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Abstract

An overview of the homometallic phosphine-Au(I)alkynyl complexes reported in the literature from 2010-2018 have been collected and reported in this review article. They have been classified for better understanding, between mononuclear and polynuclear compounds. Their luminescent properties have been discussed along the text and the specific absorption and emission data collected in Annex I. This type of compounds are being used for a wide range of applications in fields such as biomedicine, chemosensors or luminescent materials among others and their interest is increasing in the last years. Some particular examples have been also selected herein.

Keywords Gold(I); luminescence; phosphine; alkynyl; applications

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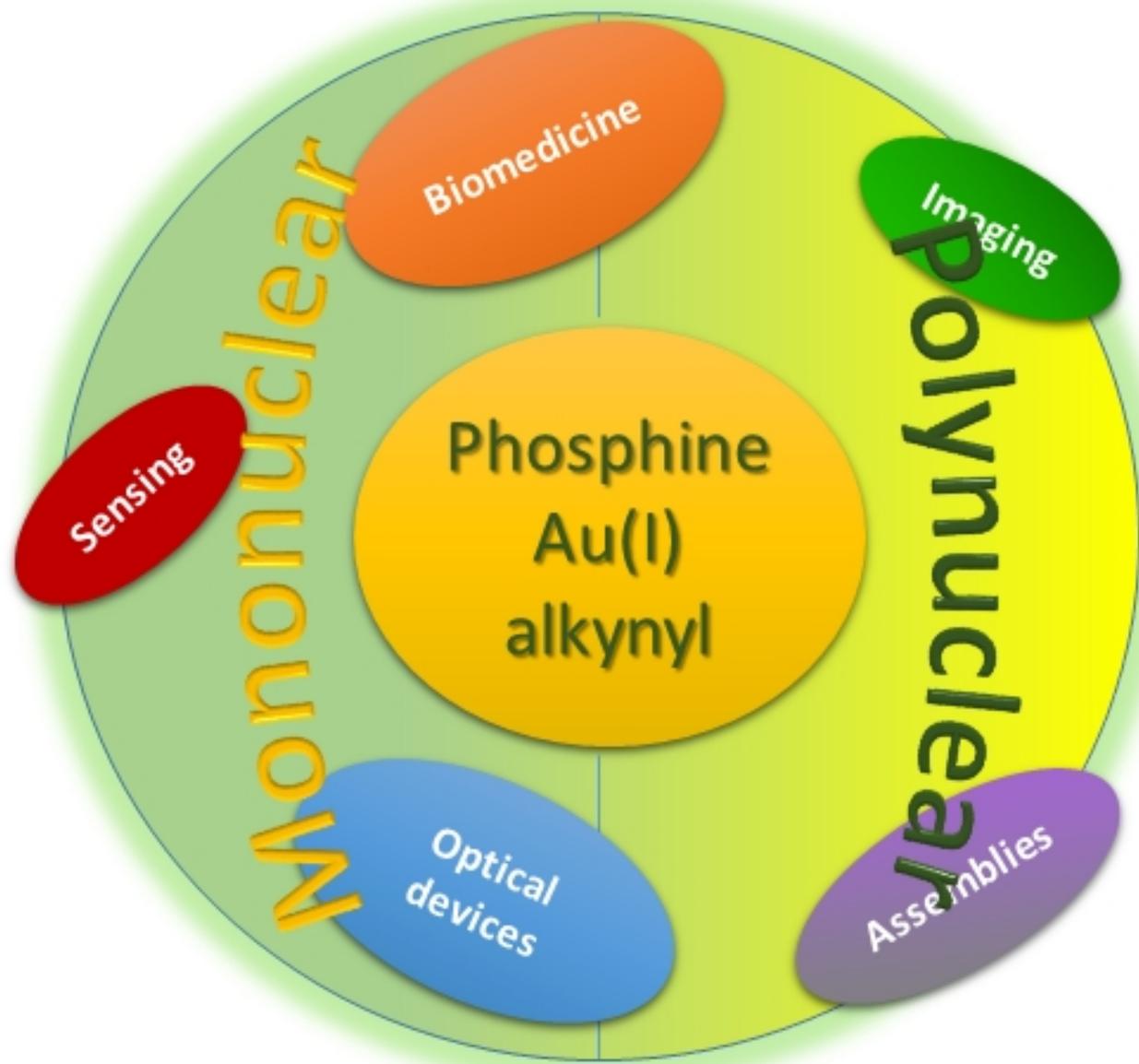
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Luminescent Phosphine Gold(I) Alkynyl complexes. Highlights from 2010 to 2018.

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Abstract

An overview of the homometallic phosphine-Au(I)alkynyl complexes reported in the literature from 2010-2018 have been collected and reported in this review article. They have been classified for better understanding, between mononuclear and polynuclear compounds. Their luminescent properties have been discussed along the text and the specific absorption and emission data collected in Annex I.

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Keywords: Gold(I), luminescence, phosphine, alkynyl, applications

1. Introduction

The photophysical properties of coinage-metal complexes, and in particular, gold(I) compounds have been intensely studied in the last two decades due to their fascinating versatility as well as the promising potential for technological applications in very different research fields such as optoelectronics, biological activity, chemosensors, mechanochromism, materials etc.[1–10] All these properties are based on the study of the luminescence characteristics of these type of compounds, which often depend dramatically on the presence of meta-metal interactions (aurophilicity). This phenomenon that is usually considered to be an origin of intense photoemission is also responsible for the formation of the families of multimetallic aggregates, which demonstrate exceptional diversity of composition, stereochemistry, and, consequently, physical properties.[11] The linear coordination of Au(I) atoms favors these aurophilic contacts. Regarding this, the ligands occupying the two coordination positions will have a direct influence on the establishment of aurophilic contacts and determine the architecture of the resulting possible inter- or intramolecular assemblies and corresponding luminescence. The linearity driven by alkynyl-derived ligands (alkynyl-chromophores, for luminescent species) can be considered as ideal candidates to be coordinated to the metal atom for this goal.

Solubility will also determine possible aurophilic contacts, being able to display intrinsic aggregation induced emission (AIE) at low solubility conditions.[12] Phosphines are one of the main ligands well-known to modulate solubility due to their great diversity and consequent physical properties. Accordingly, phosphine-Au(I)-alkynyl complexes are great candidates to analyze in detail their luminescent properties and they have been extensively investigated in this field. A wide variety of transitions, e.g. (metal-perturbed) intra-ligand transitions, metal-centred transitions and ligand-to-metal charge transfer, are thought responsible for these luminescent properties.

For all these reasons above, we are convinced that luminescent phosphine-Au(I)-alkynyl compounds reported in the last years deserve a compilation, analysis and overview of their properties and main applications. Au-C≡CR fragments have proved to be useful and versatile building blocks in the design of numerous organometallic compounds and materials with rich optical properties also because of their possible establishment of $M \cdots \pi(C \equiv C)$ interactions, which may affect also their luminescence.[13] But, due to the

huge number of these complexes and supramolecular assemblies reported in the literature, we have restricted this review article to homometallic derivatives.

The work is divided into two wide classifications: mononuclear and polynuclear complexes. Within each of these two large groups, we have tried to organize the compounds in a simple way depending on the organic part of the molecule linked to the alkynyl moiety (aliphatic and aromatic groups) and the polynuclear compounds depending on the fact that the alkynyl moiety is located as a bridging moiety or at the pending arms. Additionally, absorption and emission data of all compounds, together with aurophilic distances (for those having X-ray crystal structure) are collected in Annex I.

Chart 1 shows the chemical structure of the phosphines present in all compounds of this review with their short name, for better understanding purposes.

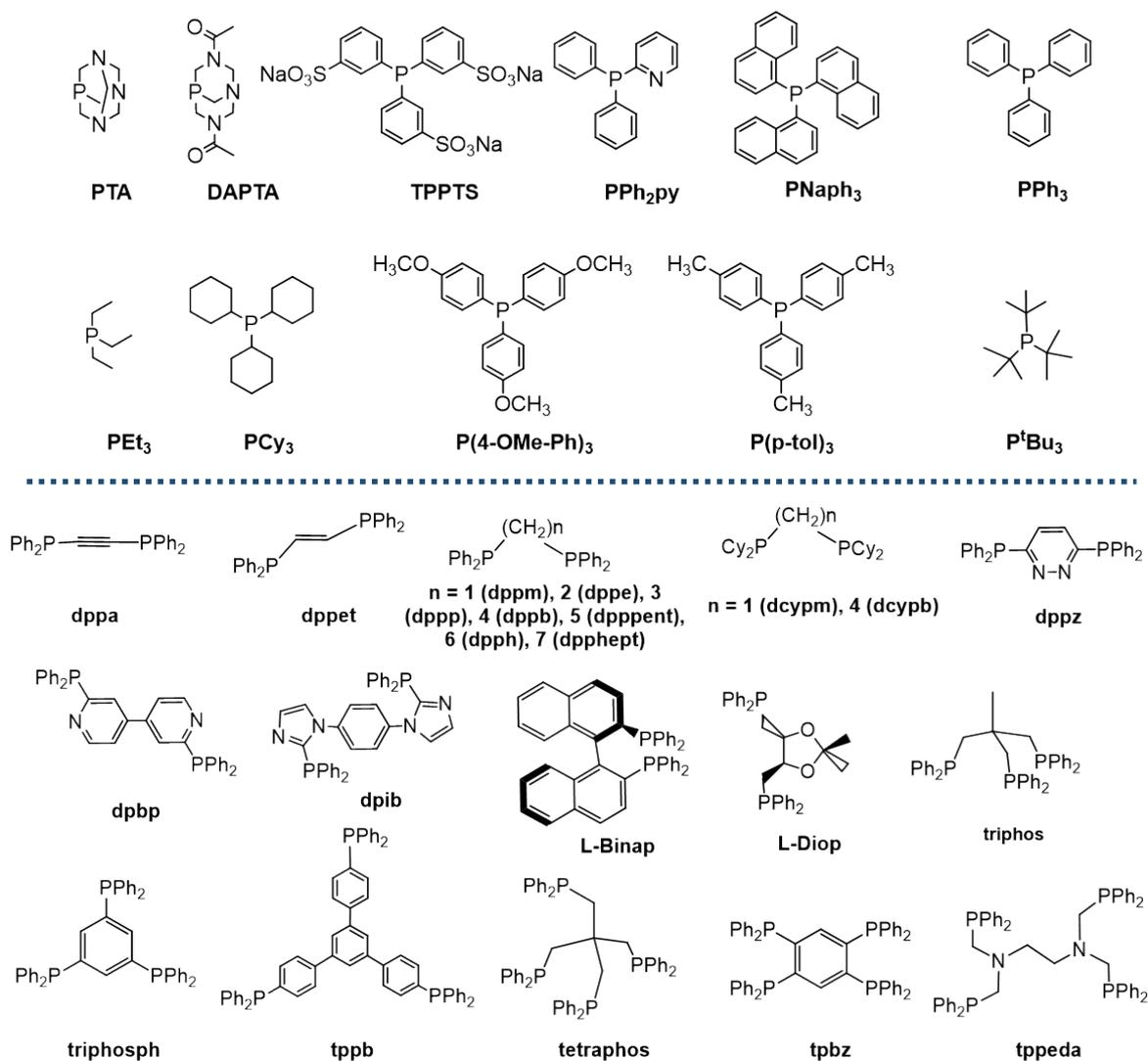


Chart 1. Chemical structure of the abbreviated monophosphines (above) and polyphosphines (below) used in this review.

