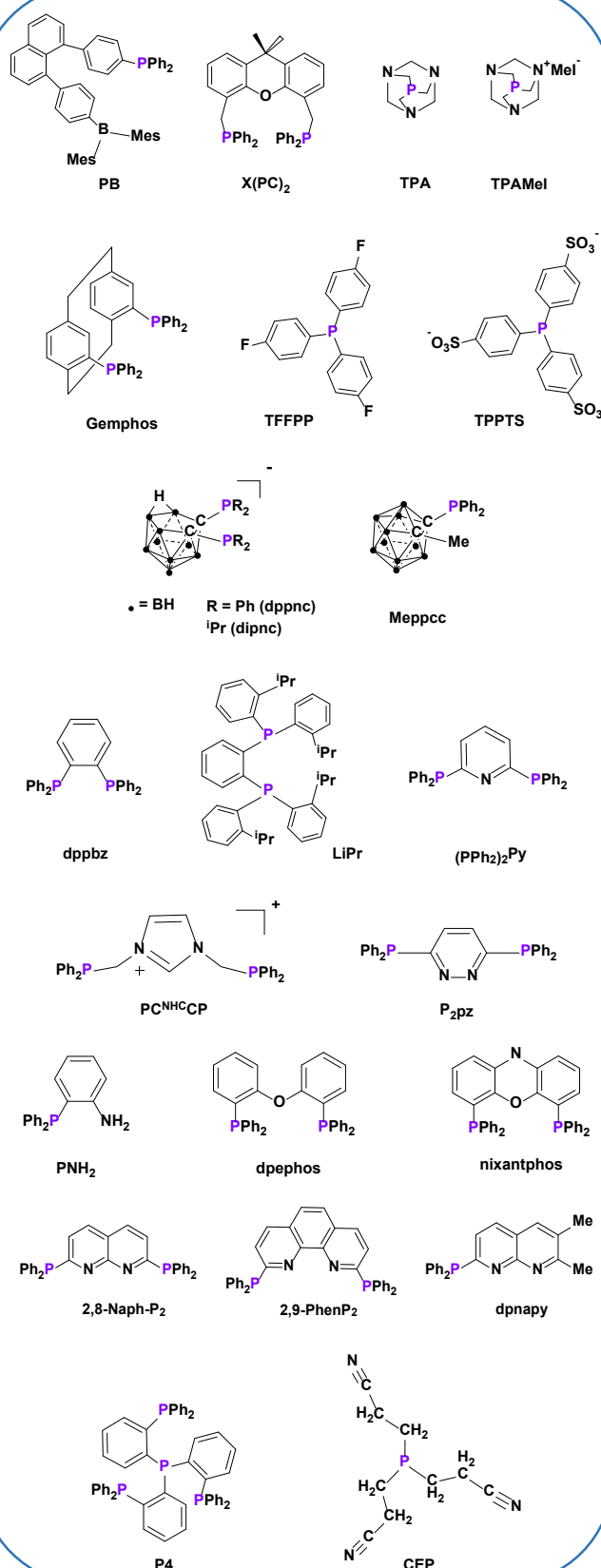


Figure 2. Some phosphane ligands used in the design of emissive three-coordinated gold complexes.

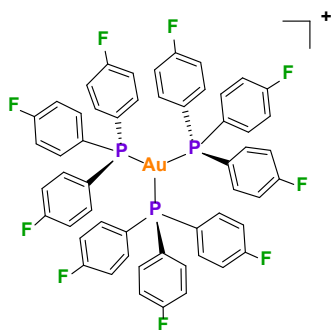


Figure 6. Chemical structure of $[\text{Au}(\text{TFFPP})_3]^+$.

The blue emission shown by $[\text{Au}(\text{PNH}_2)_3]\text{OTf}$ in the solid state at room temperature is attributable to the phosphane ligand, but at 77 K an additional emission is observed in the green region.^[29]

The water soluble complexes $[\text{Au}(\text{TPA})_3]^+$ and $[\text{Au}(\text{TPPTS})_3]^{3-}$ are emissive both in the solid state and in solution. As reported in previous studies for other diphosphanes, equilibria studies in water solution reveal an increment of the emissive behaviour when the three-coordinated species is supposed to be predominant.^[19,20b,30] Emission of complex $[\text{Au}(\text{TPPTS})_3]^{3-}$ has been widely studied, including pH influence, reversible quenching by oxygen in water, and the enhancement of the luminescent for different PNIPAM-co-allylamine hydrogel systems. Emission dependence on the temperature and pH has also been studied for these hydrogels.^[31]

Complexes $[\text{Au}(\text{MeTPA})_3]\text{X}_3$ ($\text{X} = \text{I}, \text{PF}_6$) display similar temperature dependent emission in the green-red region in the solid state. At lower temperatures two bands may be observed at about 590 and 680 nm, and upon rising the temperature only the band at lower energies is observed.^[32] The crystal structure of $[\text{Au}(\text{MeTPA})_3]\text{I}_3$ displays a distorted trigonal planar geometry environment for the gold center, with the iodide atom displaying a weak interaction ($\text{Au}-\text{I} = 2.936(1) \text{ \AA}$), perpendicular to the AuP_3 plane. Such interaction has not been reported for other tris(phosphane) gold complexes. This environment around the gold center seems to be the same upon anion exchange in $[\text{Au}(\text{MeTPA})_3](\text{PF}_6)_3$.

The emission of the mononuclear complex $[\text{Au}(\text{dnapy})_3]^+$ is shifted up to 30 nm to higher or lower energies upon coordination to Cu(I) or Cd(II) to afford heterodinuclear complexes $[\text{AuM}(\text{dnapy})_3]^{n+}$, in which Cu(I) and Cd(II) show distorted trigonal planar or trigonal prismatic environments, respectively (Figure 7).^[33]

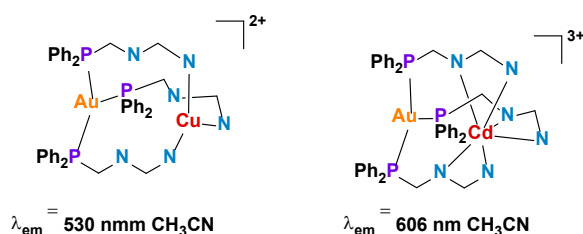


Figure 7. Heterodinuclear complexes with dnapy.

