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Polypyridyl-functionalizated alkynyl gold(I) metallaligands supported by tri- and tetradentate phosphanes

Montserrat Ferrer,[a,*] Leticia Giménez,[a] Albert Gutiérrez,[a] Joao Carlos Lima,[b] Laura Rodríguez,[a,c] Manuel Martínez,[a] Avelino Martín,[d] Rakesh Puttreddy [e] and Kari Rissanen[e]

[a] *Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica. Universitat de Barcelona, c/ Martí i Franquès 1-11 08028 Barcelona, Spain.*

[b] *LAQV-REQUIMTE, Departamento de Química, Universidade Nova de Lisboa, Monte de Caparica, Portugal.*

[c] *Institut de Nanociència i Nanotecnologia (IN^{2}UB). Universitat de Barcelona, 08028 Barcelona, Spain*

[d] *Departamento de Química Inorgánica, Campus Universitario-Edificio de Farmacia, Universidad de Alcalá, 28871 Alcalá de Henares, Spain*

[e] *Department of Chemistry, University of Jyväskylä, POB 35, 40014 Jyväskylä, Finland*

Abstract

A series of alkynyl gold(I) tri and tetratopic metallaligands of the type [Au_3(C≡C-R)$_3$(μ_3-triphosphane)] (R = 2,2'-bipyridin-5-yl or $C_{10}H_7N_2$, 2,2':6',2''-terpyridin-4-yl or $C_{15}H_{10}N_3$; triphosphane = 1,1,1-tris(diphenylphosphanyl)ethane or triphos, 1,3,5-tris(diphenylphosphanyl)benzene or triphosph) and [Au_4(C≡C-R)$_4$(μ_4-tetraphosphane)] (R = $C_{10}H_7N_2$, $C_{15}H_{10}N_3$; tetraphosphane = tetrakis(diphenylphosphanylmethyl)methane or tetraphos, 1,2,3,5-tetrakis(diphenylphosphanyl)benzene or tpbz, tetrakis(diphenylphosphaneylmethyl)-1,2-ethylenediamine or dppeda) were obtained in

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moderate to good yields. All complexes could be prepared by reaction between the alkynyl gold(I) polymeric species $[Au(C\equiv C\text{-}R)]_n$ and the adequate polyphosphane. An alternative strategy that required the previous synthesis of the appropriate acetylacetonate precursors $[Au_n(acac)_n(\mu_n\text{-polyphosphane})]$ ("acac method") was assayed, nevertheless only the polyacac derivatives $[Au_3(acac)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos, triphosph) and $[Au_4(acac)_4(\mu_4\text{-tetraphos})]$ could be isolated and characterized.

All compounds were characterized by IR, multinuclear NMR spectroscopy and ESI(+) mass spectrometry. The X-ray crystal structure of complexes $[Au_4(C\equiv C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tetraphos})]$ and $[Au_4(C\equiv C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tpbz})]$ showed the involvement of all the gold atoms in close intramolecular Au···Au contacts as well as intermolecular π stacking interactions between the aromatic rings of the polypyridyl ligands.

The photophysical properties of the synthesized compounds were carefully studied and used as a probe of their possible use as multidentate ligands for Cu(I) and Zn(II). The UV-Vis speciation studies of the complexation reactions were conducted via metal titration and, in most of cases the dangling units of the ligand have found to behave in a fairy independent way. While in the case of Cu(I) multiple equilibria exist in solution a single complex is detected for Zn(II) under the conditions studied.

Introduction

Gold(I) molecular materials have become an evolving field of research in late decades due to their promising applications in such fields as sensing,[1-3] non-linear optics,[4-6] catalysis,[7-10] therapeutics[11-13] and bioimaging.[11, 12, 14] This interest in gold(I) complexes mainly arise from their rich luminescence properties[1, 15-19] as well as their predisposition to establish aurophilic interactions.[20-24]

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In particular, gold(I) alkynyl systems[25, 26] are specially attractive due to the preference for linear two-coordinate geometry of gold(I), together with the linearity of the alkynyl unit and its π-unsaturated nature. These privileged features have made alkynyl gold(I) complexes ideal candidates as building blocks to assemble a great variety of organometallic supramolecular structures that frequently present aurophilic interactions and significant luminescent properties.[22, 27-37]

In addition to the possibility of establishing aurophilic interactions, the functionalization of the alkynyl moiety with N- donor groups in gold(I) alkynyl compounds provides an alternative and/or complementary approach to obtain heterometallic and/or multicomponent complexes with a wide range of geometries. With this in mind, we synthesized a series of phosphane gold(I) ethynylpyridine complexes that, in spite of bearing terminal N-donor pyridine groups,[38, 39] did not allow to build up heterometallic assemblies. All the attempts to use the named pyridine derivatives in self-assembly reactions resulted in either complex mixtures in solution or very insoluble materials that could not be characterized.

After the failure of the pyridine appended gold(I) species to act as metallaligands, and as a rational extension of our studies, we directed our attention to the use of polypyridyl-functionalized alkynyl ligands such as 5-ethynyl-2,2'-bipyridine and 4'-ethynyl-2,2':6',2''-terpyridine to obtain our targeted gold(I) donor compounds. These polydentate N- donors should facilitate and stabilize the coordination of a wide range of d- and f-block metallic units through polypyridyl chelation to the prefabricated gold(I) akynyl compounds.[40] Moreover, the possibility of the incorporation of photo- and/or redox-active metal fragments in combination with the known luminescent properties of alkynyl gold(I) compounds could give rise to interesting properties suitable for potential applications.

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In fact, some research groups have recently described the synthesis of alkynyl gold(I) complexes with terminal 2,2'-bipyridine[41-46] or 2,2':6',2''-terpyridine units.[41, 47-50] Interestingly, however, in spite of the stability of these metallaligands, a limited number of reports on the supramolecular coordination chemistry of these species can be found in the literature. Some years ago, Chem and col. described the isolation of tetrametallic Au_2Ln_2 (Ln= lanthanide) arrays formed by the establishment of aurophilic interactions.[42] Very recently, Vicente and col. reported the obtention of appealing supramolecular architectures like triple-stranded helicates,[51, 52] helical dimers,[53] rigid-rod complexes and coordination oligomers.[54]

Noteworthy, all the reported alkynyl gold(I) compounds with pendant polypyridyl moieties mentioned above are supported by mono or diphosphanes as auxiliary ligands, and consequently are able to act as mono or ditopic metallaligands. However, neither tri nor tetratopic analogous systems have been described so far. Indeed, although phosphanes and diphosphanes have been widespread used as ligands in the chemistry of alkynyl gold(I) compounds,[25] the number of derivatives based on tri or tetradentate phosphanes is rather limited,[36, 39, 55-59] despite their potential in the construction of multimetallic assemblies. The use of tri or tetratopic building blocks should increase the complexity of the obtained heterometallic frameworks, allowing the obtention of architectures with a great diversity of nuclearities and/or topologies and unique properties.[60]

Given these considerations, we describe herein the preparation and characterization of a series of different tri and tetraphosphane alkynyl gold(I) derivatives with appended bipyridine or terpyridine moieties, suitable for participating in coordination reactions. The photophysical properties of the synthesised compounds together with a preliminary

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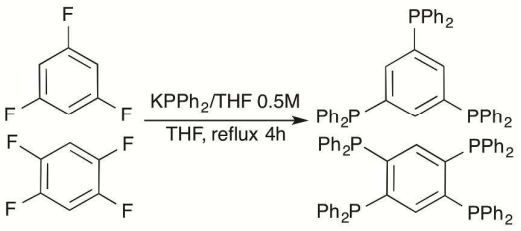
spectrophotometric study of how these properties are modified when they coordinate to d^{10} ions like Cu(I) and Zn(II) are also reported.

Results and discussion

Synthesis of poly(diphenylphosphanyl)benzene ligands

The tri- and tetraphosphanes with benzene core used in this work (i. e. triphosph and tpbz) are interesting and versatile ligands in coordination chemistry due to the possibility of obtaining polynuclear derivatives. However, they have been barely explored most probably owing to their laborious and no reproducible synthesis. Since their preparation from PPh_3 and Na metal in dry liquid ammonia described by McFarlane and col., only one report dealing with an improved obtention of tpbz (from PPh_2Cl and Na metal in THF as starting materials) can be found in the literature.[61] However, the latter method is time consuming and the reported yield is only moderate. In this work we have improved significantly the synthesis of both poly(diphenylphosphanyl)benzene ligands by refluxing 4 hours commercially available potassium diphenylphosphide in THF and the adequate fluoroarene (Scheme 1). This method was assayed after the work of James and col.,[62] who described it for other polyphosphanes and resulted in a significant improvement of the reproducibility and the yield of the desired compounds.



Scheme 1. Synthesis of poly(diphenylphosphanyl)benzene ligands

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Synthesis of alkynyl gold(I) complexes

Except for the case of tpbz and dppeda derivatives, two methods were used to prepare the targeted polynuclear alkynyl gold(I) compounds. (Schemes 2 and 3) Although the general method used to synthesize related compounds involves direct reaction between the polymer $[Au(C\equiv C\text{-}R)]_n$ and the free phosphanes (**polymer method**),[41, 42, 50, 55] the laborious syntheses of 5-ethynyl-2,2'-bipyridine, 4'-ethynyl-2,2':6',2''-terpyridine and the moderate yields of these reactions prompted us to assay an alternative strategy based on the reaction of the acetylacetonato phosphane complexes with the terminal alkynes ("**acac method**").[63, 64] In fact, the acac derivatives $[Au_3(acac)_3(\mu_3\text{-tripod})]$ and $[Au_3(acac)_3(\mu_3\text{-triphos})]$ proved to be useful as intermediates in the obtention of supramolecular metallocriptands.[65]