2. Mononuclear complexes

The mononuclear compounds present the general formulae $R_3P-Au-C\equiv C-R_1$ (Figure 1) where R_1 can be an aliphatic or aromatic group.

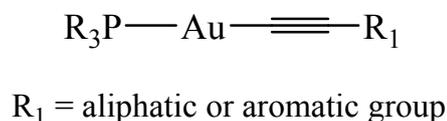


Figure 1. General chemical structure of the mononuclear complexes.

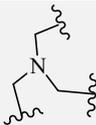
2.1. Phosphine-gold-alkynyl- R_1 ($R_1 = \text{aliphatic}$)

The only examples of this type of complexes were reported by M. Laguna, P. Dyson and co-workers (see Table 1) in 2010[14] where they analyse the antiproliferative activity of gold(I) alkyne complexes containing water-soluble phosphines PTA and DAPTA. All of them were synthesized by the reaction of $AuClPR_3$ with the alkynyl ligand under basic conditions to deprotonate the terminal alkynyl proton and able coordination to gold(I) atom.

The compounds display solid state broad emission bands when they were excited at *ca.* 370-380 nm with maxima centred in the range 485-505 nm. The origin of the emission was attributed to a $\pi \rightarrow \pi^*(C\equiv C)$ or $\sigma(Au-P) \rightarrow \pi^*(C\equiv C)$ transitions, as reported for similar Au(I) alkynyl phosphane derivatives. The influence of aurophilic contacts in these emissions cannot be excluded for structural similarity with related compounds. This emission was assigned in global, considering other non-aliphatic derivatives. For this reason, in these particular cases, the lack of chromophores in the chemical structure of the compounds precludes a pure intraligand emission and reinforces the involvement of $Au \cdots Au$ contacts in the recorded emission band.

The compounds show comparable and, in some cases, better antiproliferative effect than cis-platin and auranofin. They were shown to enter cells, and since they do not damage DNA, they probably exert their *in vitro* antiproliferative effect via interactions with critical proteins/enzymes in keeping with other gold complexes.

Table 1. Chemical structure of the aliphatic gold(I) phosphine complexes reported in the literature.

| R_1 | PR_3 | Reference |
|---|--|-----------|
| C_4H_9 —  | PTA (1a), DAPTA (1b) | [14] |
| C_5H_{11} —  | PTA (2a), DAPTA (2b) | [14] |
| CH_2OH —  | PTA (3a), DAPTA (3b) | [14] |
| $C(CH_3)_2OH$ —  | PTA (4a), DAPTA (4b) | [14] |
| CPh_2OH —  | PTA (5a), DAPTA (5b) | [14] |
| $CMeEtOH$ —  | PTA (6a), DAPTA (6b) | [14] |
|  | PTA (7a), DAPTA (7b) | [14] |

2.2. Phosphine-gold-alkynyl- R_1 (R_1 = aromatic chromophore)

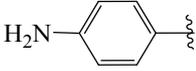
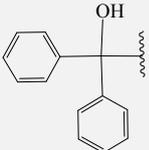
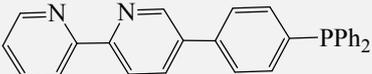
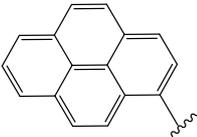
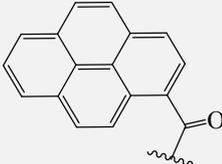
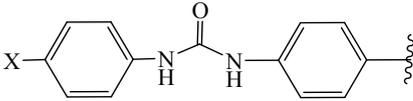
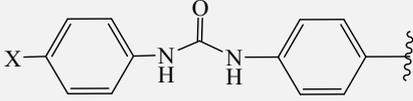
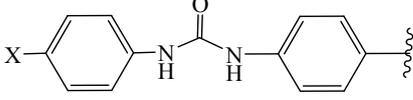
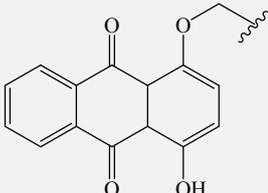
This is the largest class of compounds and for this reason we decided to divide them depending on the type of aromatic moiety coordinated to the alkynyl moiety being C-aromatic group or aromatic groups containing at least one heteroatom.

Two general methods are used for the synthesis of the compounds: i) deprotonation of alkynyl moiety and making it react with $AuClPR_3$ compounds (as described above); ii) synthesis of $[AuC\equiv CR_1]_n$ polymer and subsequent reaction with PR_3 which is being more a preferred synthetic procedure since it gives often higher yields and the reaction is cleaner and frequently faster.

2.2.1. C-aromatic derivatives

The photophysical properties of **8a** and **8b** were assigned to a $\pi \rightarrow \pi^*(C\equiv C)$ or $\sigma(Au-P) \rightarrow \pi^*(C\equiv C)$ transitions,[14] as described for their analogous aliphatic compounds displayed in Table 1, while mainly IL transitions centred on the alkynyl ligand were attributed in the case of **8c**. The lower-energy absorptions around 300 nm correspond to $\sigma \rightarrow \pi$ transitions from the Au-P bond to the antibonding orbitals of the aromatic rings.[15]

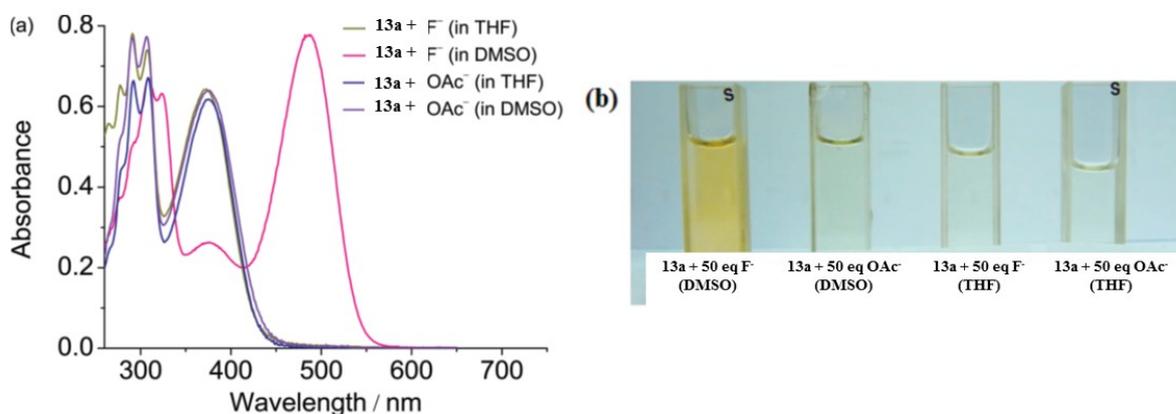
Table 2. Chemical structure of the C-aromatic gold(I) phosphine complexes reported in the literature.

| R₁ | PR₃ | Reference |
|--|---|------------------|
| Ph | PTA (8a), DAPTA (8b) PPh ₂ py(8c) | [14] [15] |
|  | PTA (9a), DAPTA (9b), PNaph ₃ (9c), PPh ₃ (9d), PEt ₃ (9e) | [16] |
|  |  (10) | [17] |
|  | PEt ₃ (11) | [18] |
|  | PEt ₃ (12) | [18] |
|  X = NO ₂ (13a), CF ₃ (13b), Cl (13c), H (13d), CH ₃ (13e), ^t Bu (13f), OCH ₃ (13g) | PCy ₃ (13a-g) | [19] |
|  X = NO ₂ (14a), OCH ₃ (14b) | PPh ₃ (14a-b) | [19] |
|  X = H (15a), OCH ₃ (15b) | P(4-OMe-Ph) ₃ (15a-b) | [19] |
|  | PPh ₃ (16) | [20] |

Intense room- and low-temperature luminescence both in solution and in the solid state was recorded for **8c** centred at ca. 440 nm (solution) or 470 nm (solid state) assigned to an IL π - $\pi^*(C\equiv C)$ or $\sigma(Au-P)$ - $\pi^*(C\equiv C)$ transition. Similar assignment was done for their analogous compounds **17c** and **51**, containing the same chromophore (Tables 3 and 5 below). IL fluorescence emission was also recorded for aniline derivatives **9a-e** based on $^1[\pi$ - $\pi^*(ethynylaniline)]$ transition.[21] An additional lower energy band at 420–470 nm with lower intensity was recorded for the compounds with higher tendency to establish aurophilic contacts and was assigned to $^3[\pi$ - $\pi^*(ethynylaniline)]$ emission.[16] Excitation of dichloromethane solutions of **10** at the intraligand absorption bands does not give to any significant emission.[17] On the contrary, when the bipyridyl group is located at the alkynyl-chromophore part of the molecule (R_1), fluorescence IL bands were recorded (compound **27**, Table 3). The authors rationalize this behaviour to a quenching by photoinduced electron transfer (PET) from the N lone pairs in the bipyridine part.[22]

D. Plazuk and co-workers described very recently that compound **12** undergo ligand scrambling in solution to form mixtures containing $[(Ar-CO-C\equiv C)_2Au]^-$ and $Au(PEt_3)_2^+$, while such behaviour was not observed in the lack of carbonyl moiety (compound **11**).[18] Weak or moderate fluorescence in solution and in the solid state with lifetimes of nanoseconds. Moreover, these compounds exhibited delayed fluorescence with lifetimes of hundreds of microseconds in the solid state.