The use of diphosphanes, that tend to act in a chelate mode, represents an excellent strategy in the synthesis of three-coordinated complexes. Despite its stoichiometry, complex $[\text{Au}(\text{dpephos})_2]\text{BF}_4$ does not show a tetrahedral coordination but a distorted three coordination around the gold atom because of

one of the Au-P distances $3.9788(8) \text{ \AA}$ is very long, probably due to bite angle of dpephos. The complex is blue emissive in THF solutions at room temperature, THF glasses and in the solid state.^[34]

Rigid carborane diphosphanes also favor three coordination in $[\text{Au}\{(\text{PR}_2)_2\text{C}_2\text{B}_9\text{H}_{10}\}\text{L}]$ ($\text{L} = \text{monophosphane}$) with the anionic *nido*-carborane diphosphanes dppnc ($\text{R} = \text{Ph}$) or dpinc ($\text{R} = \text{'Pr}$). These complexes are yellow-green emitters.^[35,36] The partial degradation of the carborane diphosphane governs the emissive behavior. For the high emissive $[\text{Au}\{(\text{PR}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}\}(\text{PPh}_3)]$ zero field splitting between the I and III triplet sublevels (Figure 8) have been determined, and the corresponding values $[47 (\text{R} = \text{'Pr})$ and $29 (\text{R} = \text{Ph}) \text{ cm}^{-1}]$ point out not to pure metal centered transitions, but charge transfer transitions, in which the phosphorus orbitals may be involved, as responsible of their highly emissive behavior.^[37]

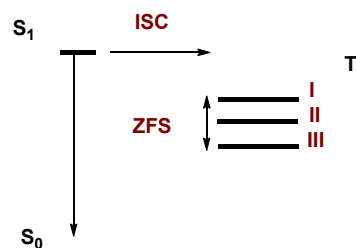


Figure 8. Schematic orbital molecular diagram illustrating zero field splitting.

2.2. Polynuclear complexes

Whereas the use of rigid diphosphanes with small bite angle may favor mononuclear three-coordinated complexes, the use of diphosphanes with more flexible and/or long skeletons leads to polynuclear complexes. In some of these derivatives the long gold...gold distances preclude aurophilic interactions. Probably the simplest stoichiometry and geometry corresponds to $[\text{Au}_2(\mu\text{-P}^{\text{A}}\text{P})\text{L}_2]$ as in $[\text{Au}_2(\mu\text{-dppp})(\text{P}^{\text{A}}\text{P})_2]$ (dppp = bis(diphenylphosphano)propane; $\text{P}^{\text{A}}\text{P} = \text{dppnc}, \text{dpinc}$) (Figure 9), whose emissions resemble those of the three-coordinated analogous mononuclear species $[\text{Au}\{(\text{PR}_2)_2\text{C}_2\text{B}_9\text{H}_{10}\}\text{L}]$ ($\text{R} = \text{Ph}, \text{'Pr}; \text{L} = \text{monophosphane}$).^[35a,36]

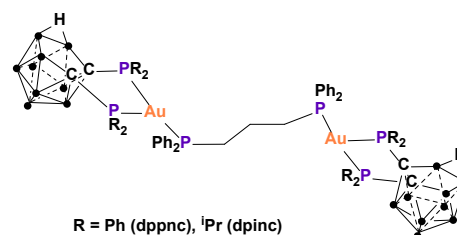


Figure 9. Complexes $[\text{Au}_2(\mu\text{-dppp})(\text{P}^{\text{A}}\text{P})_2]$.

Dinuclear complexes with three diphosphane ligands bridging the gold centers of stoichiometry $[\text{Au}_2(\text{P}^{\text{A}}\text{P})_3]^{2+}$ are also represented. IL transitions seem in many cases responsible for the transitions. In compound $[\text{Au}_2\{(\text{PPh}_2)_2\text{Py}\}_3](\text{ClO}_4)_2$ (Figure 10) the energy of the shoulder observed at higher energies (about 415 nm) seems to be originated by IL transitions. An additional more intense band is observed at about 520 nm.^[38]

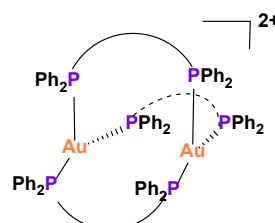


Figure 10. Chemical structure of $[\text{Au}_2\{(\text{PPh}_2)_2\text{Py}\}_3]^{2+}$.

Encapsulation of one alkaline cation avoids diphosphane dissociation of the $[\text{Au}_2(\text{P}^\wedge\text{P})_3]^{2+}$ core with the diphosphane 2,8-Naph-P₂. Emission of $[\text{Au}_2\text{K}(2,8\text{-Naph-P}_2)_3](\text{ClO}_4)_3$ (Figure 11) is solvent dependent.^[39]

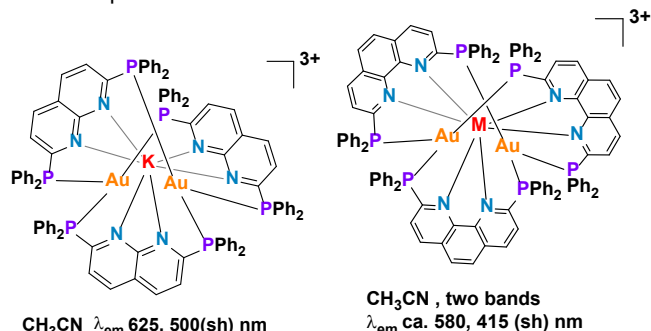


Figure 11. Encapsulation of K⁺ in $[\text{Au}_2(2,8\text{-Naph-P}_2)_3](\text{ClO}_4)_2$ and compounds $[\text{Au}_2\text{M}(2,9\text{-Phen-P}_2)_3](\text{PF}_6)_3$

Complexes $[\text{Au}_2\text{M}(2,9\text{-Phen-P}_2)_3](\text{PF}_6)_3$ (M = Li, Na, K, Cs), with an analogous naphthyridine ligand display dual emissions in MeCN solution, one emission at about 410 and the other near 560 nm. That at higher energy resembles that of the ligand, whereas the other is the only one observed in the solid state for M = Na with very low intensity.^[40]