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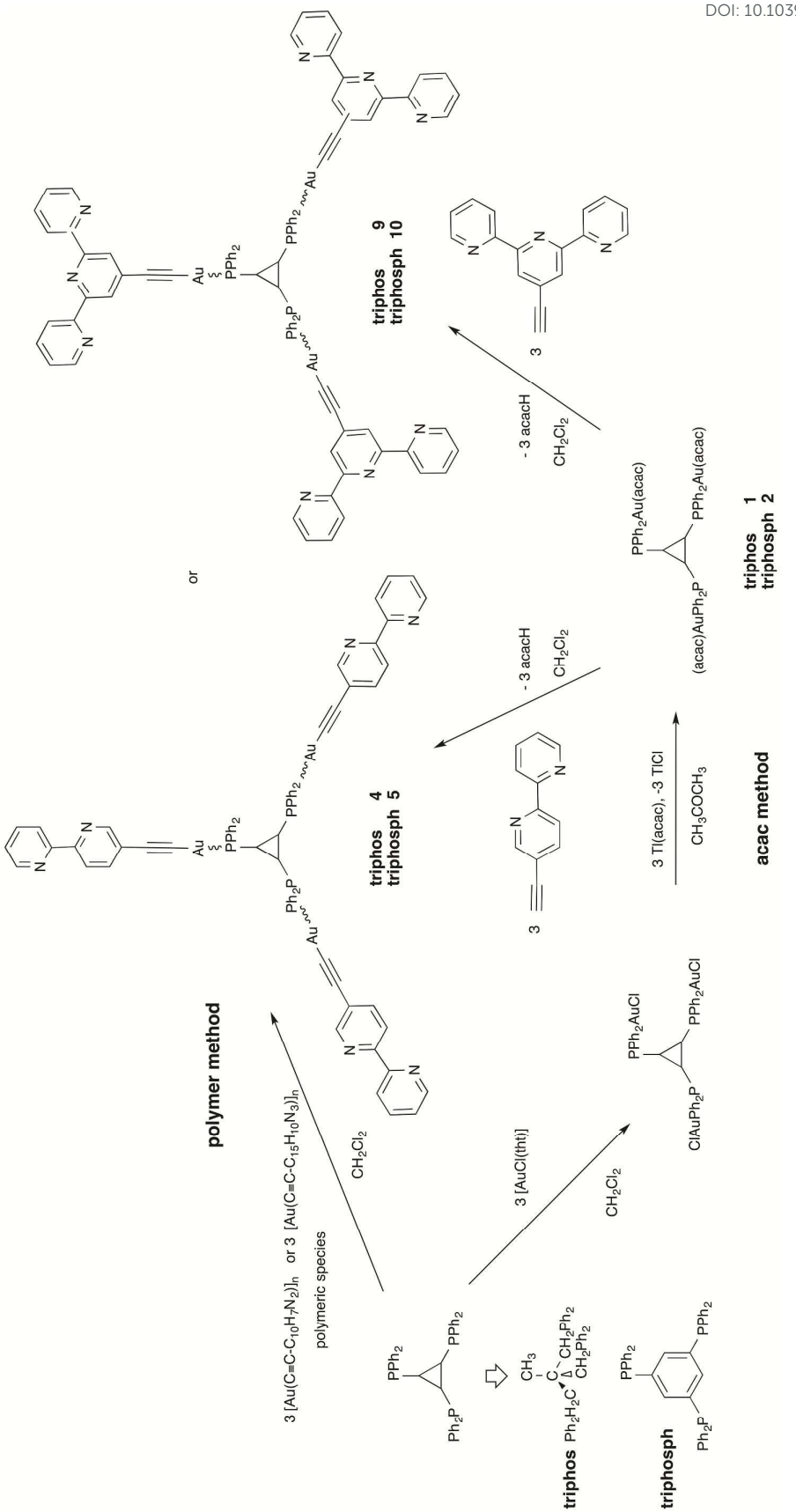

Scheme 2. Synthesis of tritopic gold(I) metallaligands

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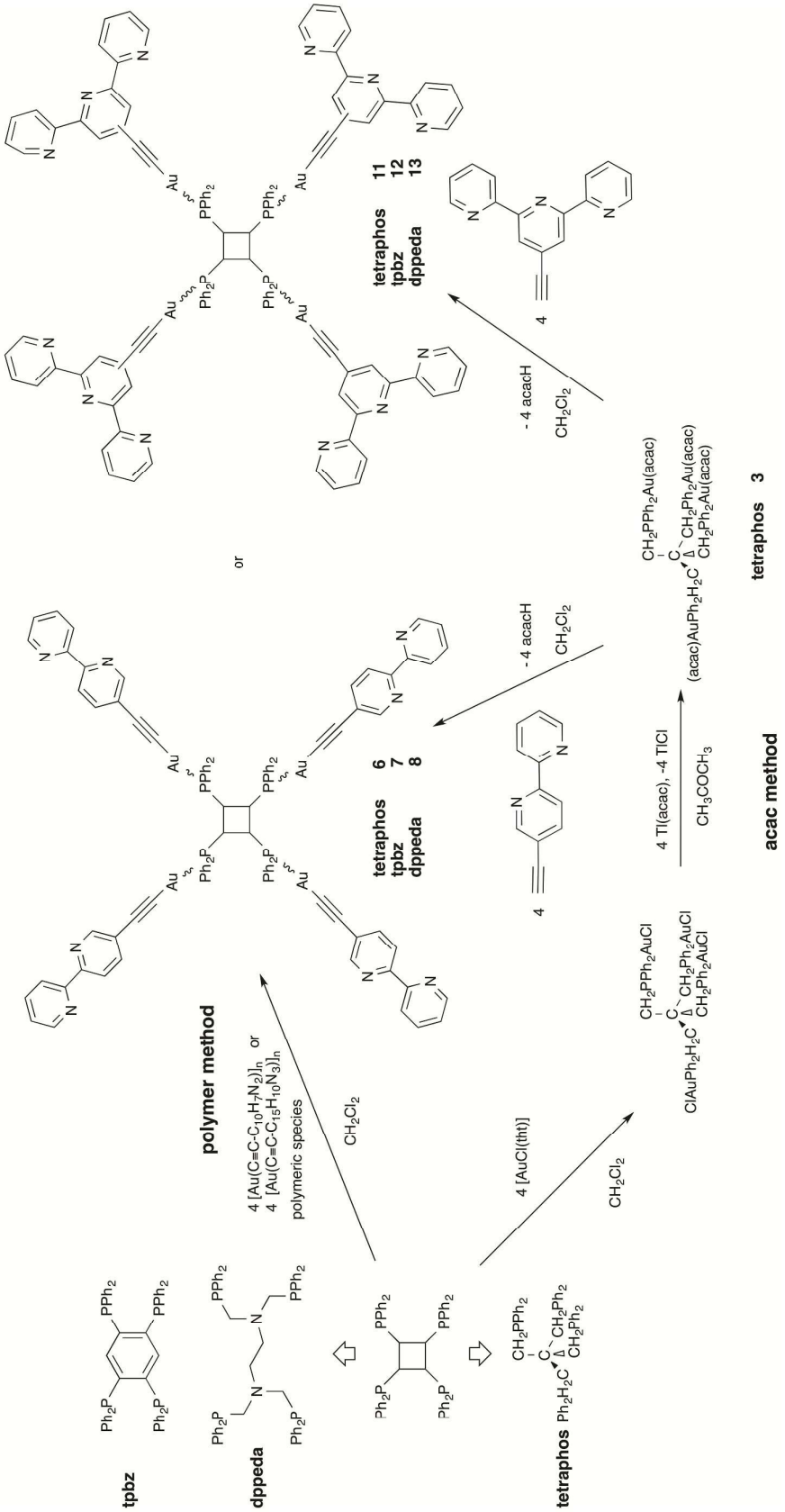

Scheme 3. Synthesis of tetratopic gold(I) metallaligands

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Polymer method. Compounds $[Au_3(C{\equiv}C\text{-}C_{10}H_7N_2)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos (**4**), triphosph (**5**)) and $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tetraphosphane})]$ (tetraphosphane = tetraphos (**6**), tpbz (**7**), dppeda (**8**) were obtained in moderate to good yields by reacting $[Au(C{\equiv}C\text{-}C_{10}H_7N_2)]_n$ with the adequate tri- or tetraphosphane in 3:1 and 4:1 molar ratio, respectively. Analogously, $[Au_3(C{\equiv}C\text{-}C_{15}H_{10}N_3)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos (**9**), triphosph (**10**)) and $[Au_4(C{\equiv}C\text{-}C_{15}H_{10}N_3)_4(\mu_4\text{-tetraphosphane})]$ (tetraphos (**11**), tpbz (**12**), dppeda (**13**)) were obtained by reacting $[Au(C{\equiv}C\text{-}C_{15}H_{10}N_3)]_n$ and the appropriate polyphosphane.

"Acac method". The acac derivatives $[Au_3(acac)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos (**1**), triphosph (**2**)) $[Au_4(acac)_4(\mu_4\text{-tetraphos})]$ (**3**), were obtained by reacting a 10% excess of the required quantity of Tl(acac) with the appropriate chloro(polyphosphane)gold(I) compound in acetone solution in the dark. The reaction progress was monitored by ^{31}P NMR spectroscopy and complete consumption of the starting gold(I) compound was observed after 48h for **1**, one week for **2** and 72h for **3**. At this point, the ^{31}P NMR spectra showed one singlet downfield shifted *ca*. 20 ppm with respect to the corresponding chloro precursors, accordingly with the complete substitution of the chloro by the acetylacetonate ligands. In the case of compounds $[Au_3(acac)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos (**1**), triphosph (**2**)), the ^1H NMR spectra display a doublet at *ca.* 2.5 ppm with $^3J(P\text{-}H) \approx 11Hz$ assigned to the CH of acac ligand. This fact together with the presence in the IR spectra of two strong broad vibrations below 1600 cm^{-1} is consistent with a κC^2 coordination mode for this ligand, typically found in gold(I) derivatives.[66-68] After their isolation in solid state and their characterization by elemental analyses, IR and NMR spectroscopies, compounds **1**-**3** were reacted with the terminal alkynes 5-ethynyl-2,2'-bipyridine and 4'-ethynyl-2,2':6',2''-terpyridine in the suitable molar ratio and the expected gold(I) derivatives

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$[Au_3(C{\equiv}C\text{-}R)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos (**4** and **9**), triphosph (**5** and **10**)) and $[Au_4(C{\equiv}C\text{-}R)_4(\mu_4\text{-tetraphos})]$ (**6** and **11**) were obtained in moderate yield after long reaction times (from 4h for **4** to 3 days for **11**). As a general trend, longer reaction times and lower yields are observed by increasing the number of phosphorus centres (tri to tetraphosphanes) and the bulkiness of the polypyridyl ligand (bipyridyl to terpyridyl). Tpbz compound could not be synthesized by this method due to the impossibility of preparation of the corresponding tetrachloro species. In the case of dppeda, the reaction between Tl(acac) and the tetrachoro species did not allow the obtention of the desired acac derivative. A complex set of signals in the ^{31}P NMR spectra of the reaction solution was obtained instead of the expected singlet.

Obviously, in this case, the "acac method" did not bring improvement to the more general method based on the use of polymeric alkynyl gold(I) species although allowed us to prepare a series of polynuclear acetylacetonato gold(I) derivatives that can have a widespread use as reactive species in organometallic synthesis.

Characterization of alkynylgold(I) complexes

Complexes **4-13** were characterized by elemental analyses, IR and (^1H, ^{31}P, ^{13}C) NMR spectroscopies and ESI(+) mass spectrometry. Due to the chemical equivalence of the P atoms within each compound, $^{31}P\{^1H\}$ NMR spectra show one sharp singlet, which is shifted *ca.* 50 ppm downfield from that corresponding to the free polyphosphanes and slightly shifted upfield compared to that of the parent acac compounds.