Urea based gold(I) acetylide complexes **13a-g**, **14a-b** and **15a-b** were synthesized and characterized by H.-Y. Chao's group. X-ray crystal structures of some of the compounds



could be solved and demonstrate the presence of aurophilic contacts in some of the compounds.[19] Intense luminescence in the visible light regime was recorded for the compounds both in the solid state and in degassed THF solutions that were assigned to $^3(\pi\pi^*)$ excited state of the acetylide ligands of the complexes. The population of the triplet state is promoted by the presence of the gold atoms due to spin orbit coupling (SOC) which is enhanced by the aurophilic bonds. **13a-g** were used as sensors for anion recognition processes. It was observed that in THF, the substituent R on the acetylide ligand of complexes influences on the anion-binding ability, with the $\log K$ values of **13a-13g** toward the same anion being **13a** the best host. A dramatic colour change toward F^- in DMSO was observed, providing an access of naked eye detection of F^- (Figure 1). On the other hand, the substituent on the phosphine ligand (compounds **14** and **15** vs **13**) of complexes has little effect on $\log K$ values with the same anion.

Figure 1. UV-vis spectra (a) and colors (b) of **13a** ($1.98 \cdot 10^{-5}M$) in THF or DMSO in the presence of 50 equiv of F^- or OAc^- . Reprinted with permission from Ref. [19].
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Useful room-temperature anthraquinone-based visible luminescence was recorded by J.A. Pope and co-workers for **16**, which allowed their successful application as fluorophores in cell imaging microscopy.[20] Analogous data is recorded for the polynuclear **38-40** (see below Table 4). The UV-visible absorption properties of the ligands comprise IL $\pi-\pi^*$ (both aryl and alkynyl) transitions of $<310 \text{ nm}$, with a broadened lowest energy contribution expected to comprise significant charge transfer character arising from O(alkoxy)-to-quinone transitions. The broad, unstructured visible absorption

characteristics of the complexes can be wholly attributed to the appended anthraquinone chromophores. The visible emission spectra at *ca.* 500-600 nm (with some shifts, depending on the nature of the appending groups at the anthraquinone chromophore) in aerated MeCN are quite broad in appearance consistent with a charge transfer dominated excited state.

2.2.2. Heteroatom-aromatic derivatives

IL [π - π^* (alkynyl)] origin transitions have been displayed for all compounds with some charge transfer character, which probably arise from mixings of metal-to-ligand charge-transfer (MLCT) character. The corresponding fluorescence or phosphorescence assignment is based on the Stokes' shift, lifetime measurements and/or effect of oxygen in the recorded emission intensity and supported by DFT calculations. In some cases,[15,23–26] the vibronically structured emission band with progressional spacings of 1400-2000 cm^{-1} are also indicative of an intraligand origin.

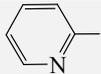
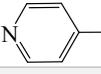
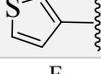
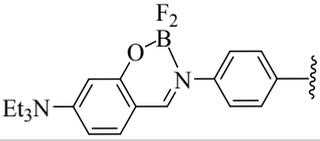
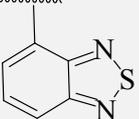
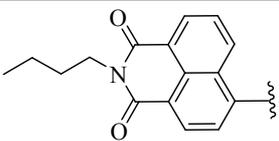
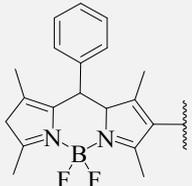
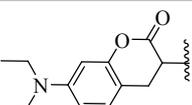
Delayed Fluorescence (DF)[27] was also recorded by C.-M. Che group for **21**, **22** and **24** with luminescent lifetimes in the order of microseconds.[28] A carefully photophysical study determines that two different mechanisms for DF can be involved being triplet-triplet annihilation (TTA) or germinate electron-hole pair (GP) recombination.[29] Very high fluorescence quantum yields (between 70-90%) were recorded for **21**, **22** and **24**. Changing the auxiliary ligand from PCy_3 to RNC and NHC results in negligible changes in the nanosecond transient absorption (ns-TA) spectra and excited state absorption life time (τ_{ESA}), suggesting that auxiliary ligand has little effect on the photophysics of the gold(I) arylacetylide complexes.

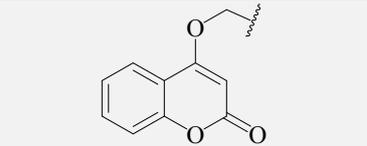
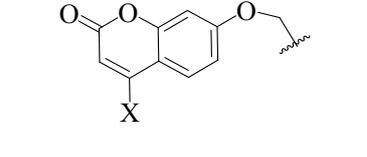
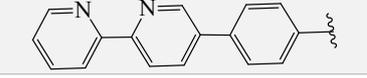
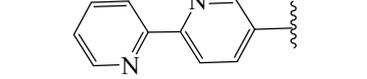
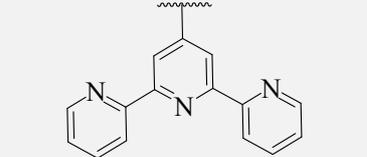
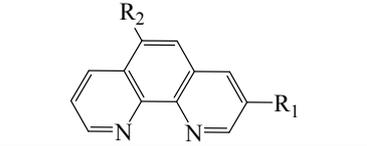
Strong $S_1 \rightarrow T_1$ intersystem crossing induced by SOC was observed to be relevant in the case of coumarin derivatives **25** and **26** at 77K. ISC was very effective thanks to the presence of the gold heavy atom being responsible of quantitative phosphorescence emission in some cases.[30] In depth photophysical characterization of compounds **28a-b** and **29c-d** was able to demonstrate the fast population of triplet state by the presence of gold(I) in recent studies developed in our group.[31]

In general, organic solvents were used to accomplish the solubilisation of the compounds in solution. Nevertheless, the formation of very long fibres and luminescent

organometallic hydrogels was observed for compounds **18**, **26c**, **28** and **29c-d** when water is used as solvent (Figure 2). A clear identification of the formation of these aggregates in solution can be found when broadening appear in the vibronically structured absorption bands.[23–25,32,33] 1D and 2D NMR, DFT calculations, optical, fluorescence and electronic microscopy together with in depth photophysical analysis shows the formation of these supramolecular assemblies and points out the presence of Au(I) and possible aurophilic contacts in this process.

Table 3. Chemical structure of the heteroatom-aromatic gold(I) phosphine complexes reported in the literature.

| R₁ | PR₃ | Reference |
|---|--|------------------|
|  | PTA (17a), DAPTA (17b), PPh ₂ py (17c) | [14,15] |
|  | TPPTS (18a), PTA (18b), DAPTA (18c) | [23,24,34] |
|  | PTA (19a), DAPTA (19b) | [14] |
|  | PPh ₃ (20) | [35] |
|  | PCy ₃ (21) | [28] |
|  | PCy ₃ (22) | [28] |
|  | PCy ₃ (23) | [28] |
|  | PCy ₃ (24) | [28] |

| | | |
|--|---|--------------|
|  | PTA (25a), DAPTA (25b) | [30] |
|  | PR ₃ = PTA, X = H (26a) PR ₃ = PTA, X = Me (26b) PR ₃ = DAPTA, X = H (26c) PR ₃ = DAPTA, X = Me (26d) PR ₃ = TPPTS, X = H (26e) | [30] [34] |
|  | PCy ₃ (27) | [17] |
|  | PR ₃ = PTA (28a), DAPTA (28b) | [25] |
|  | PPh ₃ (29a), P(p-tol) ₃ (29b), PTA (29c), DAPTA (29d) | [25,36] |
|  | R ₁ = C≡CAuPPh ₃ ; R ₂ = H (30a) R ₁ = H; R ₂ = C≡CAuPPh ₃ (30b) | [26] |

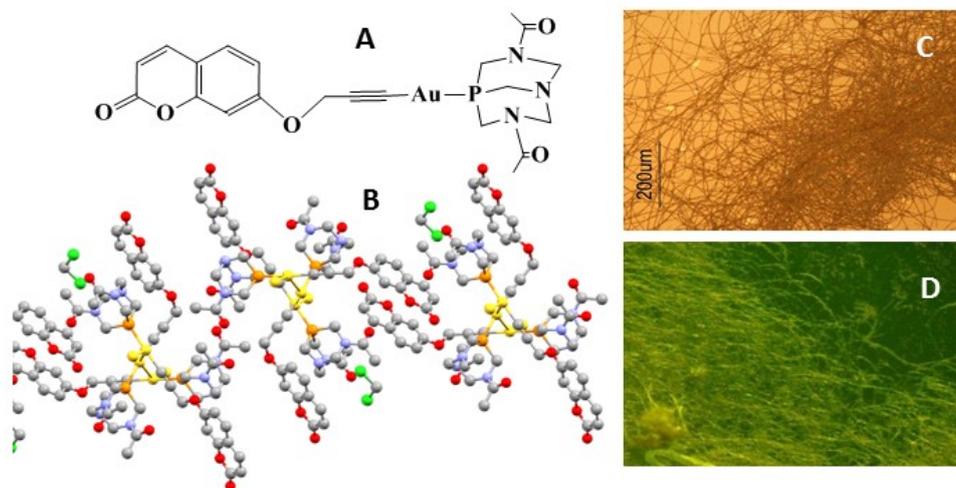


Figure 2. (A) Chemical structure of the Au(I) complex **26c** that forms hydrogels; (B) X-ray crystal structure (a-view) of **26c** showing the Au...Au and π - π weak contacts; (C) optical microscopy image of the resulting fibers; (D) fluorescence microscopy image of the resulting fibers.

3. Polynuclear complexes

Polynuclear complexes are particularly relevant from luminescence point of view since their emission may be affected by the presence of a higher number of heavy atoms that

can not only induce a stronger ISC process but also possible establishment of aurophilic contacts. We divided in this review polynuclear complexes into two large groups: those containing AuPR₃ moiety at the terminal position (being the alkynyl-chromophore as a linker) and those containing a polyphosphine as a linker (being the alkynyl-chromophore at the terminal positions). A particular case is the chemical structure of compounds **48** that can be included in both groups since they contain both alkynyl bridge and phosphine bridge ligand and we decided to include them in the first group based on the presence of the chromophore at terminal position.