Polymeric structures of stoichiometry $[\text{Au}(\text{P}^\wedge\text{P})_{1.5}]_n^{n+}$ have been obtained with the diphosphanes *trans*-(Ph₂P-CH=CH-PPh₂) (*t*-dppey) and Ph₂P-(CH₂)₄-PPh₂ (dppb) which lead very similar blue-purple emissive solids (λ_{em} = 420 nm) (Figures 12a and 12b). The data point out to the origin of the emission mainly focussed on the three-coordinated gold centers with no contribution of extended conjugation in complex with *t*-dppey.^[41] The dual emission observed for the polymer with the P2pz [Figure 12c, (λ_{em} = 493 and 540 nm in CH₂Cl₂)] appears at the same emission energies than that of the non-coordinated diphosphane, pointing out to an IL origin.^[42]

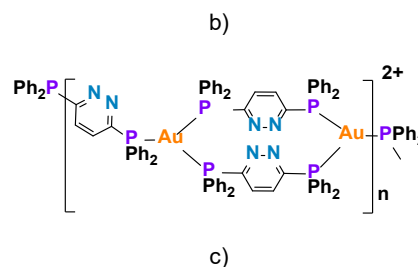
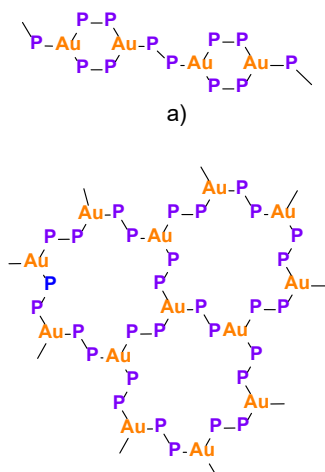


Figure 12. Different arrangements in polynuclear gold complexes with gold coordinated to three phosphorus atoms.

The tetradentate ligand tris(2-(diphenylphosphino)ethyl)amine (NP₃) acts in a tridentate mode through the three phosphorus atoms in the formation of the mononuclear $[\text{Au}(\text{NP}_3)]^+$ or dinuclear $[\text{Au}(\text{NP}_3)_2]^{2+}$, which are afforded depending on the stoichiometric conditions. The dinuclear species does not exhibit aurophilic interactions and both the mono and dinuclear complexes display yellow emissions.^[43]

3. $[\text{AuXP}_2]$ complexes (X = halogenide)

From the structural point of view, these complexes may be classified as i) mononuclear, containing two monophosphane ligands or a diphosphane in a chelate mode; ii) dinuclear derivatives in which the diphosphane acts in a bridging mode or iii) more complicated polynuclear structures (Figure 13).

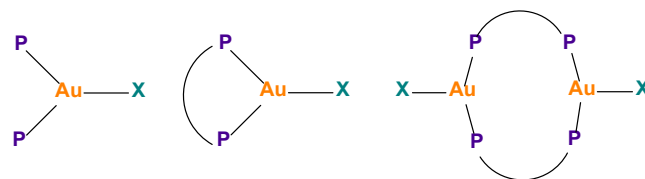


Figure 13. Some of the arrangements observed in $[\text{AuX}(\text{P}^\wedge\text{P})]$ complexes.

From the data reported it seems that for these $[\text{AuXP}_2]$ complexes, packing and crystallization processes may be very important in their luminescent properties, as different crystallization forms may allow or not weak interactions involving the halide atoms, leading to vapo-chromic or mechano-chromic species. It seems that very distorted structures which adopt almost T conformations may favour TADF behaviour (as seems to be confirmed in part 4 of this review).

3.1. Mononuclear complexes

Crystal environment is responsible of the different emissive origin and color of different polymorphs of $[\text{AuCl}(\text{PPh}_3)_2]$, for which photocrystallographic studies have been carried out. For the green emissive polymorph **A**, the ground state distances approach the excited state ones upon cooling, although below 177 K intermolecular interactions modify this trend. These changes have a deep effect in both emission intensity and lifetimes.^[44] As explained above for the analogous $[\text{AuL}_3]^+$ species,^[21-23] two main structural changes are proposed as responsible for the emissions observed upon excitation: the shrinkage of the $[\text{AuL}_3]$ unit or distortion from a triangle to a T-shaped structure. In the $[\text{AuCl}(\text{PPh}_3)_2]$ polymorphs, taking into account the results of the photocrystallographic studies, shrinkage of the molecule by photoexcitation is proposed as the origin of the green phosphorescence of polymorph **A**. Blue emission is observed for polymorph **B**, for which photodifference

Fourier map was carried out in order to analyze the electron density change between excited and ground states, as very small differences in the geometry of both states were observed. The C-H...Cl interactions (Figure 14) lead to an aggregate structure in polymorph **A** based on dimers, whereas for polymorph **B** no dimer formation is observed and orientation of the molecules is very different, observing a linear disposition (Figure 14). Shortening of the M-L bonds is induced by photoexcitation in the **A** polymorph, but this shortening is restricted in the **B** polymorph form and instead of the bond-shrunk state, a charge transfer transition is proposed as responsible of its blue emission.^[45]

The free monophosphane-borane PB is emissive. The presence of a U linker between the phosphine and borane units allows through space charge transfer emission (TSCT). It shows solvent dependent emission. In most of the solvents studied dual emission is observed at about 400 and 500 nm with quantum yields from ≈ 1 (THF or acetone) to $\approx 30\%$ (hexane, toluene). Through theoretical studies, emissions have been assigned to charge transfer transitions. Those at higher energy originated from the S_1 excited state, corresponding to $P \rightarrow BPh$ (π) transitions and those at lower energy originated from the S_2 excited state, assigned to $Mes(\pi) \rightarrow BPh(\pi^*)$ transitions. In the blue emissive compound $[Au(PB)_2Cl]$ the gold atom displays an unusual T environment. In contrast with the ligand, it displays no dual emission. The lower energy emission is not observed, which is consistent with the proposed nature for this emission in the PB free ligand.^[46]