^1H NMR and $^{13}C\{^1H\}$ NMR spectra are indicative of the high symmetry of the molecules according with single bipyridyl or terpyridyl environment. A complete assignment of proton and carbon NMR signals of both phosphanes and polypyridyl alkynyl ligands can be found in the Experimental Section. This assignment was fully

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supported by COSY, gHSQC and gHMBC 2D experiments (for NMR spectra see Supporting information). Regarding the $^{13}C\{^{1}H\}$ NMR spectra, two doublets corresponding to the carbon atoms of the acetylene unit bonded to Au are observed at *ca* 140 (C_α) and 102 (C_β) with coupling constants around 140 and 25 Hz, respectively. In the particular case of tpbz derivatives (compounds **7** and **12**) the resonances of the acetylenic carbons appear as a multiplets or apparent triplets due to second order effects that can be attributed to a large ^{31}P-^{31}P coupling transmitted through the aromatic ring and/or the existence of intramolecular Au···Au interactions in solution. As it will be seen later on, this aurophilic interaction has been observed in solid state for the bipy derivative (**7**). In addition to satisfactory NMR analysis the structure of the compounds in solution was supported by mass spectrometry. Generally, the MS ESI(+) spectra of the obtained compounds display an intense peak that corresponds to that of the double protonated $[M+2H^+]^{2+}$ species together with the $[M\text{-}C{\equiv}C\text{-}R]^+$ signal that arises from the loss of either bipyridyl or terpyridyl fragments from the corresponding parent compound. Moreover, in certain cases, additional peaks resulting from polyprotonation are found. For instance, compound $[Au_4(C{\equiv}C\text{-}C_{15}H_{10}N_3)_4(\mu_4\text{-tpbz})]$ (**12**) shows signals due to mono- $[M+H^+]^+$, di- $[M+2H^+]^{2+}$ tri- $[M+3H^+]^{3+}$ and tetraprotonated $[M+4H^+]^{4+}$ species.

Crystallographic Studies

The crystal structures of $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tetraphos})]$ (**6**) and $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tpbz})]$ (**7**) were determined by single-crystal X-ray diffraction. The molecular structure of compound **6** along with the selected bond distances and bond angles are shown in Figure 1. The unit cell of the compound contains two different molecules where some differences can be found. Although both molecules display a

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conformation that favours the establishment of aurophilic interactions between pairs of branches, these are significantly stronger for the molecule on the right (Au(1A)-Au(2A) 2.9445(12) and Au(3A)-Au(4A) 3.0356(10) Å) than for the molecule on the left of the figure 1 (Au(1)-Au(2) 3.259(3) and Au(3)-Au(4) 3.0310(11) Å). This conformation is similar to that found for the closely related compound $[Au_4(C_6F_4C_5H_4N)_4(\mu_4\text{-tetraphos})]$ where rather long (3.343(1) Å) intramolecular Au···Au interactions were found between adjacent units.[69] On the other hand, this disposition contrasts with that described for the chloride derivative $[Au_4Cl_4(\mu_4\text{-tetraphos})]$, where a pair of gold centres lie far apart while the other two show a gold-gold contact of 3.34 Å.[70] Interestingly, only three compounds bearing gold atoms in the four legs of tetraphos have been structurally characterized. An inspection of the structure packing reveals the formation of a supramolecular arrangement (figures S43 and S44 in Supporting Information) as a result of the establishment of intermolecular π-π interactions between the bipyridine units attached to Au(2)-Au(2), Au(3)-Au(3A) or Au(4)-Au(4A) pair of arms. The shortest π-π contacts (intercentroid distance = 3.56 Å) are established between the bipyridyl rings of the Au(2) arms of neighbour molecules. As a result of the presence of these intermolecular interactions, the Au(2)-C≡C-$C_{10}H_7N_2$ moiety displays a particularly small value of the C≡C-$C_{10}H_7N_2$ angle (C(1C)-C(1B)-C(16) 165(6)°) if it is compared with those found for the rest of analogous angles (*ca.*175°). Interestingly, a search on CSD revealed that among the 157 hits containing C≡C-$C_{10}H_7N_2$ fragments only five display values lower than 166° for the mentioned angle,[52, 71-74] in such a way that the formation of helicates,[52] cages[71] or stacking interactions[74] are favoured.

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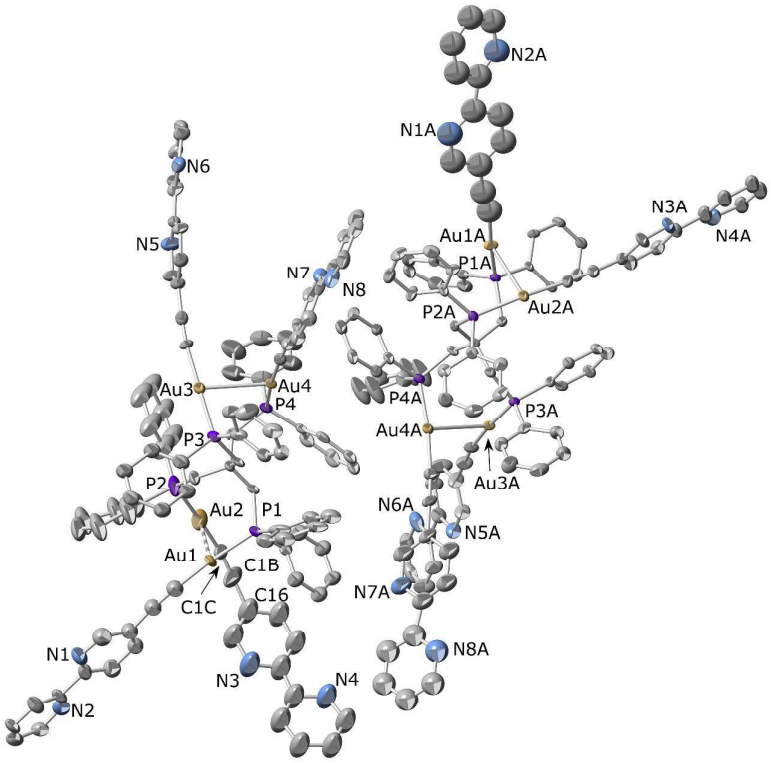

Figure 1. Molecular structure of compound $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tetraphos})]$ (**6**) showing the two different class of molecules found in the crystal. Thermal ellipsoids are draw at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (º): Au(1)-Au(2) 3.259(3), Au(3)-Au(4) 3.0310(11), Au(1A)-Au(2A) 2.9445(12), Au(3A)-Au(4A) 3.0356(10), Au(1)-P(1) 2.260(5), Au(1)-C(1) 1.93(3), Au(2)-P(2) 2.220(8), Au(2)-C(1C) 1.910(17), Au(3)-P(3) 2.290(6), Au(3)-C(25) 2.00(2), Au(4)-P(4) 2.273(4), Au(4)-C(37) 2.045(18), Au(1A)-P(1A) 2.287(4), Au(1A)-C(1A) 2.07(6), Au(2A)-P(2A) 2.287(4), Au(2A)-C(13A) 2.006(19), Au(3A)-P(3A) 2.269(4), Au(3A)-C(25A) 2.01(2), Au(4A)-P(4A) 2.275(4), Au(4A)-C(37A) 2.006(19); P(1)-Au(1)-C(1) 172.9(10), P(2)-Au(2)-C(1C) 175.3(10), P(3)-Au(3)-C(25) 177.0(8), P(4)-Au(4)-C(37) 173.0(5), P(1A)-Au(1A)-C(1A) 171.9(17), P(2A)-Au(2A)-C(13A) 171.7(6), P(3A)-Au(3A)-C(25A) 173.6(7), P(4A)-Au(4A)-C(37A) 173.6(6), Au(1)-C(1)-C(2) 170(3), Au(2)-C(1C)-C(1B) 162(4), Au(3)-C(25)-C(26) 173(2),

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Au(4)-C(37)-C(38) 172.2(19), Au(1A)-C(1A)-C(2A) 167(7), Au(2A)-C(13A)-C(14A) 175(2), Au(3A)-C(25A)-C(26A) 171(2), Au(4A)-C(37A)-C(38A) 173(2), C(1)-Au(1)-Au(2) 94.5(10), C(25)-Au(3)-Au(4) 100.5(6), C(1A)-Au(1A)-Au(2A) 99.5(17), C(25A)-Au(3A)-Au(4A) 95.9(6), P(2)-Au(2)-Au(1) 83.3(3), P(4)-Au(4)-Au(3) 89.39(13), P(2A)-Au(2A)-Au(1A) 83.60(12), P(4A)-Au(4A)-Au(3A) 85.59(11), C(1C)-C(1B)-C(16) 165(6).

The molecular structure of compound $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tpbz})]$ (**7**) (Figure 2) compares well with that of the closely related $[Au_4(C{\equiv}C\text{-}C_6H_5)_4(\mu_4\text{-tpbz})]$ described by Yam and col.[55] Analogously to the latter, the arrangement of every two adjacent Au-C≡C-$C_{10}H_7N_2$ moieties displays a crossed geometry, although their relative disposition with respect to the central benzene core is not the same. In fact, an angle of 0° is formed by the symmetry related Au(1)-Au(2) and Au(1*)-Au(2*) axes in the phenyl derivative while an almost perpendicular disposition (71.4°) is found between Au(1)-Au(1A) and Au(2)-Au(2A) in compound **7**. Besides, the distances between adjacent Au units in compound **7** (Au(1)-Au(1A) 3.077(2) and Au(2)-Au(2A) 3.118(2) Å) are shorter than in the phenyl derivative that displays a unique contact of 3.1541(4) Å. A comparison between the structures of compounds **6** and **7** reveals a cisoid disposition of the N atoms within each bipyridyl unit (torsion angle between pyridine rings: 11.6° and 28.8° for py_{N1}-py_{N2} and py_{N3}-py_{N4}, respectively) that contrasts with the transoid conformation determined for compound **6** (torsion angle between pyridine rings: 3.47°-20.79°).

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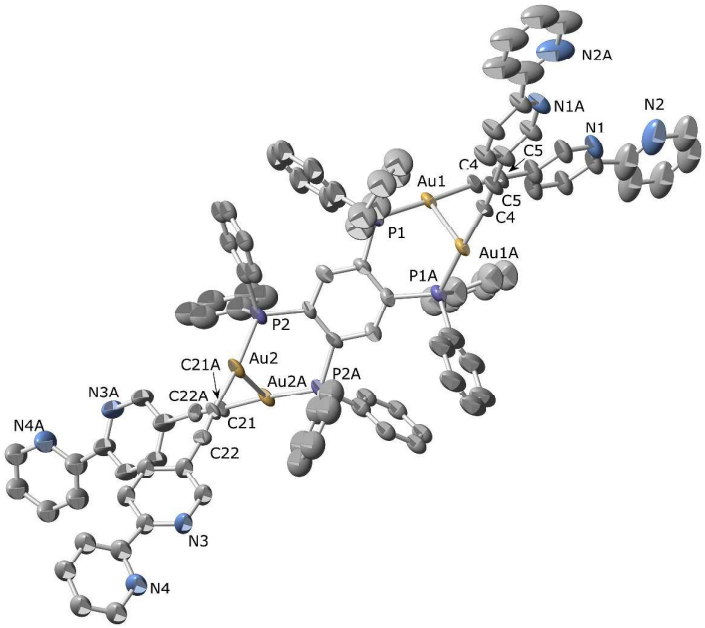

Figure 2. Molecular structure of compound $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tpbz})]$ (**7**). Thermal ellipsoids are draw at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (º): Au(1)-Au(1A) 3.077(2), Au(2)-Au(2A) 3.118(2), Au(1)-P(1) 2.290(6), Au(1)-C(4) 2.07(2), Au(2)-P(2) 2.294(6), Au(2)-C(21) 2.03(2), C(4)-C(5) 1.13(3), C(21)-C(22) 1.19(3); P(1)-Au(1)-C(4) 176.9(6), Au(1)-C(4)-C(5) 174(2), P(2)-Au(2)-C(21) 174.3(7), Au(2)-C(21)-C(22) 175(2), C(4)-Au(1)-Au(1A) 102.9(6), P(1)-Au(1)-Au(1A) 80.2(2), C(21)-Au(2)-Au(2A) 107.1(7), P(2)-Au(2)-Au(2A) 78.0(2).