3.1. Alkynyl bridged complexes (terminal Au-PPh₃)

The general scheme of the compounds of this group is displayed in Chart 2 and their chemical structures are collected in Table 4. The flexibility and type of the R linker will be of great relevance in the resulting luminescence and will be discussed below.

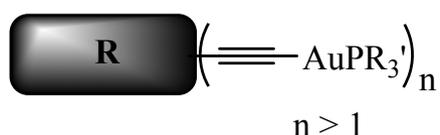


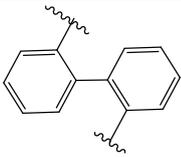
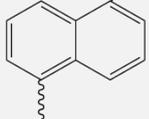
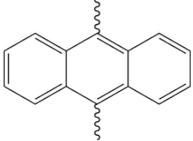
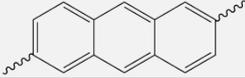
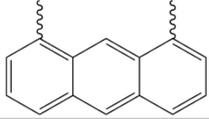
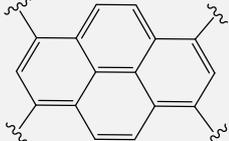
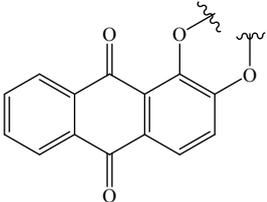
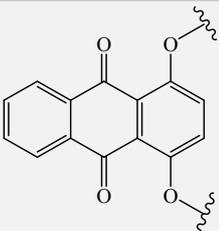
Chart 2. General scheme of the alkynyl bridged complexes.

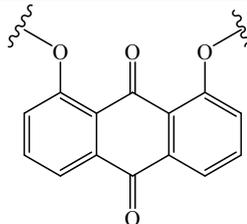
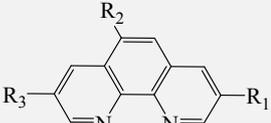
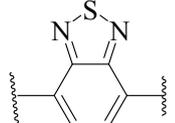
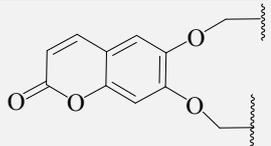
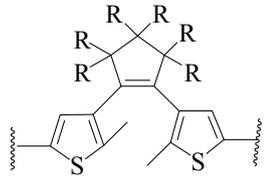
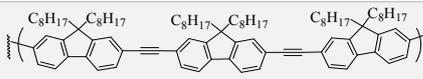
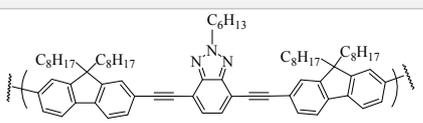
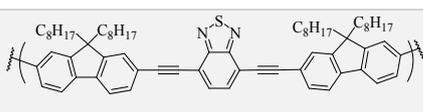
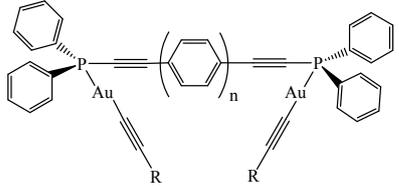
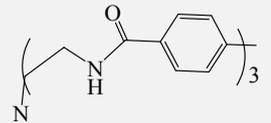
The emission spectra of the compounds are centred on metal perturbed IL transitions mixed in some cases with $\sigma-\pi^*$ MLCT states. The Stokes' shift and lifetimes in the order of nanoseconds or microseconds have determined the fluorescence or phosphorescence emission respectively. Thus, ¹IL $\pi \rightarrow \pi^*(\text{C} \equiv \text{C})$ transitions were assigned for **32**, **34-40**, **42**, **44-47** and **48c-f** while phosphorescence ³[$\sigma(\text{Au-P}) \rightarrow \pi^*(\text{C} \equiv \text{C})$] or metal perturbed ³IL emissions were ascribed for **31**, **33**, **41**, **43**, **48a-b** and **49**. The presence of the Au(I) atom has been determined as the responsible for the triplet state population by ISC and the resulting phosphorescence emission. An uncommon situation is compound **31b** displaying phosphorescence in solution while fluorescence in solid state. The ease in establishing aurophilic contacts on these complexes due to its flexibility in the case of compounds **31** (intramolecular contacts) or in an intermolecular way, in the case of **33**, may favour the ISC process and the resulting phosphorescence.

Small shifts on the emission wavelength of a series of compounds **32** have been explained by F. Mohr group by the fact that stronger donor ligands make the gold(I) center more

electron rich, thus increasing the energy level of the $\sigma(\text{Au-P})$ orbital which results in a slightly lower $\sigma-\pi^*$ emission energy.[37]

Table 4. Chemical structure of the polynuclear gold(I) phosphine complexes containing alkynyl bridge ligands reported in the literature.

| R | PR'₃ | Reference |
|---|--|------------------|
| (CH ₂) ₃ | PPh ₃ (31a), PPh ₂ py (31b) | [15] |
|  | PEt ₃ (32a), PCy ₃ (32b), P ^t Bu ₃ (32c), PPh ₃ (32d), PTA (32e) | [37] |
|  | P(<i>p</i> -tol) ₃ (33) | [38] |
|  | PPh ₃ (34) | [39] |
|  | PPh ₃ (35) | [39] |
|  | PPh ₃ (36) | [39] |
|  | PPh ₃ (37) | [40] |
|  | PPh ₃ (38) | [20] |
|  | PPh ₃ (39) | [20] |

| | | |
|---|---|------|
|  | PPh ₃ (40) | [20] |
|  | R ₁ = C≡CAuPPh ₃ ; R ₂ = H; R ₃ = C≡CAuPPh ₃ (41a) R ₁ = C≡CAuPPh ₃ ; R ₂ = C≡CAuPPh ₃ ; R ₃ = H (41b) | [26] |
|  | PPh ₃ (42) | [35] |
|  | PTA (43a), DAPTA (43b) | [34] |
|  | R=H, L=PCy ₃ (44a) R=H, L=PPh ₃ (44b) R=F, L=PCy ₃ (44c) R=F, L=PPh ₃ (44d) | [41] |
|  | PPh ₃ (45) | [42] |
|  | PPh ₃ (46) | [42] |
|  | PPh ₃ (47) | [42] |
|  | R = Ph- <i>p</i> ; n = 0 (48a), 1 (48b), 2 (48c), 3 (48d) O ^t Bu; n=3 (48e) ^t Bu; n=3 (48f) | [43] |
|  | PPh ₃ (49a) PPh ₂ py (49b) | [44] |

Cellular imaging utilizing the anthraquinone-based fluorescence of **38-40** showed that the agents are able to access organelles within the cytoplasm, in line with the suggested mode of gold cytotoxicity that involves mitochondrial inhibition.[20] It is possible that the phenomena of photobleaching and cell damage are linked, as photobleaching usually

involves the generation of toxic species (e.g., oxygen radicals) through the reaction of the luminophore excited state with material in the environment (Figure 3).

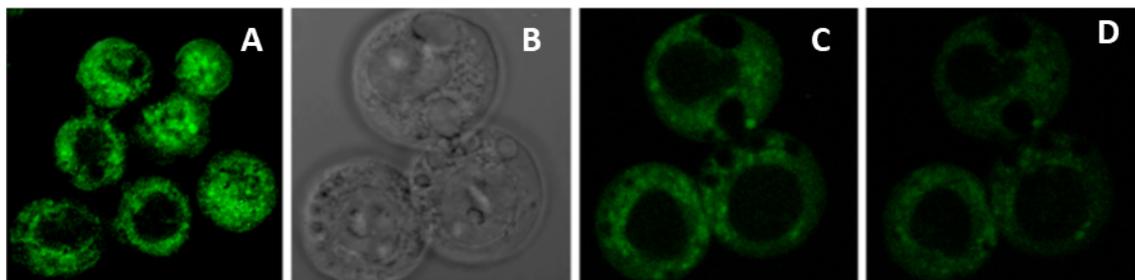
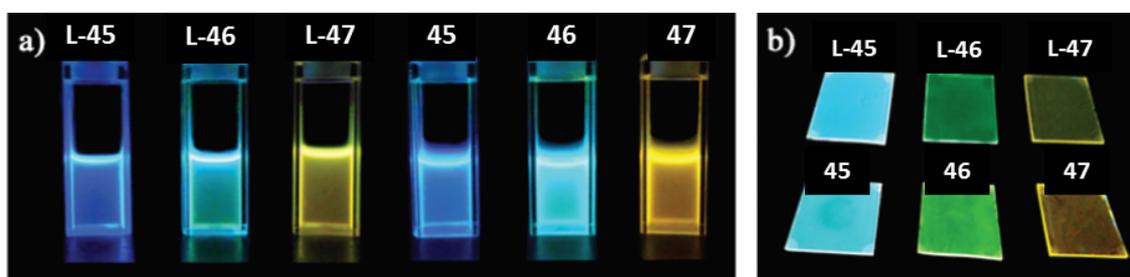


Figure 3. Images of MCF-7 cells incubated with **39** ($100\mu\text{g mL}^{-1}$, $4\text{ }^{\circ}\text{C}$, 30 min), excited at 405 nm, acquired 530–580 nm showing: (A) cytoplasmic distribution (overlaid luminescence and transmitted light); (B) appearance of vacuoles upon irradiation (transmitted light only); (C and D) photobleaching (luminescence only). Reprinted with permission from Ref. [20]

The photochromic behavior of the DTE alkynylgold(I) derivatives **44** were developed and studied by S.H. Liu group.[41] They exhibited fluorescence in CH_2Cl_2 solutions. In each case, the emission energy was found to change upon variation of both the linking moieties and the auxiliary phosphine ligands. It was observed a direct correlation between the recorded emission wavelength and the electronic density of both R substituent and phosphine with red-shifted emissions for hexafluorinated compounds and PCy3 derivatives that increases the electron-density in the Au(I) centers.[41] The fluorescence intensity decreased along with the photochromism on going from the ring-opened to the ring closed form upon irradiation at 302 nm. The small Stokes' shift suggest fluorescence origin.