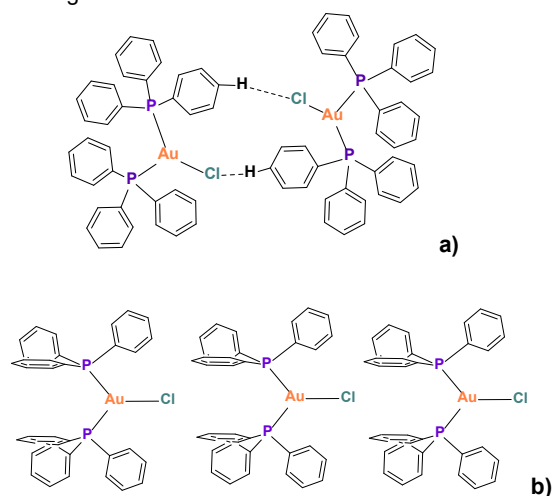


Figure 14 a) Aggregates in the crystal structure of polymorph **A** of $[AuCl(PPh_3)_2]$. b) molecular orientation of the molecules in polymorph **B** of $[AuCl(PPh_3)_2]$

Complexes $[Au(L^iPr)X]$ ($L^iPr = 1,2$ -bis(bis(2-isopropylphenyl)phosphino)benzene; $X = Cl, I$)^[47] exhibit distorted trigonal planar structures with very different Au-P distances, especially the chloride compound. Their quantum efficiencies in 2-MeTHF are less than 1% but very high quantum yields have been reported for crystals at 77 K. Quantum chemical studies for $[Au(L^iPr)I]$ indicate a strong intraligand charge-transfer character. TADF behaviour has been proposed for both complexes. Study of the dependence of the lifetime with the temperature has led to $\Delta E(S_1-T_1)$ 950 and 870 cm^{-1} , higher than those obtained by comparing the emission maxima at 293 and 77 K.

Compound $[Au\{X(PC)_2\}Cl]$, with the analogous to xantphos diphosane $X(PC)_2$, is not emissive in dichloromethane solution,

but in the solid state displays an structured blue-green emission, red shifted compared to that of the free diphosphane.^[48]

3.2. Dinuclear complexes

The structure of $[Au\{\mu-(PC^{NHCP})\}Cl]_2$ consists on a dinuclear unit in which the PC^{NHCP} ligand bridges two gold atoms which show distorted three-coordinated environment (Figure 15). The Au-Cl distances are considerably long (Au-Cl 2.7088(15) Å), compared with other three-coordinated $[Au(P^{\wedge}P)Cl]$ complexes, probably due to the H...Cl interactions exhibited by the chloride atoms inside of the molecular cavity. The compound is weakly emissive in dichloromethane solution and in the solid state its luminescence is dominated by a blue emission with quantum yield of 14%.^[49]

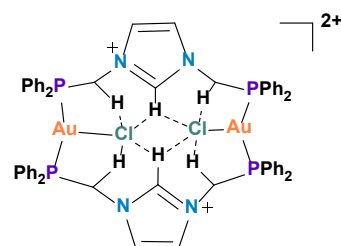


Figure 15. Schematic representation of $[Au(PC^{NHCP})Cl]$ complex including some of the H...Cl interactions.

Two reversible interconvertible polymorphs of $[Au(dppe)]_2$ with very different gold...gold distances have been reported. The α -orange emissive form (which displays longer Au...Au distance) changes to the green emissive polymorph upon air exposure (Figure 16). Addition of acetone leads again to the green luminescent form. Air exposure for hours of both polymorphs leads to an irreversible transformation to a new green emissive form which seems to change to a fourth orange polymorph.^[50]

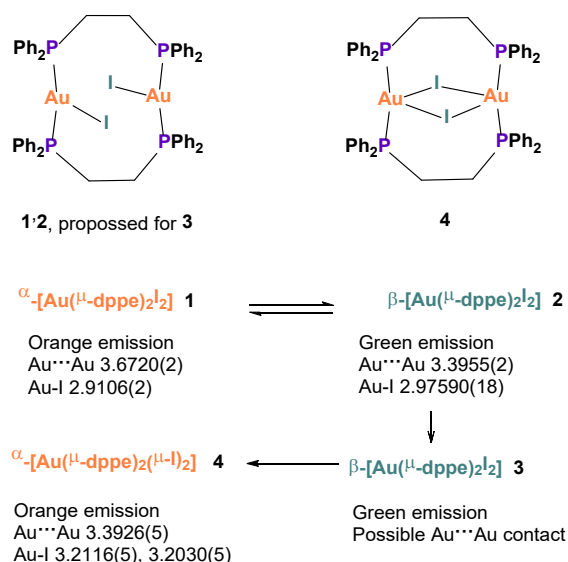


Figure 16. Schematic structures, transformations and main structural data (bond distances in Å), of emissive polymorphs of $[Au_2(dppe)_2]_2$.

4. $[AuPE_2]^{n+}$ ($n = 0, +1$) and $[AuP_2E]^{n+}$ ($n = 0, +1$) complexes ($E =$ different donor atoms)

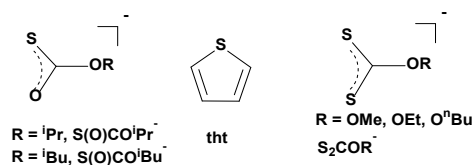
Complexes of this type containing a phosphine and another ligand with different donor atoms [Figure 17, sulfur, sulfur-oxygen, nitrogen and carbon] have been reported. Not only the donor atom, but the nature of the hole ligand is needed for the understanding of the emissive behaviour. The reported data suggest some ideas which should be confirmed by further studies. Thus, among S donor ligands, for dithiolates the emission seems to be originated by IL transitions and the origin may be more complicated for other ligands. The reported complexes with N donor ligands are chelate ligands which contain pyrrolidine anions and IL transitions are relevant in the luminescent properties. From the C donor ligands perhalophenyl ligands lead to very distorted (T shaped) structures which display TADF behaviour and the use of carbene ligands lead in many cases to high quantum yield solids.