Photophysical characterization

Absorption and emission spectra of all the complexes were recorded in 10^{-6} M dichloromethane solution at room temperature and the obtained data are summarized in Table 1.

All complexes display a vibronically resolved absorption profile centered at *ca*. 320 nm for bipy (**4**-**8**) and at *ca*. 290 nm for terpy (**9**-**13**) derivatives (Figures S45 and S46 in

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Supporting Information) that is attributed to the stretching vibrations of the bipyridyl and terpyridyl moieties in the excited state.

Table 1. Absorption and emission data in 10^{-6} M dichloromethane solution and solid-state emission at room temperature for compounds **4-13**.

Compound	λ_{abs} nm (10^{-3} ε, $M^{-1}cm^{-1}$)	λ_{em}, nm
4	318 (97.7), 330 (84.3)	392, 500 w, 536 sh (CH_2Cl_2)
		401, 505, 546, 606 (solid)
5	316 (145.0), 332 (138.6)	383, 497 w, 539 sh (CH_2Cl_2)
		429, 474, 511, 557 (solid)
6	319 (198.1), 333 (198.4)	385, 502 w, 530 w (CH_2Cl_2)
		400, 506, 542, 585 (solid)
7	320 (277.5), 334 (242.3)	374, 396, 501, 539 (CH_2Cl_2)
		423, 503[d], 604 sh, 599 (solid)
8	318 (229.2), 331 (226.5)	375, 403, 498 w, 537 sh (CH_2Cl_2)
		423, 502, 547, 581 sh (solid)
9	277 (172.1), 288 (157.0), 311 sh	340 sh, 354, 439 w, 476 w (CH_2Cl_2)
	(44.5), 332 sh (90.9)	407, 556w (solid)
10	276 (200.7), 290 (195.6), 317 sh	338 sh, 353, 433 w, 473 w (CH_2Cl_2)
	(37.6), 331 sh (27.1)	407, 516, 568 (solid)
11	277 (263.4), 294 sh (224.5), 319 sh	339 sh, 353, 439 w, 476 sh (CH_2Cl_2)
	(71.1), 333 sh (38.6)	407, 507, 563 (solid)
12	266 (371.3), 277 (395.0), 297 sh	366, 480 sh (CH_2Cl_2)
	(265.7), 321 sh (118.0), 334 sh (69.9)	407, 500, 582 (solid)
13	266 (295.2), 276 (316.0), 291 sh	356, 475 (CH_2Cl_2)
	(247.1), 319 sh (74.2), 332 sh (51.4)	407, 523, 560 (solid)

Taking into account the observed vibrational spacings and previous reports dealing with Au(I) compounds containing the same aromatic chromophores,[41, 42, 50, 52] we assign these bands to intraligand transitions of [π→π*-(C≡C-$C_{10}H_7N_2$)] or [π→π*-(C≡C-$C_{15}H_{10}N_3$)] character. A lower intensity broad band or tail above 350 nm is also

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observed in all complexes and can be assigned to a σ*(Au···Au)–π* transitions according to theoretical calculations.[75] The latter transitions have been found in related complexes recently reported by us.[76-78] The vibronic structured bands are broad and not completely defined even at low concentrations, which are assigned to excitonic splitting where Au···Au and π□π intramolecular stacking interactions are present between the arms of the dissolved complexes, as observed in previous studies carried out in our group.[39] The extinction coefficients at the maximum of the absorption band increase with the number of chromophores present in the molecules. These are higher than those reported by analogous diphosphane derivatives,[29, 41, 50] showing slight deviations of the monotonic increase due to differences in the intramolecular stacking interactions, where higher broadening leads to lower extinction coefficient at the maximum of the band.

All complexes are emissive at room temperature in solution and in solid state. Emission spectra in dichloromethane solutions were recorded upon excitation of the samples at 330 nm (**4**-**8**) and 290 nm (**9**-**13**) (Figure 3) and a dual emission was observed in all cases with maxima at *ca*. 400 nm and 530 nm for bipyridyl derivatives and at *ca.* 350 nm and 475 nm for terpyridyl complexes. The fact that complexes which contain the same alkynyl moiety present similar emission profiles, and comparing them with previous studies reported in the literature,[40, 41] let us attribute the recorded emissions to metal perturbed, alkynyl ligand based, ^{1}IL [π→π*] (higher energy emission) and ^{3}IL [π→π*] (lower energy emission) states. In all cases the presence of the Au heavy atom is expected to favour intersystem crossing and phosphorescence emission, which can be enhanced by the proximity of several Au atoms. The higher intensity of the phosphorescence band for the tetranuclear complex [Au_4(C≡C-$C_{10}H_7N_2$)$_4$(μ_4-tpbz)] (**7**) may result from a higher proximity between the arms through favouring Au···Au interactions, which in the case of the analogous compound [Au_4(C≡C-$C_{15}H_{10}N_3$)$_4$(μ_4-

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tpbz)] (**12**) could be hampered by the voluminous terpyridine ligand. As showed above, the X-ray molecular structure of compound **7** shows that all the gold centres of the compound are involved in rather short intramolecular aurophilic interactions. The emissions observed in solid state at 298K (λ_{exc}= 370 nm for **4-8** and 350 nm for **9-13**) are comparable to that obtained in deoxygenated dicloromethane solutions.

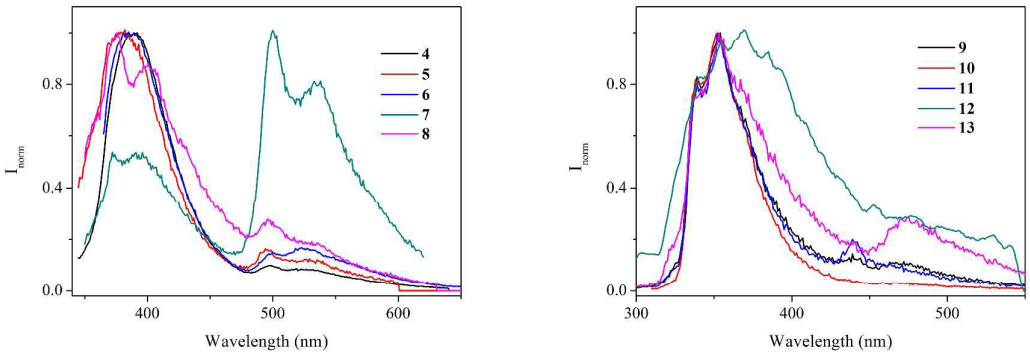

Figure 3. Normalized emission spectra of 10^{-6} M deoxygenated dichloromethane solutions of **4-8** (left) and **9-13** (right). λ_{exc} (**4-8**) = 330nm; λ_{exc} (**9-13**) = 290 nm.

Titration studies

As indicated in the introduction, one of the main aims of this work was to obtain bipyridyl and terpyridyl functionalized polygold compounds able to coordinate to cationic metallic species. To exploit the potential of the titled compounds in this regard, we envisaged the evaluation of the cation-binding ability of the obtained complexes by solution titrations.

As a starting point, we report here studies of the interaction of the bipyridine-containing compounds **4-7** with cations such Cu^{+} and Zn^{2+}. Changes in the absorption and emission bands of the polynuclear alkynyl gold(I) compounds have been monitored in order to evaluate the cation-metallaligand interaction.

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The addition of increasing amounts of $[Cu(CH_3CN)_4]BF_4$ to a 10^{-6} M dichloromethane solution of the complexes **4**-**7** displays, in all cases, a bathochromic shift of the maximum of the $\pi \rightarrow \pi^*$ absorption band of the bipyridyl moiety from *ca*. 330 nm (free complex) to *ca.* 350 nm (adduct). This behaviour is typical of the coordination of cations to the N,N-bidentate site of the bipyridine moiety and has been normally attributed to the transoid to cisoid isomerization of the heteroaromatic core.[79-81] (Figure 4 for compound **5** and figures S47-S49 for compounds **4**, **6** and **7** in Supporting Information).

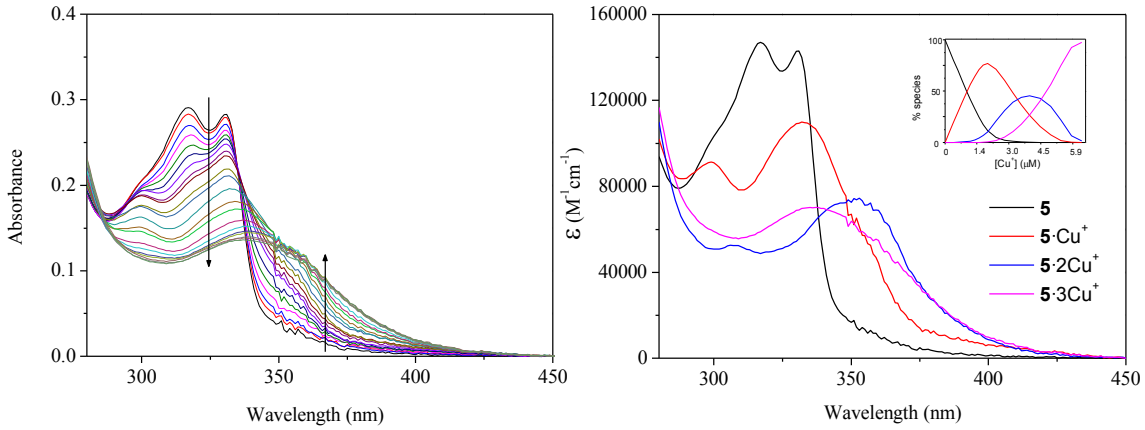

Figure 4. Absorption spectra of a 10^{-6} M dichloromethane solution of **5** upon addition of different amounts of $[Cu(CH_3CN)_4]BF_4$ (left). Spectra of individual species obtained from Spectit factorial analyses (right). Inset shows calculated speciation of the species formed upon titration.

The titrations showed the absence of well-defined isosbestic points, pointing to the presence of at least two new absorbing species formed during the addition of Cu^+ cation. The fitting procedure of the obtained data performed with a nonlinear least-squares algorithm implemented in the Specfit software[82] allowed the calculation of the stability constants (β_{1n}) for the studied equilibria (Table 2). In the case of metallaligands

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with three arms the coordination of Cu^+ to the different bipyridine units gave rise to the coexistence of either $[\mathbf{4}\cdot 2Cu^+]^{2+}$ and $[\mathbf{4}\cdot 3Cu^+]^{3+}$ or $[\mathbf{5}\cdot 1Cu^+]^+$, $[\mathbf{5}\cdot 2Cu^+]^{2+}$ and $[\mathbf{5}\cdot 3Cu^+]^{3+}$ (Figure 4). In the case of tetraphos and tpbz derivatives **6** and **7**, the fitting analysis was consistent with the formation of species with a pair number of coordinated Cu^+ i. e. $[\mathbf{6/7}\cdot 2Cu^+]^{2+}$ and $[\mathbf{6/7}\cdot 4Cu^+]^{4+}$ indicating that, in this case, symmetric coordination is favoured over other stoichiometric possibilities.