The modulation of the π -acceptor groups by increasing the strength of acceptor units in between two fluorene moieties of **45-47** results in significant perturbation in the photonic properties, demonstrating the tuning of the fluorescence emission maxima. Most importantly, the strategy to incorporate benzothiadiazole in between the two fluorene units attached through alkynyl spacers has successfully rendered yellow emission with important application as yellow emitters.[42] The solid state PL spectra for all the compounds were recorded as thin films spin coated on quartz substrates for device applications, such as organic light emitting diodes, organic solid state lasers, organic field-effect transistors, nonlinear optics, and organic photovoltaics (OPV).[45] The



resulting emission makes these compounds interesting for optoelectronic devices since it was observed that the efficiency of the optoelectronic devices depends on the solid state emission.

Figure 4. Visual appearance of **45-47** and corresponding alkynyl ligands (**L-45-47**) demonstrating the tuning of emission wavelength in (a) 1,2-DCE and (b) thin films (spincoated on a quartz plate), showing an appreciable amount of emission even in the solid state (under UV illumination at 365 nm). Reprinted with permission from Ref. [42].

The classification of fluorescence or phosphorescence in compounds **48** was made by P.-T. Chou and co-workers based on the associated radiative decay rate constant (k_r), for which the fluorescence and phosphorescence are in the range of 10^7 - 10^9 s⁻¹ and $\ll 10^5$ s⁻¹, respectively. Very emission fluorescence quantum yields of *ca.* 99% were recorded in dichloromethane solutions for **48d-f** (with $n = 3$) pointing out the important role of increasing polyaromaticity for this property.[43]

The formation of aurophilic contacts can be also used with chemosensing purposes. In this way, changes on the recorded luminescence upon establishing/breaking of Au...Au bonds will be used as a on/off sensing process. This process was explored for cation sensing with compounds **49**.[44] It was observed a $^3(\pi\pi^*)$ emission at 472 nm upon addition of Ag⁺ into DMSO solution of **49a** and **49b** being a colorimetric sensor turning on and changing the emission color from blue-violet (very weak, DMSO background emission) to blue-green (strong, Figure 5a). **49a** shows its higher selectivity and competitiveness for Ag⁺ over other metal ions studied (Figure 5b).

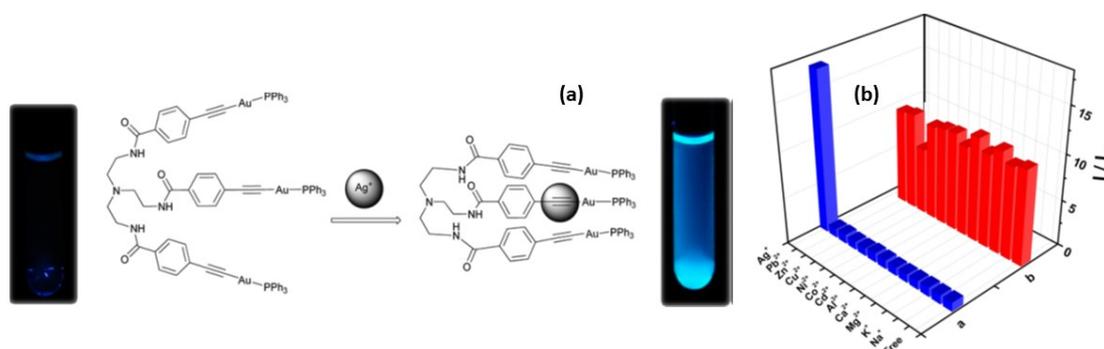


Figure 5. (a) Schematic representation of the colorimetric sensor **49a** in the selective recognition of Ag⁺; (b) (Row a) Relative emission intensity at 472 nm of **49a** (5.0×10^{-5} mol dm⁻³, $\lambda_{\text{exc}} = 311$ nm) with 2 equiv of various metal ions. (Row b) Relative emission intensity at 472 nm of **49a** (5.0×10^{-5} mol dm⁻³, $\lambda_{\text{exc}} = 311$ nm) + 1 equiv. Ag⁺ in the

presence of various metal ions (2 equiv for Cu^{2+} ; 10 equiv for Na^+ , K^+ , Ca^{2+} , and Al^{3+} ; 5 equiv. for others). Reprinted with permission from Ref. [44]

3.2. Phosphine bridged complexes (terminal $\text{Au-C}\equiv\text{C-R}_1$)

The major number of examples found in the literature of this group are dinuclear compounds although some few examples of tri- and tetranuclear complexes are also recently found and they are collected here.

The emission spectra recorded upon excitation samples of compounds **50** at around 300nm display high-energy emission at 350 nm, tentatively assigned to the $^1[\pi-\pi^*(\text{ethynylaniline})]$ transition and a lower energy band, as a shoulder, at 420-470 nm with lower intensity, assigned to $^3[\pi-\pi^*(\text{ethynylaniline})]$ emission. The resulting phosphorescence has been ascribed to the presence of aggregates with a direct influence on the aniline intersystem crossing process. For this, mononuclear compounds with no intermolecular contacts do not display this emission band (see above discussion for compounds **9**). X-ray crystal structures evidence the presence of $\text{Au}\cdots\text{Au}$, $\text{N-H}\cdots\text{C}_{\text{sp}}$, $\text{C-H}\cdots\pi$, and $\pi-\pi$ interactions in the 3D crystal packing (Figure 6).[16]

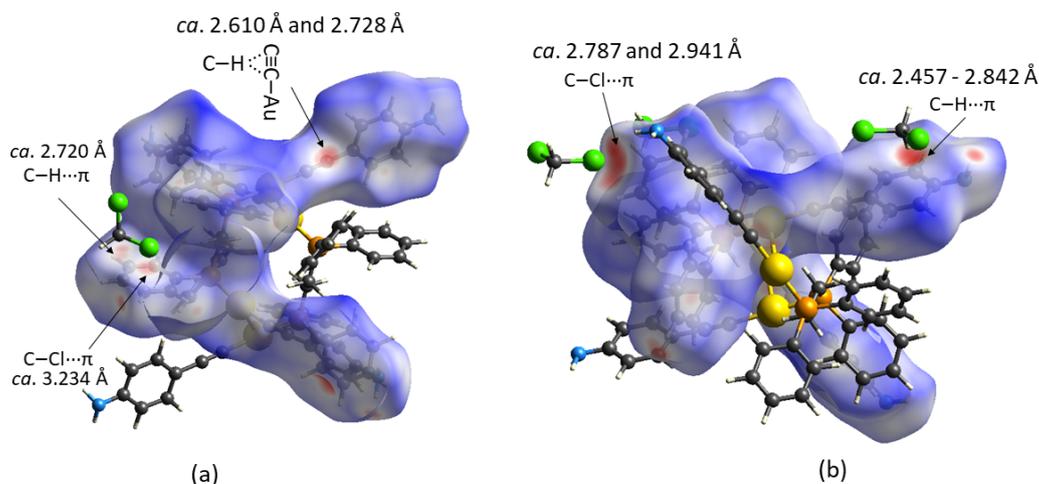


Figure 6. Hirshfeld surfaces of **50c** displaying (a) $\text{C-H}\cdots\text{C}_{\text{sp}}$, $\text{C-H}\cdots\pi$ and $\text{C-Cl}\cdots\pi$, and (b) $\text{C-Cl}\cdots\pi$ short contacts. Colour scale is between -0.4096 (red) and 1.5391 (blue) au. Reprinted with permission from Ref.[16]

The biological activity of these compounds have been analyzed by our group in detail and compared with that of their monodentate analogues **9a-e**. Although monodentate tertiary phosphine ligands have displayed broad applications in the development of anticancer gold complexes, the use of diphosphine ligands is not so extensively exploited.[46–48] The presence of the same chromophoric unit in all the complexes allowed us to perform a systematic analysis of the effect of the phosphane on the biological activity of the complexes and draw some important conclusions. Thus, it was concluded that nuclearity modulates the cancer cell lines selectivity and that phosphine and flexibility affects the resulting cytotoxicity. Increased apoptosis is observed when there is an increase in intracellular ROS, being a mechanism of action of gold(I) anticancer drugs not much explored.

On the other hand, the biological activity of low emissive $^3[\pi-\pi^*(C\equiv C)]$ compounds **52** was less relevant, analyzed against TrxR enzyme, due to their low solubility in biological medium.[49]

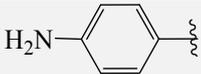
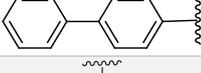
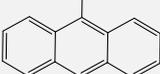
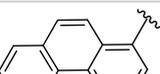
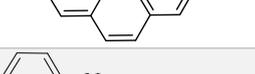
The nature of the chromophore on the population of triplet state was analyzed in compounds **53**, **55** and **56** where 3IL , 1IL transitions and no significant luminescence (due to well-known quenching effect of the azobenzene group) was recorded respectively both with dppe and dppp diphosphines.[50] Compounds **54** behave as **55** with 1IL transitions in all cases and thus, it seems that SOC is more favored for polybenzene than for those complexes containing fused carbon-aromatic groups as well-known organic luminophores such as pyrene and anthracene.

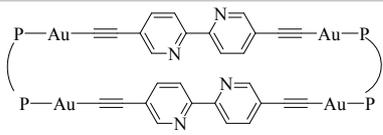
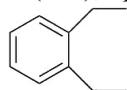
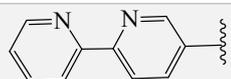
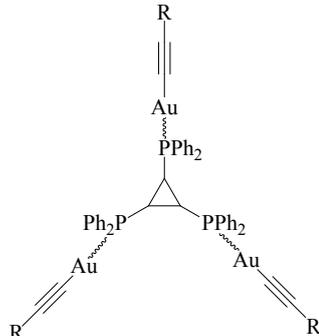
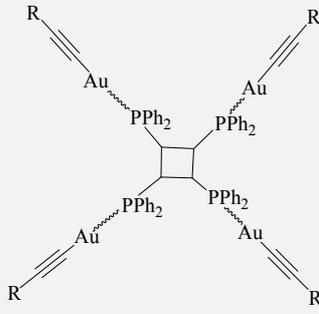
Dual emission was recorded for **57**, **59-62** upon excitation of the samples around 300 nm both in solid state and in solution. The higher energy emission was assigned to $^1IL \pi-\pi^*$ transitions centered in the aromatic rings of phenylalkynyl and phosphine ligands while the lower energy emission band was attributed to $\sigma(Au-P)\rightarrow\pi^*(Ar_{bridge})$ [51] or to $^3IL \pi-\pi^*$ transitions.[52–54] The macrocyclic structures **59** were described by Li and co-workers to behave as energy donors for Yb(III) NIR emission and very nice heterometallic zinc, iron and cobalt/gold trihelicates were reported by Gil-Rubio, Vicente and co-workers.[53] In this case, only Zn/Au-heterometallic helicates are luminescent, not cobalt and iron, as expected for their paramagnetic properties. The presence of intramolecular stackings were detected in solution by absorption spectra in the work of

Ferrer and co-workers[54] by the presence of a low tail above 300 nm assigned to $\sigma^*(\text{Au}\cdots\text{Au})-\pi^*$ transitions[55] together with higher broadening[56] leading to lower extinction coefficient at the maximum of the bands. Changes on absorption and emission data were used for the detection of Zn^{2+} and Cu^+ species.