4.1. Complexes with E = S donor atom

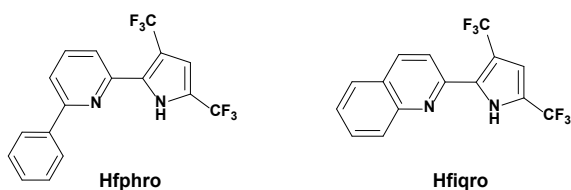
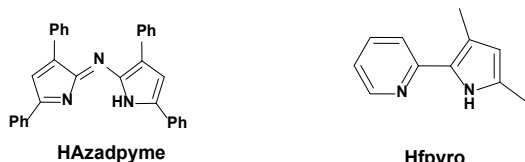
The poorly soluble $[\text{Au}(\text{GemPhos})(\text{tht})]\text{ClO}_4$ compound displays very different Au-P distances to the phosphorus atoms of the rigid diphosphane. It exhibits temperature dependent emission at about 520 nm^[51] in the solid state.

The crystal structures of the complexes $[\text{Au}(\text{CEP})_2(\text{S}_2\text{COEt})]$ and $[\text{Au}(\text{PPh}_3)_2(\text{S}_2\text{COEt})]$ show an irregular three-coordinated gold center, because is coordinated only by one of the sulfur atoms of the xanthate ligand, although the Au-S distances are both long, 2.745 and 2.53 Å, respectively. The blue emission (λ_{em} ca. 490 nm) of the xanthate complexes $[\text{Au}(\text{CEP})_2(\text{S}_2\text{COR})]$ both in acetonitrile solutions and solid state has been assigned to IL perturbed transitions. However, compound $[\text{Au}(\text{PPh}_3)_2(\text{S}_2\text{COEt})]$ is not emissive, which has been attributed to a stronger Au-S bond, leading to quenching of the emission through a LMCT excited state.^[20a]

Other similar complexes are the monothiocarbonate complexes $[\text{Au}\{\text{S}(\text{O})\text{CO}^i\text{Pr}\}(\text{PPh}_3)_2]$ and $[\text{Au}\{\text{S}(\text{O})\text{CO}^i\text{Bu}\}(\text{PPh}_3)_2]$ which are not emissive in solution. The weak blue-green emission observed in the solid state at room temperature is increased at 77 K.^[52]



S-donor ligands



N-donor ligands

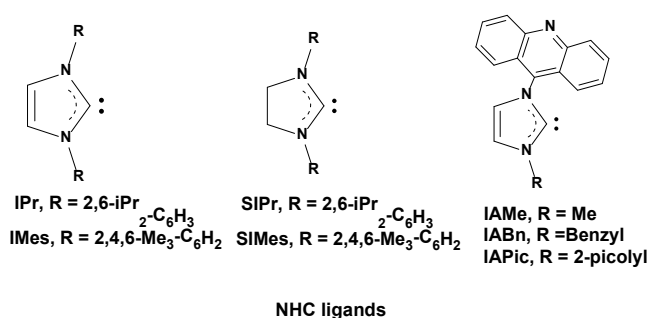


Figure 17. Selection of different ligands used in the design of emissive three-coordinated gold complexes discussed in Section 4, classified attending to their coordinating atoms at gold.

The mechanochromic blue emissive mononuclear $[\text{Au}(\text{nixantphos})(\text{SCN})]$ leads, upon grinding, to the red emissive dinuclear ionic compound $[\text{Au}(\text{nixantphos})]_2(\text{SCN})_2$. This transformation is reversible upon exposition of $[\text{Au}(\text{nixantphos})]_2(\text{SCN})_2$ to ethanol vapors.^[53] This behaviour could be understood as consistent with the pseudohalide nature of the SCN ligand, leading to different bonding shapes and thus to mechanochromic response as shown for other $[\text{AuXP}_2]$ complexes in Section 2.

4.2. Complexes with E = N donor atom

These examples correspond to the stoichiometry $[\text{Au}(\text{N}^-\text{N})(\text{PPh}_3)]^+$ in which N⁻N is a bidentate nitrogen-based ligand (Figure 18). Deprotonation of HAzadpyme, Hfpyro and Hfqiroy and addition of $[\text{AuCl}(\text{PPh}_3)]$ lead to complexes in which the gold atom is coordinated by the phosphorus atom of the PPh₃ ligand and to both nitrogen atoms of the ligand with very different Au-N distances, displaying distorted trigonal planar environments for the gold atoms. Compound $[\text{Au}(\text{fphro})(\text{PPh}_3)]$ displays linear coordination with Au-N distances 2.061(2) and 3.004(2) Å.

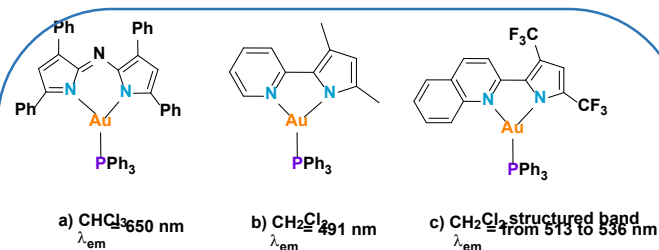


Figure 18. Compound $[\text{Au}(\text{Azadpyme})(\text{PPh}_3)]$ a), $[\text{Au}(\text{fpyro})(\text{PPh}_3)]$ b), $[\text{Au}(\text{fqiroy})(\text{PPh}_3)]$ c). For values in other media see table 1.

In complex $[\text{Au}(\text{Azadpyme})(\text{PPh}_3)]$ the Au-N distances are about 2.1 and 2.4 Å. It is luminescent both in CHCl_3 and 2-MeTHF. In 2-MeTHF at 77 K, peak to peak separation of the band structure corresponds with Azadpyme vibronic modes which is consistent with intraligand transitions as responsible of the emission.^[54] In complexes $[\text{Au}(\text{N}^-\text{N})(\text{PPh}_3)]$ [N⁻N = fpyro, fqiroy] the Au-N distances are about 2.1 and 2.6 Å. They are emissive in the blue-green region.^[55] For these complexes, according to theoretical studies the gold atom acts as external heavy atom with no contribution of the d orbitals in the transitions which originate the emissions.

Thus, for these $[\text{Au}(\text{N}^{\wedge}\text{N})(\text{PPh}_3)]$ complexes the IL bands may be tuned by careful selection of the $\text{N}^{\wedge}\text{N}$ ligand from the red to the blue region of the visible spectrum. Φ in solution for the three $[\text{Au}(\text{N}^{\wedge}\text{N})(\text{PPh}_3)]$ complexes are below 0.15 but in the solid state $\Phi = 0.4$ for $[\text{Au}(\text{fpyro})(\text{PPh}_3)]$.