Table 2. Calculated stability constants of studied complexes.

Ligand/cation	$\log(\beta_{11})$	$\log(\beta_{12})$	$\log(\beta_{13})$	$\log(\beta_{14})$
4/Cu$^+$		15±1	20±1	
5/Cu$^+$	10±1	19±1	28±1	
6/Cu$^+$		20±1		35±1
7/Cu$^+$		15±1		28±1
4/Zn^{2+}			15±1	

Emission titrations gave very interesting profiles. As it can be seen in Figure 5 for compound **5** and in Figures S47-S49 in Supporting Information for the rest of compounds, the addition of copper(I) salt to a dichloromethane solutions of compounds **4**-**7** induced a decrease on both fluorescence and phosphorescence bands of the hosts.

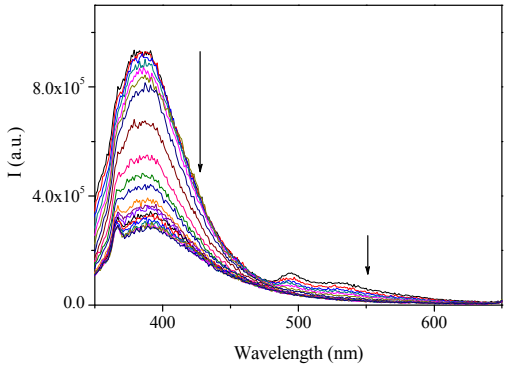

Figure 5. Emission spectra of a 10^{-6} M dichloromethane solution of **5** upon addition of different amounts of $[Cu(CH_3CN)_4]BF_4$.

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Similar behaviour has been reported for Cu^{+} titrations on organic fluorophores that contain appended 5-ethynyl-2,2'-bipyridyl fragments.[83] In contrast, the emission spectra recorded for the 1:1 complex (after adding 1 equivalent of $[Cu(CH_3CN)_4]BF_4$ in deoxygenated samples display an increase of both fluorescence and phosphorescence emission bands (Figure S50 in Supporting Information), which could be related with the presence of an equilibrium between singlet and triplet states as observed in systems that present activated delayed fluorescence.

Additionally, the possibility of interaction with other cations able to coordinate to bipyridyl units, such as Zn^{2+} was envisaged. Preliminary experiments carried out with **4** as a representative compound of these series showed changes in absorption and emission spectra that present noteworthy differences from those obtained with Cu^{+}. (Figure S51 in Supporting Information). On the one hand, a progressive decrease of the host absorption bands with a concomitant development of a longer wavelength transition was observed. The observation of a well-defined isosbestic point at 338 nm is indicative of a neat interconversion between the uncomplexed and complexed states, which contrasts with the equilibrium among various species found in the case of Cu^{+} addition. Fitting of the titration data[82] gave a single stability constant value (Table 2) that corresponds to the formation of $[\mathbf{4}\cdot 3Zn^{2+}]^{6+}$ as unique species. On the other hand, the emission titration results in a red-shifted and clearly enhancement (15-fold) of the fluorescence band of compound **4**, which is in agreement with a binding-induced conformational restriction of the bipyridine moiety by Zn^{2+}chelation.[84]

Conclusions

An improved method for obtaining polyphosphanyl benzene phosphanes has been developed.

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Trinuclear and tetranuclear phosphane alkynyl gold(I) systems with appended bipyridyl or terpyridyl moieties has been obtained using two different methods. While the reaction between the gold(I) polymeric species $[Au(C\equiv C\text{-}R)]_n$ and the adequate polyphosphane (polymer method) afforded the desired compounds in good yield in all the cases, the "acac method" implied long reactions times and only allowed the synthesis of a limited number of complexes due to the impossibility of isolating the adequate polyacetylacetonate precursor. In spite of this, the new isolated poly "acac" species $[Au_3(acac)_3(\mu_3\text{-triphosphane})]$ (triphosphane = triphos, triphosph) and $[Au_4(acac)_4(\mu_4\text{-tetraphos})]$ are reactive species that can be widely used as a precursors in organometallic synthesis.

All the prepared compounds are luminescent at room temperature in solution and in solid state and exhibit dual emissions that have been assigned to gold perturbed, alkynyl ligand based, ^{1}IL $[\pi\rightarrow\pi^*]$ and ^{3}IL $[\pi\rightarrow\pi^*]$ states.

Dissimilar behaviour has been found on studying the absorption and emission properties of the synthesized bipyridyl metallaligands upon complexation with closed-shell cations like Cu^+ and Zn^{2+}. Absorption titrations showed a clean process for Zn^{2+} while complex equilibria that involve the simultaneous formation of various absorbing species are detected for Cu^+. In emission titrations, a quenching or an enhancement of the fluorescence in the resulting supramolecular aggregates are observed on adding Cu^+ or Zn^{2+}, respectively.

Finally, we have demonstrated that the species reported here have a great potential as chelating or bridging polytopic metallaligands with interesting photophysical properties. For this reason, further studies of the reactivity of the complexes reported here against a wide range of metallic cations as well as of the properties exhibited by the resulting species are currently in progress.

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Experimental Section

General Methods.

All manipulations were performed under prepurified nitrogen atmosphere using Schlenck-tube techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use, or alternatively from a Solvent Purification System (Innovative Technologies).

Literature methods were used to prepare [AuCl(tht)],[85] Tl(acac),[86] [Au(C≡C-$C_{10}H_7N_2$)]$_n$,[41] 5-trimethylsilylethynyl-2,2'-bipyridine,[87] 4'-ethynyl-2,2':6',2"-terpyridine, [87, 88] tetrakis(diphenylphosphanylmethyl)methane (tetraphos),[70] *N, N, N', N'*-tetra(diphenylphosphanylmethyl)-1,2-ethylenediamine (dppeda),[89, 90] [$(AuCl)_3(\mu_3$-triphos)],[91] [$(AuCl)_3(\mu_3$-triphosph)],[92] [$(AuCl)_4(\mu_4$-tetraphos)],[70] and [$(AuCl)_4(\mu_4$-dppeda)].[93] All other reagents were obtained from commercial suppliers and used as received.

Infrared spectra were recorded on a FT-IR 520 Nicolet Spectrophotometer. ^{1}H NMR (δ(TMS) = 0.0 ppm), ^{31}P{^{1}H} NMR (δ(85% H_3PO_4) = 0.0 ppm), ^{13}C{^{1}H} NMR (δ(TMS) = 0.0 ppm), spectra were obtained at 250, 300, 400 or 500 MHz with Varian and Bruker spectrometers at 25 ºC unless otherwise stated. Elemental analyses of C, H, and N were carried out at the Centres Científics i Tecnològics (Universitat de Barcelona). ESI-MS mass spectra were recorded on a LC/MSD TOF Argilent Technologies 61969A spectrometer in H_2O:CH_3CN (1:1) solutions. Absorption spectra were recorded on a Varian Cary 100 Bio spectrophotometer. Emission and excitation spectra were recorded on a Horiba-Jobin-Yvon SPEX Nanolog spectrofluorimeter. Solutions were prepared with spectroscopic grade solvents. Titrations were carried out by addition of aliquots of 10^{-4} M solutions of the cations prepared in dichloromethane to

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the host solution (10^{-6} M in dichloromethane). Absorption and emission spectra were measured after each addition.

X-Ray Structure Determination

Crystal data for complexes **6** and **7** are presented in the Supporting Information (Table S1).

Data for [Au_4(C≡C-$C_{10}H_7N_2$)$_4$(μ_4-tetraphos)] (**6**) was collected at 120.0 K on a dual source Rigaku Oxford SuperNova diffractometer equipped with an Atlas detector using mirror-monochromated Cu-Kα radiation (λ = 1.54184 Å). The data collection and reduction were done using the program *CrysAlisPro*[94] and the intensities were corrected for absorption using the Gaussian face-index absorption correction method.[94] The structure was solved with direct methods (SHELXS) [95, 96] and refined by full-matrix least squares on F^2 using the OLEX2,[97] which utilizes the SHELXL module.[95, 96] No attempt was made to locate the hydrogens for disordered organic molecules in the unit cell. Constraints (EADP) and restraints (ISOR) commands are used where appropriate to suppress the alerts for large displacement parameter in checkcif. For a few aromatic rings and C-C bond distances, constraints (AFIX) and restraints (DFIX) commands were to suppress Hirshfeld differences for non-hydrogen atoms in A and B-alerts. Two of the Au-atoms are severely disordered, and attempts to resolve high electron residual density create additional A and B-alerts. Finally, continuous four Fourier cycles of refinement were performed till the convergence is achieved. The final refinement convergence was achieved at R_1 = 0.1094 and wR_2 = 0.2561 for intensities I>2(I) with largest peak/hole in the final difference map as 8.516/-3.240 e/Å^3.

The intensity data sets for [Au_4(C≡C-$C_{10}H_7N_2$)$_4$(μ_4-tpbz)] (**7**) were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream

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700 unit. The structure was solved, by using the WINGX package,[98] by direct methods (SHELXS-2013)[95, 96, 99] and refined by least-squares against F^2 (SHELXL-2014).[95, 96, 99] All the hydrogen atoms were positioned geometrically and refined by using a riding model. Crystals of compound **7** diffracted very weakly, and only data collections up to $\theta = 23°$ could be performed. Crystals of compound **7** crystallized with a huge number of solvent molecules, but it was not possible to get sensible chemical models for them. The Squeeze procedure of the PLATON[100] package was employed to remove the contribution of that electronic density to the structure factors, obtaining a solvent accessible volume equivalent to 21% of the unit cell volume. EADP constrains were applied to bipyridine and phenyl ring atoms to suppress the alerts for large displacement parameter in checkcif. The final refinement convergence was achieved at $R_1 = 0.092$ and $wR_2 = 0.223$ for intensities I>2(I) with largest peak/hole in the final difference map as 3.139/-1.577 e/Å^3.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and Characterization

Preparation of 5-ethynyl-2,2'-bipyridine

The compound was prepared by a modified procedure of the deprotection of the trimethylsilylethynyl group described by Ziessel in ref. 87.

To a solution of 500 mg of 5-trimethylsilylethynyl-2,2'-bipyridine (obtained by a copper-catalyzed Sonogashira coupling)[87] in 50 ml of MeOH, KF (140 mg, 2.41 mmol) was added and the mixture was stirred overnight at room temperature. The resulting suspension was evaporated to dryness under vacuum and the residue was chromatographed on silica and eluted with CH_2Cl_2/MeOH (100:2) to yield a darkish

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solid that contains copper as impurity. The solid was dissolved in 100 mL of chloroform acidified with a few drops of $HCl_{(aq)}$ and the mixture stirred for 3 hours at RT. After this time the red suspension was filtered through celite and extracted (3x100 mL) with 15.5% $NH_{3(aq)}$ saturated with EDTA. The organic layer was separated, washed with brine and dried over $MgSO_4$. The resulting solution was evaporated to dryness and the crude product purified by vacuum sublimation at 70°C to yield a white crystalline solid, which gave analytical data identical to those previously reported.[87] Yield: (303 mg, 85%).