The fine-tuning of (phenyl)*n*-bridged bimetallic Au(I) complexes lead to the capability of harnessing fluorescence versus phosphorescence via distance- and state-dependent intersystem crossing was studied by P.T. Chou and co-workers for compounds **58**. [57] This very nice example shows how $\pi\pi^*$ chromophore emission energy can be fine-tuned via the insertion of different numbers of phenylene spacers. It was also demonstrated for the first time in a systematic manner the decrease of rate constant for $S_1 \rightarrow T_1$ intersystem crossing (ISC) k_{isc} as the increase of the effective distance in an in depth photophysical characterization analysis.

Table 5. Chemical structure of the polynuclear gold(I) phosphine complexes containing phosphine bridge ligands reported in the literature.

| R₁ | P[^]P | Reference |
|---|---|------------------|
|  | dppa (50a), dppt (50b), dppe (50c), dppp (50d) | [16] |
|  | dppe (51) | [15] |
|  | dppm (52a), dppb (52b); dcypm (52c), dcypb (52d) | [49] |
|  | dppe (53a), dppp (53b) | [50] |
|  | dppb (54a), dpppent (54b), dpph (54c) | [58] |
|  | dppe (55a), dppp (55b) | [50] |
|  | dppe (56a), dppp (56b) | [50] |
| Ph | dppz (57a), dpbp (57b), dpib (57c) | [51] |
| Ph | $\text{Ph}_2\text{P} \left(\text{C}_6\text{H}_4 \right)_n \text{PPh}_2$ $n = 1-5$ | [57] |

| | | |
|--|---|------|
| | $n = 1$ (58a), 2 (58b), 3 (58c), 4 (58d), 5 (58e) | |
|  | dppm (59a), dppp (59b), dpppent (59c), dppe (59d),  (59e) | [52] |
|  | dpphept (60a), L-Binap (60b), L-Diop (60c) | [53] |
|  | R = 2,2'-bipy; PR ₃ = triphos (61a) R = 2,2'-bipy; PR ₃ = triphosph (61b) R = terpy; PR ₃ = triphos (61c) R = 2,2'-terpy; PR ₃ = triphosph (61d) R = Ph; PR ₃ = tppb (61e) | [54] |
|  | R = 2,2'-bipy; PR ₃ = Tetraphos (62a); R = 2,2'-bipy; PR ₃ = tpbz (62b), R = 2,2'-bipy; PR ₃ = dppeda (62c) R = 2,2'-terpy; PR ₃ = Tetraphos (62d); R = 2,2'-terpy; PR ₃ = tpbz (62e), R = 2,2'-terpy; PR ₃ = dppeda (62f) | [54] |

4. Conclusions and Prospectives

Phosphine-Au(I)-alkynyl complexes are a hot-topic of research on the last two decades and their potential applications become more diverse and of great interest in different fields. **Biomedical, photoelectronics and chemosensing are detected as the most studied and promising applications thanks** to their exiting luminescent properties and the relatively easy way to modify the chemical structure to introduce different chromophores well-designed depending on the desired property.

The main number of examples of this type of complexes reported in the literature are mononuclear containing aromatic chromophores but the number of polynuclear complexes is increasing in the last years.

The linearity of these complexes due to the Au(I) center and the alkynyl moiety makes the compounds suitable for establishing **intra- or** intermolecular contacts which are suitable in a large number of cases by the presence of Au(I)⋯Au(I) contacts. Other weak interactions are also present in these aggregates, **opening a relatively recent** and newer field of research based on Au(I) metallogelators. In particular, the aurophilic contacts have a direct and strong influence on the resulting luminescence and mainly phosphorescence. This is due to the presence of the Au(I) heavy atom, which is observed to enhance SOC in a large number of cases, inducing triplet state population and, as a result, phosphorescence. This property is expected to be even more favoured in the presence of aurophilic contacts and is of great interest for OLEDs applications. In anycase, in depth photophysical studies on this type of molecules is starting to be performed in the last years and this will be of great importance for the understanding of the observed transitions and, as a result, the better design of new molecules.

After around 20 years of emerging research on this field and, taking into consideration all the established knowledge, we are convinced that luminescent Au(I) complexes and, in particular, phosphine-Au(I) alkynyl complexes will continue growing on interest in the next years. **Some important points have been already detected such as: i) the biological properties depend strongly on the phosphine solubility and the selectivity against particular cancer cell lines is directly correlated to the nuclearity (from mono and polynuclear phosphines). The chromophore does not play any significant effect on the biological activity, only in their solubility and luminescence as fluorescence markers; ii) intermolecular Au⋯Au contacts may favour phosphorescence emission by enhancing the ISC process and can be used in sensing processes; iii) the luminescent properties of the Au(I) complexes is in general driven and located at the chromophore, although perturbed and affected by the heavy atom. Nevertheless, phosphorescence is not always displayed, as expected for heavy atom effect; iv) DF is gaining attention with fluorescence emissions with lifetimes in the order of microseconds with complexes derived from benzothiadiazole, coumarin or bodipy; v) the phosphine auxiliary ligands only play a direct effect on the resulting luminescence when contain a chromophore in their chemical structure; vi) the largest emission quantum yields measured among all the reported complexes contain benzothiadiazole, coumarin, naphthalimide and polyphenyl chromophores in their chemical structure and all of them are fluorescence emission.**

Acknowledgements

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Appendix I

| Compound | Au··Au (Å) | Medium (T, K) | Abs. $\lambda_{\text{max}}/\text{nm}$ (\square , $\text{M}^{-1}\cdot\text{cm}^{-1}$) | $\lambda_{\text{em}}/\text{nm}$ (τ , μs) | Reference |
|---|------------|-------------------------------------|---|---|-----------|
| Mononuclear complexes | | | | | |
| Phosphine-gold-alkynyl-R_1 (R_1 = aliphatic) | | | | | |
| 1a | | Solid (298K) | | 486 | [14] |
| 1b | | Solid (298K) | | 490 | |
| 2a | | Solid (298K) | | 473 | [14] |
| 2b | | Solid (298K) | | 498 | |
| 3a | | Solid (298K) | | 491 | [14] |
| 3b | | Solid (298K) | | 481 | |
| 4a | | Solid (298K) | | 496 | [14] |
| 4b | | Solid (298K) | | 498 | |
| 5a | | Solid (298K) | | 502 | [14] |
| 5b | | Solid (298K) | | 487 | |
| 6a | | Solid (298K) | | 504 | [14] |
| 6b | | Solid (298K) | | 488 | |
| 7a | | Solid (298K) | | 486 | [14] |
| 7b | | Solid (298K) | | 495 | |
| Phosphine-gold-alkynyl-R_1 (R_1 = aromatic) | | | | | |
| <i>C-aromatic derivatives</i> | | | | | |
| 8a | | Solid (298K) | | 499 | [14] |
| 8b | | Solid (298K) | | 534 | |
| 8c | | Solid (77K) | | 429, 452, 467, 493. | |
| | | CH_2Cl_2 (298K) | 237 (33027), 267 (26389)283 (26050) | 429, 450, 460, 472, 490. | |
| 9a | | H_2O | 290 (16000) | 352, 470 | [16] |
| 9b | | H_2O | 292 (19500) | 354, 459 | |
| 9c | | THF/ H_2O (1:1) | 298 (41100), 381 (6700) | 342 | |
| 9d | | THF/ H_2O (1:1) | 315 (18400) | 353 | |
| 9e | | THF/ H_2O (1:1) | 310 (20900) | 358 | |
| 10 | | CH_2Cl_2 (298 K) | 307 (62000), 268 (27000), 255 (29000) | -- | [17] |

| | | | | | |
|------------|-----------|---|---|--|------|
| 11 | 3.1887(6) | CH ₂ Cl ₂ (298 K) Solid (298K) | 248 (40 040), 280 (29 080), 291 (52 100), 342 (18 800), 359 (44 350), 379 (69 600) | 390 446, 472, 502, 520 (max.). <i>DF solid</i> (50μs): 523 (τ ₁ =670 μs) | [18] |
| 12 | | CH ₂ Cl ₂ (298 K) Solid (298K) | 290 (22900), 382 (26600), 401 (25080) | 448 500, 585 (max), 588. <i>DF solid</i> (50μs): 531 (max, τ ₁ =539 μs, τ ₂ 81=μs) | [18] |
| 13a | | THF (298K) Solid (298K) | 263 (sh,12500), 276 (23300), 288 (30800), 301 (28600), 345 (24000) | 443 (max, 6.5), 474. 525 (<0.1) | [19] |
| 13b | | THF (298K) Solid (298K) | 266 (sh, 18700), 280 (sh, 35300), 295 (60 400), 311 (63200). | 443, 475. | |
| 13c | | THF (298K) Solid (298K) | 264 (sh, 20000), 279 (36600), 293 (58900), 310 (58700). | 443, 479, 505, 528. 443, 476. | |
| 13d | | THF (298K) Solid (298K) | 264 (sh, 22300), 279 (28500), 293 (54400), 310 (55200) | 440, 479, 530 (sh). 444, 474. | |