4.3. Complexes with E = C donor atom

The crystal structures of the neutral complexes $[\text{Au}(\text{dppbz})\text{R}]$ ($\text{R} = \text{perhalophenyl ligand: } (\text{C}_6\text{Cl}_2\text{F}_3, \text{C}_6\text{Cl}_5)$) show very different Au-P distances and one of the P-Au-C angles $[163.99(14) \text{ and } 163.8(3)^\circ]$ closed to linearity. Theoretical studies for compound $[\text{Au}(\text{dppbz})(\text{C}_6\text{Cl}_2\text{F}_3)]$ lead to metal-ligand (phosphorous of the diphosphane) to ligand (benzene ring of the diphosphane) (MLL'CT) charge transfer transitions as the origin of the emission. TADF emission of complexes $[\text{Au}(\text{dppbz})\text{R}]$ ($\text{R} = (\text{C}_6\text{F}_5, \text{C}_6\text{Cl}_2\text{F}_3, \text{C}_6\text{Cl}_5)$, Figure 19) has been studied, through the analysis of lifetimes at different temperatures, and estimated values for $\Delta E(\text{S}_1-\text{T}_1)$ range from 656 to 1165 cm^{-1} (Table 2). These values, although a bit higher, fit well with those calculated from the difference in the wavelengths of the peak maxima at 300 and 77 K.^[56]



Figure 19. Compounds $[\text{Au}(\text{dppbz})\text{R}]$. λ_{em} in the solid state between 555 and 575 nm.

Complexes $[\text{Au}(\text{dppnc})(\text{NHC})]$ [$\text{NHC} = \text{N-heterocyclic carbene}$] (Figure 2) and $[\text{Au}(\text{dppbz})(\text{NHC})\text{OTf}]$ [$\text{OTf} = \text{SO}_3\text{CF}_3$, $\text{NHC} = \text{IPr, SiPr, IMes, Slmes}$] (Figure 20) are emissive in the blue-green region, with quantum yields from 30 up to near 100% in the solid state. The emissions of complexes with dppbz have also been studied in dichloromethane and bathochromic shifts are observed when changing from solid to dichloromethane solutions. The origin of the emissions has been studied by theoretical calculations for complexes with dppnc, and is attributed to L (diphosphane) to ML' (gold-NHC) charge transfer transitions (LML'CT). The same origin has been proposed for the complexes $[\text{Au}(\text{dppbz})(\text{NHC})\text{OTf}]$ ^[57,58] and not to metal centered transitions. Complexes $[\text{Au}(\text{dppnc})(\text{NHC})]$, with the ligands IAME, IABn and IAPic, are not emissive, which has been proposed as a consequence of the presence of the highly electron rich acridine group. The acridine unit contributes mostly to the LUMO, with no contribution of the metal and little contribution of the carbene ligand, whereas for the emissive complexes the LUMO is an antibonding combination of the NHC ligand with the $d\sigma$ gold(I) orbital.

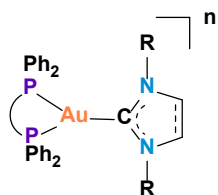


Figure 20. Gold(I) complexes with $\text{P}^{\wedge}\text{P} = \text{dpppb}$ ($n = +1$) and dppnc ($n = 0$).

Complexes with the tetradentate tris(2-diphenylphosphinophenyl)phosphane (P4) phosphane

$[\text{CuAu}(\text{P4})(\text{CN})_2](\text{PF}_6)_2$ and $[\text{AgAu}(\text{P4})(\text{CN})_2](\text{CF}_3\text{SO}_3)_2$ display tetranuclear structures in which the skeleton corresponds to an eight membered ring in which the metallic centers exhibit three-coordinated environments with negligible metal...metal interactions (Figure 21). Calculated and experimentally determined $\Delta E(\text{S}_1-\text{T}_1)$ values (Table 2) of 325 and 491 cm^{-1} have been reported for $[\text{AgAu}(\text{P4})(\text{CN})_2](\text{CF}_3\text{SO}_3)_2$, whereas the experimentally determined value for $[\text{CuAu}(\text{P4})(\text{CN})_2](\text{PF}_6)_2$ (4670 cm^{-1}) does not fit with TADF behavior.^[59] Different metal...metal interactions may be the responsible for the different emissive origin.

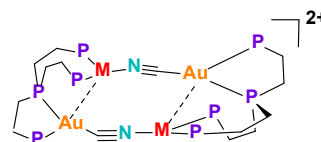


Figure 21. Schematic structure of $[\text{MAu}(\text{P4})(\text{CN})_2](\text{PF}_6)_2$ ($\text{M} = \text{Ag, Cu}$). $\lambda_{\text{em}} = 650 \text{ nm}$ ($\text{M} = \text{Cu}$), 585 nm ($\text{M} = \text{Ag}$) in the solid state.

5. Conclusion

Analysis of the examples resumed in this review may lead to the conclusion that most of the emissive three-coordinated gold(I) systems are stabilized by the use of phosphanes and specially by the use of rigid diphosphanes as ligands. Different emission energies have been reported which spread from red to blue, thus it is possible to modulate the photophysical properties upon careful selection of the gold environment, although red emitters are scarcely represented, even in examples displaying dual emission the red one may be weak. The careful selection of the ligands has a deep influence in the origin of the emission and this fact is relevant for the suitable applications of these complexes. From the data reported it seems that for $[\text{AuP}_3]^n$ complexes modification of the *classical* phosphanes though halide substitution of the phenyl hydrogens or introduction of amine groups and formation of polynuclear or polymeric species favour IL contribution for the origin of the emissions. In some complexes (mainly those containing halide or pseudohalide ligands) differences in the packing may lead to emission tuning, and other properties such as vapochromism or mechanochromism may be observed. Many of the examples displaying TADF show very distorted trigonal planar geometries which may be better described as T shaped structures.

Population of the triplet state (from triplet metal centered transitions) and relaxation via phosphorescent or delayed fluorescent processes may be useful for the design of OLEDs.