Preparation of 1,3,5-tris(diphenylphospanyl)benzene (triphosph) and 1,2,4,5-tetrakis(diphenylphosphanyl)benzene (tpbz)

The syntheses of 1,3,5-tris(diphenylphospanyl)benzene and 1,2,4,5-tetrakis(diphenylphosphanyl)benzene were based on that described for 1,2(diphenylphosphanyl)benzene.[62] From 0.75 mL of the starting fluorinated compounds (7.2 mmol of 1,3,5-trifluorobenzene and 6.7 mmol of 1,2,4,5-tretrafluorobenzene), 2.19 g (48%) and 3.06 g (56%) of the above indicated tri- and tetraphosphanes were obtained, respectively. Analytical data was identical to those previously reported.[101]

Preparation of $[Au(C\equiv C\text{-}C_{15}H_{10}N_3)]_n$

The synthesis of $[Au(C\equiv C\text{-}C_{15}H_{10}N_3)]_n$ was based on that described by $[Au(C\equiv C\text{-}C_{10}H_7N_2)]_n$.[41] [AuCl(tht)] (125 mg, 0.39 mmol) and recently distilled NEt_3 (0.16 mL, 1.17 mmol) were added to a solution of 4'-ethynyl-2,2':6',2"-terpyridine (100 mg, 0.39 mmol) in 10 ml of CH_2Cl_2. The mixture was protected from light and stirred for 2 h. The obtained yellowish suspension was concentrated to dryness under vacuum giving a yellow solid that was washed subsequently with MeOH and Et_2O and dried under

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vacuum. Yield (124 mg, 70%). Anal. Found: C, 45.70; H, 2.33; N, 9.35; Calc. for $C_{17}H_{10}AuN_3$: C, 45.05; H, 2.22; N, 9.27 %. IR ν_{max}/cm^{-1} 2119 (C≡C).

Preparation of [$Au_3(acac)_3(\mu_3$-triphos)] (1)

To an acetone solution of [$(AuCl)_3(\mu_3$-triphos)] (200 mg, 0.16 mmol), solid Tl(acac) (160 mg, 0.53 mmol) was added. The resulting mixture was protected from light and stirred for 48 h. The obtained suspension was concentrated to dryness and the residue was extracted with dichloromethane (3 x 5 mL). The combined extracts were concentrated under vaccum (5 mL) and n-hexane was added to precipitate a white solid. Yield (172 mg, 71%). IR ν_{max}/cm^{-1} 1648, 1622 (acac); 1504, 1436, 1096 (triphos). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) 7.80-7.35 (30H, br s, PPh_2), 3.09 (6H, d, $^2J(H\text{-}P)$ 10.8, CH_2-P), 2.33 (3H, d, $^3J(H\text{-}P)$ 11.4, CO-CH-CO), 1.94 (18H, s, CH_3-CO), 1.01 (3H, s, CH_3-C). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 24.9 (s, PPh_2).

Preparation of [$Au_3(acac)_3(\mu_3$-triphosph)] (2)

To an acetone solution of [$(AuCl)_3(\mu_3$-triphos)] (226 mg, 0.17 mmol), solid Tl(acac) (170 mg, 0.56 mmol) was added. The obtained mixture was protected from light and stirred for 1 week. The resulting suspension was filtered and the solid was extracted with acetone (3 x 5 mL). The combined extracts together with the filtrate were concentrated to dryness. The remaining solid was dissolved in the minimum amount of dichloromethane and n-hexane was added to precipitate a beige solid. Yield (130 mg, 50%). Anal. Found: C, 44.99; H, 3.52; Calc. for $C_{57}H_{54}Au_3O_6P_3$: C, 45.07; H, 3.58%. IR ν_{max}/cm^{-1} 1647, 1631 (acac); 1504, 1439, 1096 (triphosph). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) 7.58-7.34 (33H, m, PPh_2 + P-C_6H_3-P), 2.61 (3H, d, $^3J(H\text{-}P)$ 11.1, CO-CH-CO), 2.12 (18H, s, CH_3-CO). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 42.6 (s, PPh_2).

Preparation of [$Au_4(acac)_4(\mu_4$-tetraphos)] (3)

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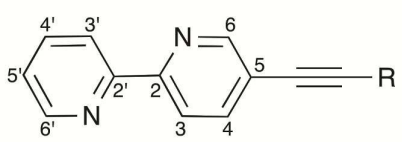
Compound **3** was synthesized following an analogous procedure to that described for compound **2**. From (300 mg, 0.17 mmol) of [$(AuCl)_4(\mu_3$-tetraphos)] and (230 mg, 0.76 mmol) Tl(acac) and a reaction time of 72 h compound **3** was obtained as a white solid. Yield (187 mg, 55%). Anal. Found: C, 43.41; H, 3.80; Calc. for $C_{73}H_{76}Au_4O_8P_4$: C, 43.99; H, 3.84%. IR ν_{max}/cm^{-1} 1652, 1622 (acac); 1504, 1435, 1096 (tetraphos). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) 7.70-6.80 (br m, PPh_2 + $CHCl_3$), 3.11 (12H, br s, CO-CH-CO + C-CH_2-P), 2.03 (24H, br s, CH_3-CO).^{31}P{^{1}H}-NMR (121.4 MHz, $CDCl_3$, 298 K) 22.8 (s, PPh_2).



Numbering Scheme

Preparation of [$Au_3(C\equiv C\text{-}C_{10}H_7N_2)_3(\mu_3$-triphos)] (4)

Polymer method: To a suspension of [$Au(C\equiv C\text{-}C_{10}H_7N_2)]_n$ (50 mg, 0.13 mmol) in CH_2Cl_2 (15 mL), the stoichiometric amount of solid triphos (28 mg, 0.04 mmol) was added and the mixture was stirred for 2 h. The resulting pale yellow solution was concentrated (5 mL) and n-hexane was added to precipitate a white solid, which was filtered off washed with n-hexane (3x5mL) and dried *in vacuo*. Yield (53 mg, 75%).

Acac method: To a solution of [$Au_3(acac)_3(\mu_3$-triphos)] (**1**) (75 mg, 0.05 mmol) in CH_2Cl_2 (15 mL), the stoichiometric amount of 5-ethynyl-2,2'-bipyridine **(**27 mg, 0.15 mmol**)** was added. The solution was stirred for 4h and concentrated to 5mL *in vacuo*. Subsequent addition of n-hexane caused the precipitation of a white microcrystalline solid, which was filtered off washed with n-hexane (3x5 mL) and dried *in vacuo*. Yield (44 mg, 50%).

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Anal. Found: C, 52.89; H, 3.42; N, 4.81; Calc. for $C_{77}H_{60}Au_3N_6P_3$: C, 52.75; H, 3.45; N, 4.79%. IR ν_{max}/cm^{-1} 2116 (C≡C); 1429, 1097 (triphos). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) 8.72 (3H, m, 6-H), 8.67 (3H, ddd, *J(H-H)* 4.8, 1.8, 0.8, 6'-H), 8.38 (3H, dt, *J(H-H)* 8.0, 1.0, 3'-H), 8.31 (dd, *J(H-H)* 8.2, 0.7, 3-H), 7.96-7.89 (12H, m, PPh_2), 7.82 (3H, dd, *J(H-H)* 8.4, 2.4, 4-H), 7.81 (3H, td, *J(H-H)* = 7.5, 1.8, 4'-H), 7.46-7.43 (18H, br m, PPh_2), 7.29 (3H, ddd, *J(H-H)* 7.5, 4.8, 1.2, 5'-H), 3.46 (6H, d, ^{2}*J(H-P)* 10.9, CH_2), 0.89 (3H, s, CH_3). ^{31}P{^{1}H}-NMR (121.4 MHz, $CDCl_3$, 298 K) 25.4 (s, PPh_2). ^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 298 K) 156.0, 153.6 (C2+C2'), 152.5 (C6), 149.4 (s, C6'), 139.9 (s, C4), 138.4 (d, ^{2}*J(C-P)* 140, P-Au-*C*≡C), 137.0 (C4'), 134.1 (d, ^{2}*J(C-P)* 14, C_{ortho}Ph), 132.1 (C_{para}Ph), 131.0 (d, ^{1}*J(C-P)* 56, C_{ipso}Ph), 129.6 (d, ^{3}*J(C-P)* 12, C_{meta}Ph), 123.7 (C5'), 122.3 (C5), 121.3 (C3'), 120.3 (C3), 101.4 (d, ^{3}*J(C-P)* 26, P-Au-C≡*C*), 42.8 (d, ^{1}*J(C-P)* 31, CH_2), 39.0 (C_q-triphos), 30.7 (CH_3). MS ESI(+) *m/z* 1573.2 (100%, $[M-C_{12}H_7N_2]^+$, calc. 1573.2), 697.1 (6%, $[M-2(C_{12}H_7N_2)]^{2+}$, calc. 697.1) 877.2 (85%, $[M+2H^+]^{2+}$, calc. 877.2), 585.1 (8%, $[M+3H^+]^{3+}$, calc. 585.1).

Preparation of $[Au_3(C{\equiv}C\text{-}C_{10}H_7N_2)_3(\mu_3\text{-triphosph})]$ (5)

Compound **5** was successfully synthesized following analogous procedures to those described for compound **4**.

Polymer method. From (50 mg, 0.13 mmol) of $[Au(C{\equiv}C\text{-}C_{10}H_7N_2)]_n$ and (28 mg, 0.04 mmol) of triphosph. Yield (50 mg, 71%).

Acac method. From (76 mg, 0.05 mmol) of $[Au_3(acac)_3(\mu_3\text{-triphosph})]$ (**2**) and (27 mg, 0.15 mmol) of 5-ethynyl-2,2'-bipyridine and a reaction time of 6 h. Yield (45 mg, 51%). Anal. Found: C, 53.23; H, 3.03; N, 4.80; Calc. for $C_{78}H_{54}Au_3N_6P_3$: C, 53.26; H, 3.09; N, 4.78%. IR ν_{max}/cm^{-1} 2110 (C≡C); 1434, 1097 (triphos). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) 8.79 (3H, dd, *J(H-H)* 2.1, 0.9, 6-H), 8.67 (3H, ddd, *J(H-H)* 4.9, 1.8, 0.9, 6'-H), 8.36 (3H, dt, *J(H-H)* 8.0, 1.1, 3'-H), 8.32 (3H, dd, *J(H-H)* 8.3, 0.9, 3-H), 7.88 (3H, dd,

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J(H-H) 8.2, 1.8, 4-H), 7.67 (3H, td, *J(H-H)* = 7.7, 1.8, 4'-H), 7.60-7.43 (33H, br m, PPh_2+$C_6H_3P_3$), 7.28 (3H, ddd, *J(H-H)* 7.8, 4.8, 1.2, 5'-H). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 42.9 (s, PPh_2). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 298 K) 156.0, 153.7 (C2 + C2'), 152.6 (C6), 149.3 (C6'), 140.3 (t, $^2J(C\text{-}P)$ 14, CH-$C_6H_3P_3$), 140.0 (C4), 137.4 (d, $^2J(C\text{-}P)$ 145, P-Au-*C*≡C), 137.0 (C4'), 134.5 (d, $^2J(C\text{-}P)$ 14, $C_{ortho}Ph$), 132.7 ($C_{para}Ph$), 129.9 (d, $^3J(C\text{-}P)$ 11, $C_{meta}Ph$), 127.7 (d, $^1J(C\text{-}P)$ 56, $C_{ipso}Ph$), 123.7 (C5'), 122.0 (C5), 121.3 (C3'), 120.4 (C3), 101.0 (d, $^3J(C\text{-}P)$ 25, P-Au-C≡*C*). MS ESI(+) *m/z* 1759.3 (15%, $[M+H^+]^+$, calc. 1759.3); 1579.2 (50%, $[M\text{-}C_{12}H_7N_2]^+$, calc. 1573.2), 880.1 (100%, $[M+2H^+]^{2+}$, calc.: 880.1).