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|------------|-----------|----------------------------|---|--------------------------|------|
| 13e | | THF (298K) | 266 (sh, 17400), 279 (33400), 293 (54900), 310 (55400) | 443, 479, 505, 518, 529. | |
| | | Solid (298K) | | 443, 475. | |
| 13f | | THF (298K) | 265 (sh, 16300), 280 (sh, 32400), 293 (51800), 310 (51400) | 440, 481, 532 (sh). | |
| | | Solid (298K) | | 444, 475. | |
| 13g | | THF (298K) | 265 (sh, 16800), 280 (sh, 33600), 293 (56400), 310 (58300) | 443, 475. | |
| | | Solid (298K) | | 440, 480, 505, 517, 529. | |
| 14a | | THF (298K) | 268 (18800), 276 (22400), 292 (28000), 305 (27900), 342 (27100). | - | [19] |
| | | Solid (298K) | | - | |
| 14b | | THF (298K) | 268 (24000), 276 (sh, 26600), 284 (sh, 30100), 299 (45900), 315 (46500) | 444, 475. | |
| | | Solid (298K) | | 440, 473, 485, 510 (sh) | |
| 15a | 3.0145(9) | THF (298K) Solid (298K) | 279 (38600), 296 (48400), 313 (49700). | 444, 474. 448, 495 | [19] |
| 15b | | THF (298K) Solid (298K) | 279 (sh, 37400), 297(52100), 314 (54000) | 443, 476 449, 503 | |
| 16 | | MeCN | 272, 324 sh, 448 | 425, 522 | [20] |

| <i>Heteroatom-aromatic derivatives</i> | | | | | |
|--|--|---|---|---|------|
| 17a | | Solid (298K) | | 510 | [14] |
| 17b | | Solid (298K) | | 541 | |
| 17c | | Solid (298K) | | 458 | [15] |
| | | Solid (77K) | | 456 | |
| | | CH ₂ Cl ₂ (298K) | 233 (47165), 267 (34792)288 (29990), 297 (29482) | | |
| 18a | | H ₂ O (298K) | 265 (22700), 276 (23500) | 410, 430, 442. | [34] |
| 18b | | H ₂ O (298K) | 235 (11100) 265 (14000), 277 (15800), 330 (6400) | 406, 423, 441, 480 sh. | [23] |
| | | CH ₂ Cl ₂ (298K) | 242 (11400), 269 (16500), 284 (20100) | 433, 555. | |
| | | (77K) | | 407, 428, 445 480 sh. | |
| | | Solid | | 407, 430, 450, 510. | |
| 18c | | H ₂ O (298K) | 231 (12900), 264 (13800), 275 (14600) | 535 | [24] |
| | | CH ₂ Cl ₂ (298K) | 237 (18200), 268 (20600), 282 (21700) | 404, 424, 442. 407, 429, 443, 480 sh. | |
| | | (77K) | | 407, 430, 445, 514. | |
| | | Solid | | 515 | |
| 19a | | Solid (298K) | | 467 | [14] |
| 19b | | Solid (298K) | | 488 | |
| 20 | | CH ₂ Cl ₂ (298K) | 239 sh (39810), 268 sh (19952), 275 (15488), 285 (14454), 413 (66069) | 478, 504 | [35] |
| 21 | | CH ₂ Cl ₂ (298K) | 265(14100),27 5 (14600),305 (9300), 311(9800), 319 (12400), 379 (6900) | 467 442, 630, 688. | [28] |

| | | | | | |
|------------|------------|---|---|---|------|
| | | EtOH/MeOH H (4:1) (77K) Solid (298K) Solid (77K) | | 504 492 | |
| 22 | | CH ₂ Cl ₂ (298K) EtOH/MeOH H (4:1) (77K) Solid (298K) | 283 (12.2·103), 333 (5600), 350 (11300), 380 (23800), 397 (25500) | 441, 613, 670, 418, 439, 462 (sh) 569, 609, 666. 403 (sh), 503. 610, 668 404 (sh), 504 627, 680 | [28] |
| 23 | 5.2726(4) | CH ₂ Cl ₂ (298K) | 280 (13500), 325 (4500), 412 (10100), 553 (40200) | 593 | [28] |
| 24 | | CH ₂ Cl ₂ (298K) EtOH/MeOH H (4:1) (77K) Solid (298K) Solid (77K) | 271 (13900), 316 (3200), 331(3200), 410 (40000), 423 (3700) | 466, 596, 652. 460, 481, 596, 653. 405 (w), 480 (sh), 515 598, 652 (sh). 409(w), 487 (max), 517 (sh),597, 654(sh). | [28] |
| 25a | | MeOH | 263 (11000), 275(8800), 302 (5000) | 359 | [30] |
| 25b | 3.235(2) | MeOH | 265 (7800), 276 (7400), 303 (4600) | 351 | |
| 26a | | MeOH | 295sh (8700), 320 (10500) | 381 | [30] |
| 26b | | MeOH | 289sh (6900), 320 (13400) | 374 | |
| 26c | 2.9789(15) | MeOH | 296sh (8600), 323 (14200) | 382 | |
| 26d | | MeOH | 289sh (8100), 321 (16700) 316 (13500) | 379 | |

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|--|--|---|---|---|------|
| 26e | | H ₂ O | | 392, 450 | [34] |
| 27 | | CH ₂ Cl ₂ (298K) | 326 (48000), 265 (10000) | 387 (0.49 ns) | [17] |
| 28a | | H ₂ O | <i>ca.</i> 310 (not reported) | <i>ca.</i> 630 (not reported) | [25] |
| | | DMSO | | <i>ca.</i> 430 (not reported) | |
| 28b | | H ₂ O | <i>ca.</i> 310 (not reported) | <i>ca.</i> 630 (not reported) | [25] |
| | | DMSO | | <i>ca.</i> 430 (not reported) | |
| 29a | | CH ₂ Cl ₂ (298K) | 276, 289 | 338, 352 | [36] |
| 29b | | CH ₂ Cl ₂ (298K) | | 339, 353 | |
| 29c | | H ₂ O | <i>ca.</i> 320, 345 (not reported) | 440, 500br (not reported) | [25] |
| 29d | | H ₂ O | <i>ca.</i> 320, 345 (not reported) | 440, 500br (not reported) | |
| 30a | | CH ₂ Cl ₂ (298K) | 328 (39000), 315 (35000), 279 (51000), 269 (45000) | 476, 510. 467, 483, 505, 519, 547, 565. | [26] |
| | | EtOH (298K) (77K) | | | |
| 30b | | CH ₂ Cl ₂ (298K) | 331 (26000), 319 (24000), 280 (36000), 275 (36000) | 532, 576. 521, 532, 568, 582, 620, 645. | |
| | | EtOH (298K) (77K) | | | |
| Polynuclear complexes | | | | | |
| <i>Alkynyl bridged complexes (terminal Au-PPh₃)</i> | | | | | |
| 31a | | CH ₂ Cl ₂ (298K) | 230 (53455) | 378 | [15] |
| | | CH ₂ Cl ₂ (77K) | | 359, 376, 393, 415, 433, 444, 457, 467, 480 | |
| 31b | | Solid (298K) Solid (77K) | | 505 500 | |

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|------------|--|---|--|--|------|
| | | CH ₂ Cl ₂ (298K) | 233 (51871), 255 (24750). | 390 | |
| | | CH ₂ Cl ₂ (77K) Solid (298K) Solid (77K) | | 416, 434, 444, 455, 466 505 500 | |
| 32a | | CH ₂ Cl ₂ | 390, 442 (s) | 459 | [37] |
| 32b | | C ₆ H ₆ | 390, 433 (s) | | |
| 32c | | CH ₂ Cl ₂ | 387, 431 (s) | 527 | |
| | | C ₆ H ₆ | 388, 433 (s) | | |
| 32d | | CH ₂ Cl ₂ | 388, 427 (s) | 482 | |
| | | C ₆ H ₆ | 389, 429 (s) | | |
| 32e | | CH ₂ Cl ₂ | 388, 447 (s) | 484 | |
| | | C ₆ H ₆ | 390, 430 (s) | | |
| | | CH ₂ Cl ₂ | - | 577 | |
| 33 | | CH ₂ Cl ₂ (298K) | 246 (89270), 330sh (27780), 344 (45450), 362 (47900) | 568 (93.1) | [38] |
| | | Solid (298K) | | 571 (0.3) | |
| | | Solid (77K) | | 575 (43.7) | |
| | | EtOH/MeO H (4:1 v/v) | | 563 (643) | |
| 34 | | CH ₂ Cl ₂ (298K) | 462 (101000), 434 (078100), 410 (038700), 275 (187000), 230 (207000) | 499 | [39] |
| 35 | | CH ₂ Cl ₂ (298K) | 412(117000), 389 (136000), 366(089700), 310(877000), 238(430000) | 445 | [39] |
| 36 | | CH ₂ Cl ₂ (298K) | 422(097600), 398 (093600), 376 (058300), 267 (567000), 228 (469000) | 455 | [39] |
| 37 | | CH ₂ Cl ₂ (298K) | 469, 441, 413, 336, 268, 228 | 540(sh), 505, 476 | [40] |
| | | Solid (298K) | 540(sh), 505, 476 | 650 (br) | |
| 38 | | MeCN | 272, 375 | 406, 538, 566 | [20] |

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|------------|--|---|--|----------------------------------|------|
| 39 | | MeCN | 266 sh, 322 sh, 406 | 415, 435 | [20] |
| 40 | | MeCN | 257, 275 sh, 382 | 491 | [20] |
| 41a | | CH ₂ Cl ₂ (298K) | 357 (75000), 337 (61000), 286 (59000), 276 (55000) | 506, 547. | [26] |
| | | EtOH (298K) (77K) | | 501, 519, 544, 562, 594, 614. | |
| 41b | | CH ₂ Cl ₂ (298K) | 327 (59000), 310 (73000), 275 (30000), 268 (31000) | 532, 576. | |
| | | EtOH (298K) (77K) | | 521, 533, 568, 583, 619, 645. | |
| 42 | | CH ₂ Cl ₂ (298K) | 269 (17378), 276 (21379), 291 (30902), 309 (35481), 324 (8912), 418 (15848) | 490 (sh), 501, 510 | [35] |
| 43a | | H ₂ O (298K) | 298 (8800), 336 (8500) | 440 | [34] |
| 43b | | H ₂ O (298K) | 300 (10100), 333 (10500) | 432 | |
| 44a | | CH ₂ Cl ₂ (298K) | 284(32200), 305(30200), 320(29500). | 416, 433 | [41] |
| 44b | | CH ₂ Cl ₂ (298K) | 275(40000), 288(40700), 312(38800) | 395, 422 | |
| 44c | | CH ₂ Cl ₂ (298K) | 283(44700), 297(52700), 312(48500) | 436, 460 | |
| 44d | | CH ₂ Cl ₂ (298K) | 301(49300), 316(47200) | 398, 442 | |
| 45 | | CH ₂ Cl ₂ (298K) | 378 (sh), 391 (103900), 396 | 426, 443 (sh) | [42] |
| | | Thin film | | 474, 504 | |
| 46 | | CH ₂ Cl ₂ (298K) | 315 (35400), 342 (42100), 360 (48700), | 462, 485 | [42] |