All these trends (and some other resumed at the beginning of each Section) are suggested from the data, but need confirmation with further studies. In this sense it should be noted that from the report of Dori *et al.* in 1970^[6] it is evident that the field of gold(I) three-coordinated emissive complexes has been widely developed, but efforts are needed in the systematization of these changes with the aim of controlling them and designing complexes with the desired properties. In addition, for some of the first gold luminescent complexes reported many data are still unknown (lifetime, quantum yield...) which would also contribute to understand the exact origin of the emissions, as well as their possible usefulness for different applications.

Table 1. Emissive properties of selected compounds.

Compound	Condition ^[a]	λ_{em} ^[b]	τ (μ s)	ϕ (%)	Ref.
[Au(PPh ₃) ₃] ⁺	solid	481	9.3		26
	CH ₃ CN	512	10		26
	CH ₃ CN	505 ^[c]			27
[Au(PPh ₂ Me) ₃] ⁺	CH ₃ CN	529 ^[c]			27
[Au(PPhMe ₂) ₃] ⁺	CH ₃ CN	525 ^[c]			27
[Au(PMe ₃) ₃] ⁺	CH ₃ CN	509 ^[c]			27
[Au(TFFPP) ₃]Cl	solid, R.T.	415			28
[Au(PNH ₂) ₃]OTf	solid	440			29
	solid 77 K	440, 500			
[Au(TPPTS) ₃] ⁸⁻	solid 77 K	486	1.9 ; 8		20b
	solid, R.T.	494			
	H ₂ O	513		4.6	
[Au(TPA) ₃] ⁻	solid 77 K	533	3.2		19, 20b
	solid, R.T.	517			
	CH ₃ CN/MeOH	520			
	H ₂ O, pH = 7	547	0.53	6.9	
[Au(MeTPA) ₃]I ₃	solid	598-686 ^[d]			32
[Au(MeTPA) ₃](PF ₆) ₃	solid	590-680 ^[d]			32
[Au(dpnpy) ₃] ⁺	CH ₃ CN	560	0.96		33
[AuCu(dpnpy) ₃] ²⁺	CH ₃ CN	530			33
[AuCd(dpnpy) ₃] ³⁺	CH ₃ CN	606	0.71		33
[Au(dpephos) ₂] ⁺	TFH	490	0.126 2.2	0.2 1.5	34
	TFH 77 K	445	1,3 10 ³ 8,4 10 ³		
	KBr disk	494	6.9	5	
[Au(dppnc)(PPh ₃)]	solid R.T.	540, 670			35b
	solid 77 K	529, 676			35b
	300 K, PMMA	534	8	50	37
	2-Me-THF, 77 K	497	15		37
	CH ₂ Cl ₂	528, 603			35b
[Au(dppnc)(PPh ₂ Me)]	solid R.T.	521, 640			35b
	solid 77 K	513, 653			
	CH ₂ Cl ₂	530, 576			35b
[Au(dppnc){P(4-MeC ₆ H ₄) ₃ }]	solid R.T.	513, 614			35b
	solid 77 K	506, 633			
	CH ₂ Cl ₂	534			
[Au(dppnc)(PPh ₂ (CH ₂) ₂ py)]	solid R.T.	510	15.2		35a
	solid 77 K	520, 670			

[Au(dppnc)(PPh ₂ OEt)] ^[e]	solid	519, 610	17.6, 12.5		35a
	solid 77 K	525, 670			
[Au(dppnc)(Meppcc)]	solid	480			36
	solid 77 K	526, 670			
[Au(dpinc)(PPh ₃)]	solid R.T.	508			35b
	solid 77 K	507			35b
	300 K, PMMA	525	12	75	37
	2-Me-THF, 77 K	508	20		37
	CH ₂ Cl ₂	514			35b
[Au(dpinc)(PPh ₂ Me)]	solid R.T.	512			35b
	solid 77 K	505			
	CH ₂ Cl ₂	512			
[Au(dpinc){P(4-MeC ₆ H ₄) ₃ }]	solid R.T.	508			35b
	solid 77 K	503			
	CH ₂ Cl ₂	512			
[Au(dpinc)(PPh ₂ (CH ₂) ₂ py)]	solid	508	15.4		35a
	solid 77 K	508			
[Au(dpinc)(PPh ₂ NHpy)]	solid	521	15.2		35a
	solid 77 K	516			
[Au(μ-dppp)(dppnc) ₂] ^[e]	solid	545, 730	11.8, 11.9		35a
	solid 77 K	540, 730			
[Au(μ-dppp)(dpinc) ₂]	solid	525	14.6		35a
	solid 77 K	520			
[Au ₂ {(PPh ₂) ₂ Py ₃ }] ²⁺	CH ₃ CN	≈ 415, shoulder	0.3		38
		≈ 520	1.8	0.18	
[Au ₂ K(2,8-Naph-P ₂) ₃](ClO ₄) ₃	CH ₂ Cl ₂	625	0.1	4	39
	CH ₃ CN	500 (shoulder) 625	0.1	4	
[Au ₂ Li(2,9-Phen-P ₂) ₃](PF ₆) ₃	CH ₃ CN	414, 585			40
[Au ₂ Na(2,9-Phen-P ₂) ₃](PF ₆) ₃	CH ₃ CN	410, 590			40
[Au ₂ K(2,9-Phen-P ₂) ₃](PF ₆) ₃	CH ₃ CN	413, 577			40
[Au ₂ Cs(2,9-Phen-P ₂) ₃](PF ₆) ₃	CH ₃ CN	419, 575			40
[Au(<i>t</i> -dppey) _{1.5}] _n ⁿ⁺	solid	≈ 420			41
[Au(dppb) _{1.5}] _n ⁿ⁺	solid	≈ 420			41
[Au(P2pz) _{1.5}] _n ⁿ⁺	CH ₂ Cl ₂	493, λ _{ex} =403 540, λ _{ex} =468			42
[Au(NP ₃)] ₂ ²⁺	solid	500			43
[Au(NP ₃)] ⁺	solid	470			43
[Au(PB) ₂ Cl]	CH ₂ Cl ₂	410	44		46
[Au(L ⁱ Pr)Cl]	solid	558	13	82	47
	solid 77 K	582	92	58	
	2-Me-THF	607	0.8	2	