Preparation of $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tetraphos})]$ (6)

Compound **6** was successfully synthesized following analogous procedures to those described for compound **4**.

Polymer method. From (50 mg, 0.13 mmol) of $[Au(C{\equiv}C\text{-}C_{10}H_7N_2)]_n$ and (25 mg, 0.03 mmol) of tetraphos. Yield (55 mg, 77%).

Acac method. From (100 mg, 0.05 mmol) of $[Au_4(acac)_4(\mu_4\text{-tetraphos})]$ (**3**) and (36 mg, 0.20 mmol) of 5-ethynyl-2,2'-bipyridine and a reaction time of 4 days. Yield (59 mg, 51%).

Anal. Found: C, 52.46; H, 3.34; N, 4.80; Calc. for $C_{101}H_{76}Au_4N_8P_4$: C, 52.43; H, 3.31; N, 4.84%. IR ν_{max}/cm^{-1} 2116 (C≡C); 1436, 1094 (tetraphos). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) 8.68 (4H, d, *J(H-H)* 4.7, 4H, 6'-H), 8.65 (4H, d, *J(H-H)* 1.6, 6-H), 8.38 (4H, d, *J(H-H)* 8.0, 3'-H), 8.31 (4H, d, *J(H-H)* 8.2, 3-H), 7.82 (4H, td, *J(H-H)* 7.8, 1.9, 4'-H), 7.73 (4H, dd, *J(H-H)* 8.2, 2.1, 4-H), 7.45 (40H, s br, 40H, PPh_2), 7.29 (4H, ddd, *J*(H-H) 7.6, 4.8, 1.2, 5'-H), 3.46 (8H, d, $^2J(H\text{-}P)$ 10.7, CH_2). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 23.2 (s, PPh_2). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 298 K) 156.0, 153.5 (C2+C2'), 152.4 (C6), 149.4 (C6'), 140.0 (C4), 138.6 (d, $^2J(C\text{-}P)$ 141, P-Au-*C*≡C),

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137.0 (C4'), 133.9, 132.1, 129.8 (br, Ph), 123.7 (C5'), 122.3 (C5), 121.3 (C3'), 120.3 (C3), 101.0 (d, $^{3}J(C\text{-}P)$ 27, P-Au-C≡*C*), 42.7 (C_q-tetraphos), 40.7 (dq, *J*(C-P) 30, 7, CH_2-tetraphos). MS ESI(+) *m/z* 2336.3 (9%, $[M+Na^+]^+$, calc. 2336.3); 2134.3 (15%, $[M\text{-}C_{12}H_7N_2]^+$, calc. 2134.3); 1157.7 (40%, $[M+2H^+]^{2+}$, calc.: 1157.7); 772.1 (20%, $[M+3H^+]^{3+}$, calc.: 772.1).

Preparation of $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-tpbz})]$ (7)

Compound **7** was obtained as a yellow microcrystalline powder by the **polymer method** exclusively. From (50 mg, 0.13 mmol) of $[Au(C{\equiv}C\text{-}C_{10}H_7N_2)]_n$ and (25 mg, 0.03 mmol) of tpbz. Yield (43 mg, 60%).

Anal. Found: C, 52.83; H, 3.03; N, 4.85; Calc. for $C_{102}H_{70}Au_4N_8P_4$: C, 52.82; H, 3.04; N, 4.83%. IR ν_{max}/cm^{-1} 2107 (C≡C); 1436, 1101 (tpbz). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) 8.81 (4H, br s, 6-H), 8.65 (4H, d, *J(H-H)* 4.9, 6'-H), 8.35 (4H, d, *J(H-H)* 8.0, 3'-H), 8.26 (4H, d, *J(H-H)* 8.2, 3-H), 7.90 (4H, dd, *J(H-H)* 8.2, 2.1, 4-H), 7.77 (4H, td, *J(H-H)* 7.8, 1.8, 4'-H), 7.40 (10H, m, PPh_2+$C_6H_2P_4$), 7.28-7.19 (br m, PPh_2 + 5'-H + $CHCl_3$). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 35.7 (s, PPh_2). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 298 K) 156.1, 153.3 (C2+C2'), 152.6 (C6), 149.3 (C6'), 144.0 (br, CH-$C_6H_2P_4$), 140.1 (C4), 139.2 (m, P-Au-*C*≡C), 136.9 (C4'), 134.9 (dd, *J(C-P)* 154, 14, CP-$C_6H_2P_4$), 134.7, 132.4, 129.6 (Ph), 128.2 (m, C_{ipso}Ph), 123.5 (C5'), 122.7 (C5), 121.3 (C3'), 120.2 (C3), 102.9 (t, *J(C-P)* 13, P-Au-C≡*C*). MS ESI(+) *m/z* 2139.3 (5%, $[M\text{-}C_{12}H_7N_2]^+$, calc. 2139.3); 1160.7 (100%, $[M+2H^+]^{2+}$, calc.: 1160.7); 773.8 (6%, $[M+3H^+]^{3+}$, calc.: 773.8).

Preparation of $[Au_4(C{\equiv}C\text{-}C_{10}H_7N_2)_4(\mu_4\text{-dppeda})]$ (8)

Compound **8** was obtained as a white solid by the **polymer method** exclusively. From (50 mg, 0.13 mmol) of $[Au(C{\equiv}C\text{-}C_{10}H_7N_2)]_n$ and (28 mg, 0.03 mmol) of dppeda. Yield (40 mg, 52%).

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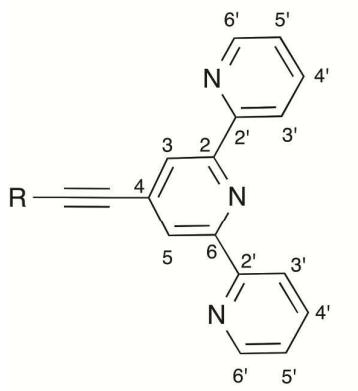
Anal. Found: C, 52.01; H, 3.43; N, 5.95; Calc. for $C_{102}H_{80}Au_4N_{10}P_4$: C, 51.96; H, 3.42; N, 5.94%. IR ν_{max}/cm^{-1} 2106 (C≡C); 1435, 1102 (dppeda). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) 8.69-8.67 (8H, br m, 6-H + 6'-H), 8.39 (4H, d, *J(H-H)* 8.0, 3'-H), 8.27 (4H, d, *J(H-H)* 8.3, 3-H), 7.81 (4H, td, *J(H-H)* 7.8, 1.8, 4'-H), 7.77-7.73 (16H, m, PPh_2), 7.68 (4H, dd, *J(H-H)* 8.2, 2.2, 4-H), 7.37-7.35 (24H, m, PPh_2) 7.29 (4H, ddd, 4H, *J(H-H)* 7.5, 4.8, 1.2, 5'-H), 4.07 (8H, s, CH_2P), 2.76 (4H, s, CH_2N). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 27.1 (s, PPh_2). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$, 298 K) 156.0, 153.5 (C2+C2'), 152.5 (C6), 149.4 (C6'), 139.9 (C4), 139.1 (d, $^2J(C\text{-}P)$ 13, $C_{ortho}Ph$), 137.0 (C4'), 134.1 (d, $^2J(C\text{-}P)$ 13, $C_{ortho}Ph$), 132.1 ($C_{para}Ph$), 123.7 (C5'), 122.3 (C5), 121.3 (C3'), 120.3 (C3), 56.6 (br, NCH_2P), 53.7 (CH_2N) (AuC≡C not observed). HRMS ESI(+) *m/z* 2178.357 (5%, $[M\text{-}C_{12}H_7N_2]^+$, calc. 2178.360); 1801.327 (15%, $[M\text{-}C_{12}H_7N_2\text{-}AuC_{12}H_7N_2]^{2+}$, calc.: 1801.329).



Numbering Scheme

Preparation of $[Au_3(C\equiv C\text{-}C_{15}H_{10}N_3)_3(\mu_3\text{-triphos})]$ (9)

Polymer method. From (60 mg, 0.13 mmol) of $[Au(C\equiv C\text{-}C_{15}H_{10}N_3)]_n$ and (25 mg, 0.04 mmol) of triphos. Yield (41 mg, 46%).

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Acac method. From (76 mg, 0.05 mmol) of $[Au_3(acac)_3(\mu_3\text{-triphos})]$ (**1**) and (39 mg, 0.15 mmol) of 4'-ethynyl-2,2':6',2"-terpyridine and a reaction time of 2 days. Yield (36 mg, 36%).

Anal. Found: C, 55.63; H, 3.53; N, 6.32; Calc. for $C_{92}H_{69}Au_3N_9P_3$: C, 55.68; H, 3.50; N, 6.35%. IR ν_{max}/cm^{-1} 2119 (C≡C); 1486, 1435, 1097 (triphos). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) 8.70 (6H, d, *J(H-H)* 4.8, 6'-H), 8.59 (6H, d, *J(H-H)* 8.1, 3'-H), 8.52 (6H, s, 3-H+5-H), 7.96-7.91 (12H, m, PPh_2), 7.84 (6H, td, *J(H-H)* 8.1, 1.8, 4'-H), 7.51-7,45 (18H, br m, PPh_2), 7.31 (6H, m, 5'-H), 3.46 (6H, d, ^{2}*J(H-P)* 10.9, CH_2), 0.92 (3H, s, CH_3). ^{31}P{^{1}H}-NMR (161.9 MHz, $CDCl_3$, 298 K) 25.3 (s, PPh_2). ^{13}C{^{1}H}-NMR (125.7 MHz, $CDCl_3$, 298 K) 156.3, 155.4 (C2+C2'+C6), 149.3 (C6'), 139.8 (d, ^{2}*J(C-P)* 139, P-Au-*C*≡C), 136.8 (C4'), 135.2 (C4), 134.0 (d, ^{2}*J(C-P)* 14, C_{ortho}Ph), 132.2 (C_{para}Ph), 130.9 (d, ^{1}*J(C-P)* 55, C_{ipso}Ph), 129.8 (d, ^{3}*J(C-P)* 11.2, C_{meta}Ph), 124.1 (C5'), 123.8 (C3+C5), 121.2 (C3'), 102.6 (d, ^{3}*J(C-P)* 24, P-Au-C≡*C*), 42.7 (d, ^{1}*J(C-P)* 27.9, CH_2), 38.9 (C_q-triphos), 31.0 (CH_3). HRMS ESI(+) *m/z* 1985.399 (45%, $[M+H^+]^+$, calc. 1985.399); 1727.300 (15%, $[M\text{-}C_{17}H_{10}N_3]^+$, calc. 1727.301); 993.203 (15%, $[M+2H^+]^{2+}$, calc.: 993.204).