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|--|--|---|---|-------------------------------------|------|
| | | | 410 (66400), 435 (sh) | | |
| | | Thin film | 322, 346, 368, 421, 446 (sh) | 519 | |
| 47 | | CH ₂ Cl ₂ (298K) | 350 (65300), 453 (33200) | 564 | [42] |
| | | Thin film | 357, 466 | 566 | |
| 48a | | CH ₂ Cl ₂ (298K) | 286(20000), 302sh(14000) | 394, 455 | [43] |
| 48b | | CH ₂ Cl ₂ (298K) | 272sh(18000), 283(21000), 294(24000), 312(22000) | 370, 482, 517 | |
| 48c | | CH ₂ Cl ₂ (298K) | 271(39000), 285(47000), 299sh(48000), 315 (56000) | 352, 370, 528, 570 | |
| 48d | | CH ₂ Cl ₂ (298K) | 271(41000), 285(48000), 325 (70000) | 375, 394, 549, 591 | |
| 48e | | CH ₂ Cl ₂ (298K) | 325(118000) | 375, 393, 547, 595 | |
| 48f | | CH ₂ Cl ₂ (298K) | 325(126000) | 375, 392, 550, 593 | |
| 49a | | DMSO | 260 (58600), 270 (66400, sh), 275 (76600, sh), 292 (106000), 305 (117000), 324 (13200, sh) | - | [44] |
| 49b | | Solid | | 472 (sh), 496 (max), 554 (sh) | |
| | | DMSO | 269 (66700, sh), 292 (90600), 305 (102000), 327 (19000, sh) | | |
| | | Solid | | 472 (sh), 497 (max), 553 (sh) | |
| <i>Phosphine bridged complexes (terminal Au-C≡C-R1)</i> | | | | | |
| 50a | | THF/H ₂ O (1:1) | 307 (20700), 404 (14400) | 350, 420 | [16] |

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| 50b | 3.316(2) | | 314 (25700), 400 (4500). | 350, 420 | |
| 50c | 3.118(1) | | 313 (19900), 382 (11900) | 350, 420 | |
| 50d | | | 310 (22000), 380 (2700) | 350, 420 | |
| 51 | | CH ₂ Cl ₂ (298K) (77K) Solid (298K) (77K) | 235 (37795), 269 (40797), 285 (40112) | 405, 450 420, 445, 460, 479 510 447 | [15] |
| 52a | | DMSO (298K) | 280 (70400), 291 (71100) | 415, 438, 461 | [49] |
| 52b | | DMSO (298K) | 270 (5006), 285 (66500) | 415, 438, 459 | |
| 52c | | DMSO (298K) | 274 (69800), 288 (66700) | 415, 438, 461 | |
| 52d | | DMSO (298K) | 276 (48900), 286 (46700) | 415, 440, 461 | |
| 53a | <i>Orthorhombic</i> <i>c</i> 3.06 | CH ₂ Cl ₂ (298K) Solid (298K) | 296 (121000), 308 (128000). | 497, 533, 575 (2.9) <i>Orthorhombic:</i> 498, 546, 583 (17.8) <i>Triclinic:</i> 491, 530, 563 (4.3). | [50] |
| 53b | | CH ₂ Cl ₂ (298K) Solid (298K) | 270sh (48000), 283sh (80000), 295 (127000), 307 (132000). | 496, 528, 573 (2.5) 495, 529, 563 (3.6) | |
| 54a | 3.339(1) | CH ₂ Cl ₂ (298K) Solid (298K) | 356 (7300), 375 (18000), 396 (36500), 420 (42100) | 430, 453, 479 492, 515 | [58] |
| 54b | | CH ₂ Cl ₂ (298K) Solid (298K) | 356 (8000), 375 (18000), 396 (36400), 420 (41900) | 430, 452, 479 496, 510 | |

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|------------|--|---|---|--|------|
| 54c | | CH ₂ Cl ₂ (298K) Solid (298K) | 356 (7800), 375 (18800), 396 (38000), 420 (43700) | 430, 453, 479 495, 512 | |
| 55a | | CH ₂ Cl ₂ (298K) Solid (298K) | 280 (22000), 290 (32000), 316 (16000), 342 (13000), 359(29000), 380 (47000). | 383, 403, 425 (0.015) 510 | [50] |
| 55b | | CH ₂ Cl ₂ (298K) Solid (298K) | 280 (22000), 290 (36000), 359 (35000), 380 (54000) | 383, 403, 425 (0.023) 510 | |
| 56a | | CH ₂ Cl ₂ (298K) | 267(13000), 274(12000), 365 (29000), 455 (2000) | --- | [50] |
| 56b | | CH ₂ Cl ₂ (298K) | 267 (4000), 274 (3800), 365 (27000), 455 sh (600) | --- | |
| 57a | | CH ₂ Cl ₂ (298K) Solid (298K) | 282sh (19000), 238 (27000), 269 (22000) | 377, 491 520 | [51] |
| 57b | 2.990(7) | CH ₂ Cl ₂ (298K) Solid (298K) | 239 (52000), 270 (34000), 282 (33000) | 375.5, 491 544 | |
| 57c | | CH ₂ Cl ₂ (298K) Solid (298K) | 256sh (6500), 268.5 (6800), 282 (5200) | 375.5, 491 421, 442, 451, 462, 487 | |
| 58a | | CH ₂ Cl ₂ | | 316, 424 | [57] |
| 58b | | CH ₂ Cl ₂ | | 333, 457 | |
| 58c | | CH ₂ Cl ₂ | | 360, 510 | |
| 58d | | CH ₂ Cl ₂ | | 373, 534 | |
| 58e | | CH ₂ Cl ₂ | | 380, 549 | |
| 59a | Au ₁ ...Au ₂ 3.096(2) Au ₃ ...Au ₄ 3.266(2) | CH ₂ Cl ₂ (298K) Solid (298K) | 230, 343, 368. | 398, 549, 589 468, 555 | [52] |

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|------------|---|---|---|--|------|
| 59b | Au ₅ ...Au ₆ 3.258 (2) | CH ₂ Cl ₂ (298K) | 233, 339, 357 | 392, 534(w), 573 | |
| 59c | | Solid (298K) CH ₂ Cl ₂ (298K) Solid (298K) | 232, 340, 358. 232, 340, 358. | 463, 549 391, 532, 572 455, 551 | |
| 59d | | CH ₂ Cl ₂ (298K) Solid (298K) | 230, 346, 368 | 392, 531, 572 456, 544 | |
| 59e | | CH ₂ Cl ₂ (298K) Solid (298K) | | 402, 542, 586 468, 556. | |
| 60a | | CH ₂ Cl ₂ | 229 (5.02), 316 (6.21), 330 (5.97) | 392 | [53] |
| 60b | | Solid CH ₂ Cl ₂ | | 432, 584, 653 378 (sh), 391, 500 (sh, w) | |
| 60c | | Solid CH ₂ Cl ₂ | 231 (12.49), 320 (9.50), 334 (9.46) | 402, 418, 513 391, 508 (w) | |
| | | Solid | 229 (5.97), 316 (7.97), 330 (7.60) | 404, 515 (sh), 589, 649 (sh) | |
| 61a | | CH ₂ Cl ₂ (298K) Solid (298K) | 318 (97700), 330 (84300) | 392, 500 w, 536 sh 401, 505, 546, 606 | [54] |
| 61b | | CH ₂ Cl ₂ (298K) Solid (298K) | 316 (145000), 332 (138600) | 383, 497 w, 539 sh 429, 474, 511, 557 | |
| 61c | | CH ₂ Cl ₂ (298K) Solid (298K) | 277 (172100), 288 (157000), 311 sh (44500), 332 sh (90900). | 340 sh, 354, 439 w, 476 w 407, 556 w | |
| 61d | | CH ₂ Cl ₂ (298K) | 276 (200700), 290 (195600), | 338 sh, 353, 433 w, 473 w | |

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|------------|---|---|--|--|------|
| 61e | | Solid (298K) | 317 sh (37600), 331 sh (27100) | 407, 516, 568 | [51] |
| | | CH ₂ Cl ₂ (298K) | 270.5 (11000), 282.5 (11000) | 360, 490 | |
| | | Solid (298K) | | 372, 520 | |
| 62a | 3.259(3), 3.0310(11), 2.9445(12), 3.0356(10) | CH ₂ Cl ₂ (298K) Solid (298K) | 319 (198100), 333 (198400). | 385, 502 w, 530 w 400, 506, 542, 585. | [54] |
| 62b | 3.077(2), 3.118(2) | CH ₂ Cl ₂ (298K) | 320 (277500), 334 (242300) | 374, 396, 501, 539. | |
| | | Solid (298K) | | 423, 503, 604 sh, 599. | |
| 62c | | CH ₂ Cl ₂ (298K) | 318 (229200), 331 (226500) | 375, 403, 498 w, 537 sh. | |
| | | Solid (298K) | | 423, 502, 547, 581 sh. | |
| 62d | | CH ₂ Cl ₂ (298K) | 277 (263400), 294 sh(224500), 319 sh (71100), 333 sh (38600). | 339 sh, 353, 439 w, 476 sh. | |
| 62e | | Solid (298K) | | 407, 507, 563. | |
| 62f | | CH ₂ Cl ₂ (298K) | 266 (371300), 277 (395000), 297 | 366, 480 sh. | |
| | | Solid (298K) | sh(265700), 321 | 407, 500, 582. 356, 475. | |
| | | CH ₂ Cl ₂ (298K) | sh(118000), 334 sh (69900). | | |
| | | | 266 (295200), 276 (316000), 291 sh(247100), 319 sh (74200), 332 sh (51400) | | |



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Luminescent Phosphine Gold(I) Alkynyl complexes. Highlights from 2010 to 2018.

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