	2-Me-THF, 143 K	638	28		
[Au(L ⁱ Pr)]	solid	549	9	92	47
	solid 77 K	569	77	74	
	2-Me-THF	596	0.7	4	
	2-Me-THF, 143 K	628	32		
[Au(X(PC) ₂ Cl)]	solid	499, 468(sh); 530, 575 (sh)	289, 290 λ_{ex} 320; λ_{em} 500		48
[Au(Gemphos)(tht)]	solid	530	≈ few		51
	solid, 18 K	515	≈ 1000		
[Au{S(O)CO ⁱ Pr}(PPh ₃) ₂]	solid	≈ 472			52
	solid 77 K	472			
[Au{S(O)CO ⁱ Bu}(PPh ₃) ₂]	solid	467			52
	solid 77 K	467			
[Au(Azadpyme)(PPh ₃)]	CHCl ₃	≈ 650		0.24	54
	2-Me-THF	≈ 720 Vibronic structure resolved at 77 K			
[Au(fpyro)(PPh ₃)]	CH ₂ Cl ₂	491	124	3.7 ^[f]	55
	solid	488		40 ^[f]	
[Au(fiqro)(PPh ₃)]	CH ₂ Cl ₂	513, 542, 585 503, 536	79.7	12 ^[f]	55
	solid	488		4 ^[f]	
[Au(dppbz)(C ₆ F ₅)]	solid	560	10.3	29	56
	solid 77 K	575	35.5		
[Au(dppbz)(C ₆ Cl ₂ F ₃)]	solid	545	20.8	16	56
	solid 77 K	570	72.7		
[Au(dppbz)(C ₆ Cl ₅)]	solid	555	19.89	11	56
	solid 77 K	585	58		
[Au(dppnc)(iPr)]	solid	500	16.2	34	57
	solid 77 K	500			
	CH ₂ Cl ₂	520	10.9		
	CH ₂ Cl ₂ 77 K	490			
[Au(dppnc)(SiPr)]	solid	520	21.8	99	57
	solid 77 K	530			
	CH ₂ Cl ₂	545	11.6		
	CH ₂ Cl ₂ 77 K	495			
[Au(dppnc)(IMes)]	solid	490	13.4	45	57
	solid 77 K	495			
	CH ₂ Cl ₂	540	12.2		
	CH ₂ Cl ₂ 77 K	500			
[Au(dppnc)(SiMes)]	solid	470	15.8	65	57
	solid 77 K	480			

	CH ₂ Cl ₂	570	11.4		
	CH ₂ Cl ₂ 77 K	490			
[Au(dppbz)(IPr)]	solid	505	14.3	80	58
	solid 77 K	510	23.9		
[Au(dppbz)(SIPr)]	solid	490	17.9	98	58
	solid 77 K	500	30.7		
[Au(dppbz)(IMes)]	solid	530	17.2	99	58
	solid 77 K	530	21		
[Au(dppbz)(SIMes)]	solid	545	10.2	59	58
	solid 77 K	525	78		
[CuAu(P4)(CN)] ₂ (CF ₃ SO ₃) ₂	solid	650	9.3	10	59
	solid 77 K	662	89.3		
[AgAu(P4)(CN)] ₂ (CF ₃ SO ₃) ₂	solid	585	3.9	45	59
	solid 77 K	588	48.9		

^[a] No temperature indicated means room temperature. ^[b] Emission maximum in nm. ^[c] Overlapped with the emission of the [SnCl₃]⁻ unit. ^[d] Temperature dependent emission. ^[e] Two emissions in the same order than their corresponding lifetimes. ^[f] Sum of fluorescence and phosphorescence.

Table 2. Reported data from fitting of lifetime values at different temperatures to equation 1^[a]

Compound ^[a]	Condition	ΔE (cm ⁻¹)	τ _(S1)	τ _(T1)	Ref.
[AuL ^I PrCl]	solid	950	50	92 ^[b]	47
[AuL ^I PrI]	solid	870	49	77 ^[b]	47
[Au(dppbz)(C ₆ F ₅)]	solid	656	240	35 ^[b]	56
[Au(dppbz)(C ₆ Cl ₂ F ₃)]	solid	966	87	73 ^[b]	56
[Au(dppbz)(C ₆ Cl ₅)]	solid	1165	39	58 ^[b]	56
[AgAu(P4)(CN)] ₂ ²⁺	solid	491	118	50	59

^[a] Equation 1: $\tau = \frac{3 + e^{-\Delta E(S_1-T_1)/K_B T}}{3\left(\frac{1}{\tau(T_1)}\right) + \left(\frac{1}{\tau(S_1)}\right)e^{-\Delta E(S_1-T_1)/K_B T}}$ K_B = Boltzman constant. ΔE

= energy gap between the first excited singlet and triplet state (see Figure 6). τ_(T1) (in μs) and τ_(S1) (in ns) correspond to lifetimes of the first excited triplet and singlet respectively. ^[b] From the experimental emission spectra at 77 K.

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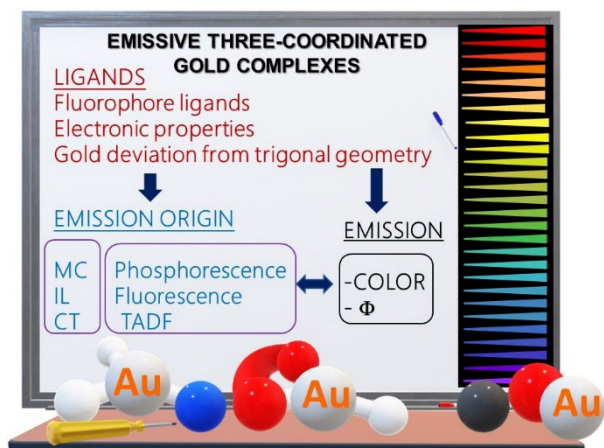
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Entry for the Table of Contents



Trigonal planar coordination at gold allows phosphorescent ^3MC transitions, but a careful selection of ligands may favor different origins as intraligand (IL) or charge transfer (CT) transitions, for the luminescence observed and thus, fluorescence or thermally activated delayed fluorescence (TADF) may be the origin of the luminescence. In addition, phenomena as mechanochromism or vapochromism may be observed. The objective of this review is to give an overview of the reported luminescent three-coordinated gold systems and to get insight into the emissive properties of these promising systems.