Preparation of $[Au_3(C{\equiv}C\text{-}C_{15}H_{10}N_3)_3(\mu_3\text{-triphosph})]$ (10)

Polymer method. From (60 mg, 0.13 mmol) of $[Au(C{\equiv}C\text{-}C_{15}H_{10}N_3)]_n$ and (25 mg, 0.04 mmol) of triphosph. Yield (31 mg, 42%).

Acac method. From (76 mg, 0.05 mmol) of $[Au_3(acac)_3(\mu_3\text{-triphosph})]$ (**2**) and (39 mg, 0.15 mmol) of 4'-ethynyl-2,2':6',2"-terpyridine and a reaction time of 2 days. Yield (24 mg, 24%).

Anal. Found: C, 56.23; H, 3.23; N, 6.32; Calc. for $C_{93}H_{63}Au_3N_9P_3$: C, 56.12; H, 3.19; N, 6.33%. IR ν_{max}/cm^{-1} 2119 (C≡C); 1435, 1100 (triphos). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) 8.69 (6H, dq, *J(H-H)* 4.8, 0.9 Hz, 6H, 6'-H), 8.58 (6H, dt, *J(H-H)* 6.0, 0.9, 3'-H),

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8.55 (6H, s, 3-H + 5-H), 7.83 (6H, td, *J(H-H)* 7.5, 1.8, 4'-H), 7.70-7.44 (33H, br, PPh_2 + P-C_6H_3-P), 7.30 (6H, ddd, *J(H-H)* 7.5, 4.8, 1.8, 6H, 5'-H). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 42.9 (s, PPh_2). $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 298 K) 156.4, 155.5 (C2 +C2'+C6), 149.3 (C6'), 140.7 (br, P-Au-*C*≡C), 136.8 (C4'), 135.1 (C4), 134.5 (d, $^2J(C\text{-}P)$ 14, $C_{ortho}Ph$), 132.7 (s, $C_{para}Ph$), 130.0 (d, $^3J(C\text{-}P)$ 12, $C_{meta}Ph$), 127.8 (d, $^1J(C\text{-}P)$ 57, $C_{ipso}Ph$), 124.1 (C5'), 123.8 (C3 + C5), 121.2 (C3'), 102.3 (br, P-Au-C≡*C*). HRMS ESI(+) *m/z* = 1991.354 (<1%, $[M+H^+]^+$, calc. 1991.353); 996.191 (<1%, $[M+2H^+]^{2+}$, calc. 996.180); 258.103 (100%, $[C_{17}H_{11}N_3+H^+]^+$, calc. 258.103).

Preparation of $[Au_4(C{\equiv}C\text{-}C_{15}H_{10}N_3)_4(\mu_4\text{-tetraphos})]$ (11)

Polymer method. From (60 mg, 0.13 mmol) of $[Au(C{\equiv}C\text{-}C_{15}H_{10}N_3)]_n$ and (28 mg, 0.03 mmol) of tetraphos. Yield (40 mg, 44%).

Acac method. From (100 mg, 0.05 mmol) of $[Au_4(acac)_4(\mu_4\text{-tetraphos})]$ (**2**) and (51 mg, 0.2 mmol) of 4'-ethynyl-2,2':6',2"-terpyridine and a reaction time 3 days. Yield (40 mg, 30%).

Anal. Found: C, 55.23; H, 3.33; N, 6.42; Calc. for $C_{121}H_{88}Au_4N_{12}P_4$: C, 55.43; H, 3.38; N, 6.41%. IR ν_{max}/cm^{-1} 2117 (C≡C); 1440, 1100 (tetraphos). ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) 8.73 (8H, ddd, *J(H-H)* 4.7, 1.8, 0.9, 6'-H), 8.60 (8H, dt, *J(H-H)* 7.9, 1.1, 3'-H), 8.44 (8H, s, 3-H + 5-H), 8.30-7.00 (overlapped with terpy signals, very br, P*Ph*$_2$), 7.85 (overlapped with P*Ph*$_2$, ddd, *J(H-H)* 8.8, 7.5, 1.8, 4'-H), 7.33 (overlapped with P*Ph*$_2$, ddd, *J(H-H)* 7.5, 4.8, 1.2 , 5'-H), 3.53 (8H, br, CH_2). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 22.9 (s, PPh_2). $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 298 K) 156.4, 155.3 (C2 +C2'+C6), 149.3 (C6'), 140.1 (d, $^2J(C\text{-}P)$ 141, P-Au-*C*≡C), 136.8 (C4'), 135.4 (C4), 133.8, 132.4, 130.0 (br, Ph), 124.2 (C3 + C5), 123.8 (C5'), 121.2 (C3'), 102.2 (d, $^3J(C\text{-}P)$ 26, P-Au-C≡*C*), 42.8 ($C(CH_2)_4$), 40.7 (d, $^1J(C\text{-}P)$ 30, $C(CH_2)_4$). HRMS ESI(+) *m/z* = 2622.491 (<1%, $[M+H^+]^+$, calc. 2622.498); 2169.438 (4%, $[M\text{-}C_{17}H_{10}N_3Au+H^+]^+$, calc.

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2169.443); 1311.749 (8%, $[M+2H^+]^{2+}$, calc. 1311.752); 258.103 (100%, $[C_{17}H_{11}N_3+H^+]^+$, calc. 258.103).

Preparation of $[Au_4(C\equiv C\text{-}C_{15}H_{10}N_3)_4(\mu_4\text{-tpbz})]$ (12)

Compound **12** was obtained as an orange microcrystalline powder by the **polymer method** exclusively. From (60 mg, 0.13 mmol) of $[Au(C\equiv C\text{-}C_{15}H_{10}N_3)]_n$ and (28 mg, 0.03 mmol) of tpbz. Yield (50 mg, 62%).

Anal. Found: C, 55.83; H, 3.13; N, 4.37; Calc. for $C_{122}H_{82}Au_4N_{12}P_4$: C, 55.76; H, 3.15; N, 6.40%. IR ν_{max}/cm^{-1} 2113 ν(C≡C); 1505, 1435, 1097 (tpbz). ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) 8.54 (8H, d, *J(H-H)* 4.5, 6'-H), 8.49 (8H, s, 3-H + 5-H), 8.40 (8H, d, *J(H-H)* 8.1, 3'-H), 7.71 (8H, td, *J(H-H)* 7.8, 1.8, 4'-H), 7.43-7.22 (m, P*Ph*$_2$ + P-C$_6$*H*$_2$-P + residual proton of $CDCl_3$), 7.18 (8H, m, 5'-H). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 35.5 (s, PPh_2). $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 298 K) 156.5, 155.1 (C2 +C2'+C6), 149.1 (C6'), 144.1 (br, CH-$C_6H_2P_4$), 139.2 (m, P-Au-*C*≡C), 136.5 (C4'), 135.7 (C4), 134.7, 132.4, 129.6 (Ph), 128.4 (m, C_{ipso}Ph), 124.3 (C3 +C5), 123.4 (C5'), 121.1 (s, C3'), 104.0 (m, P-Au-C≡*C*). HRMS ESI(+) *m/z* 2628.445 (3%, $[M+H^+]^+$, calc. 2628.450); 2371.338 (4%, $[M\text{-}C_{17}H_{10}N_3]^+$, calc. 2371.355); 1314.728 (100% $[M+2H^+]^{2+}$, calc. 1314.729); 876.817 (30%, $[M+3H^+]^{3+}$, calc.: 876.822); 657.870 (20%, $[M+4H^+]^{4+}$, calc. 657.869).

Preparation of $[Au_4(C\equiv C\text{-}C_{15}H_{10}N_3)_4(\mu_4\text{-dppeda})]$ (13)

Compound **13** was obtained as a white solid by the **polymer method** exclusively. From (60 mg, 0.13 mmol) of $[Au(C\equiv C\text{-}C_{15}H_{10}N_3)]_n$ and (28 mg, 0.03 mmol) of dppeda. Yield (40 mg, 46%).

Anal. Found: C, 54.63; H, 3.42; N, 7.32; Calc. for $C_{122}H_{92}Au_4N_{14}P_4$: C, 54.97; H, 3.48; N, 7.36%. IR ν_{max}/cm^{-1} 2116 (C≡C); 1504, 1435, 1100 (dppeda). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) 8.70 (8H, d, *J(H-H)* 4.2, 6'-H), 8.59 (8H, d, *J(H-H)* = 8.0 Hz, 3'-H),

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8.47 (8H, s, 3-H+5-H), 7.85-7.74 (24H, m, 4'-H+PPh_2), 7.41-7.30 (32H, m, 5'-H+PPh_2), 4.12 (8H, br, CH_2P), 2.73 (4H, br, CH_2N). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 298 K) 27.2 (s, PPh_2). $^{13}C\{^1H\}$-NMR (125.7 MHz, $CDCl_3$, 298 K) 156.3, 155.4 (C2+C2'+C6), 149.3 (C6'), 140.0 (d, $^2J(C\text{-}P)$ 139, P-Au-*C*≡C), 136.8 (C4'), 135.3 (C4), 134.1 (d, $^2J(C\text{-}P)$ 13, $C_{ortho}Ph$), 132.1 ($C_{para}Ph$), 129.7 (d, $^3J(C\text{-}P)$ 11, $C_{meta}Ph$), 129.3 (s, $C_{ipso}Ph$), 124.0 (C5'), 123.8 (C3+C5), 121.2 (C3'), 102.9 (d, $^3J(C\text{-}P)$ 25, P-Au-C≡*C*), 56.8 (br, NCH_2P), 53.5 (br, *C*H_2N)**.** HRMS ESI(+) *m/z* 2409.437 (40%, $[M\text{-}C_{17}H_{10}N_3]^+$, calc. 2409.439); 1205.221 (100%, $[M\text{-}C_{17}H_{10}N_3\text{+}H^+]^{2+}$, calc.1205.224); 803.818 (90%, $[M\text{-}C_{17}H_{10}N_3\text{+}2H^+]^{3+}$, calc. 803.818); 603.115 (8%, $[M\text{-}C_{17}H_{10}N_3\text{+}3H^+]^{4+}$, calc. 603.116)

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Supporting Information

^1H, ^{31}P and ^{13}C NMR spectra of the compounds, UV-VIS and emission spectra, crystallographic data and stability constants. CCDC 1559283 and 1561541 for

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structures of **6** and **7**, respectively contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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The synthesis of photophysical active polytopic alkynyl gold(I) metallaligands and preliminary studies of their interaction with metal cations are presented.