PERSPECTIVE
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Keep it tight: a crucial role of bridging phosphine ligands in the design and optical properties of multinuclear coinage metal complexes
Keep it tight: a crucial role of bridging phosphine ligands in the design and optical properties of multinuclear coinage metal complexes

Aleksandra V. Paderina, Igor O. Koshevoy and Elena V. Grachova

Copper subgroup metal ions in the +1 oxidation state are classical candidates for aggregation via non-covalent metal–metal interactions, which are supported by a number of bridging ligands. The bridging phosphines, soft donors with a relatively labile coordination to coinage metals, serve as convenient and essential components of the ligand environment that allow for efficient self-assembly of discrete polynuclear aggregates. Simultaneously, accessible and rich modification of the organic spacer of such P-donors has been used to generate many fascinating structures with attractive photoluminescent behavior. In this work we consider the development of di- and polynuclear complexes of M(i) (M = Cu, Ag, Au) and their photophysical properties, focusing on the effect of phosphine bridging ligands, their flexibility and denticity.

1. Introduction

The chemistry of coinage metals (copper, silver and gold) has been the focus of intense research and shown remarkable developments particularly since the 1990s. The organization principles of the corresponding coordination compounds, namely, stable oxidation states, typical coordination numbers, coordination polyhedra, and the nature of preferable ligands seemed to be simple and obvious at the moment when the phenomenon of metallophilicity was discovered. Metallophilicity is a dispersion force, strengthened by relativistic and correlation effects, that leads to the attraction of metal ions or atoms with filled electron shells at distances less than the sum of van der Waals radii without the formation of a covalent bond. With respect to the d10 configuration, metallophilicity has become a well-recognized and extensively studied phenomenon of crucial importance, because this part of the supporting motif controls the architecture of the supramolecular aggregate. Furthermore, introducing heteroatoms generates essential self-assembly of discrete d10 coinage metal ions and nanoclusters, subnanoclusters, as well as classical cluster compounds, including cluster compounds of main group metals, carbonyl, chalcogenide and halide transition metal clusters, where the electron density of the metallic framework is delocalized over the metal skeleton. Metallophilic interactions determine the extremely rich luminescence properties of coinage metal supramolecular systems, which can be applied to produce, for example, molecular sensors, responsive materials, light-emitting devices, labels for bioimaging, molecular containers, and reactors.

Despite their relative weakness, metallophilic interactions allow the construction of discrete three-dimensional cluster architectures and control of their physicochemical properties. Near-edge X-ray absorption (NEXAFS) and X-ray photoelectron spectroscopy (XPS) studies of coinage metal species revealed that in the ground state these systems consisted of aggregated M(i) complexes without sufficient contribution from covalent bonding. This is a fundamental difference between the aggregates of d10 coinage metal ions and nanoclusters, subnanoclusters, as well as classical cluster compounds, including cluster compounds of main group metals, carbonyl, chalcogenide and halide transition metal clusters, where the electron density of the metallic framework is delocalized over the metal skeleton. Metallophilic interactions determine the extremely rich luminescence properties of coinage metal supramolecular systems, which can be applied to produce, for example, molecular sensors, responsive materials, light-emitting devices, labels for bioimaging, molecular containers, and reactors.

There is no doubt that the accurate design of the ligand environment is necessary for the effective construction of coinage metal supramolecular aggregates. A template ligand is a principal part of the system, as its stereochemical properties, coordination ability and flexibility determine the location of M(i) atoms relative to each other. For di- and multidentate ligands, the nature of the organic linker between donor sites is of crucial importance, because this part of the supporting motif controls the architecture of the supramolecular aggregate.
additional coordinating sites with different electronic properties. Thus, the template ligand plays the leading role in the assembly of supramolecular systems based on coinage metals and determines the diversity of this type of compound.

Historically, phosphines are presumably the most popular class of ligands employed for the synthesis of coinage metal derivatives, including those with luminescence behavior. The $\lambda^3\sigma^1$-organophosphorus atom (neutral L type ligand) is an ideal site for the coordination of an M(I) ion (M is a d$^{10}$ metal) bond has a donor around the d$^{10}$ ions vary from tetrahedral (Cu(I), Ag(I), coordination number four) to trigonal and finally linear (mainly Au (i), coordination number two) geometry. With polydentate ligands in hand, comprising several phosphorus atoms connected by an appropriate linker, one gets rich opportunities to control the metal–metal interactions and influence the size and topology of the resulting d$^{10}$ aggregates (Fig. 1), which vary from phosphine-bridged dinuclear compounds to coordination cyclic or cage molecules, and ultimately to cluster species.$^{37,39}$

The ligand environment of d$^{10}$ phosphate complexes is often completed with various anionic X ligands, such as (pseudo)halides, chalcogenides, thiocyanates, arylls and alkynes. For instance, in the case of Au(i), the combination of a phosphate and an X ligand produces a neutral heteroleptic complex [(R,P)AuX], which allows for efficient Au–X interactions due to the low coordination number. The linear configuration of the Au(i) coordination environment is virtually unaffected by the electronic properties of the substituents on phosphorus and the X-bound atoms, which makes this sort of complex (real or speculative) a convenient building block for the engineering of polymeric clusters and supramolecular systems (Fig. 1). According to theoretical and experimental data, soft X ligands (–C≡CR, I, –SR) promote stronger aurophilic interactions compared with hard X donors (–Cl, –OR etc.). In addition, the free electron pair(s) on the metal-connected atoms of X groups (e.g. on the sulfur of a thiolate, on the triple bond of the alkynyl) can be used for coordination to adjacent metal ions to enhance the metal–metal bonds. Not surprisingly, soft X ligands with a pronounced ability for efficient bridging bonding (–SR, –NR, –CR, –CCR) are typically found in cluster compounds featuring metallophilic contacts.

The bridging ability of the X and phosphate ligands, aided by metallophilic bonding, is known to produce coordination polymeric species. By preventing polymerization and preparing molecular compounds, the composition and molecular architecture of these compounds are primarily regulated by the stereochemical properties and flexibility of the organic spacer in oligodentate phosphate ligands, the spatial separation of phosphorus atoms relative to one another, along with other factors, e.g. the nature of the bridging X group, its bulkiness and the presence of additional functional groups, the nature of the d$^{10}$ M(i) ion, and the stoichiometry of reagents.

A number of comprehensive reviews have been devoted to the synthesis of luminescent polymeric coinage metal-containing complexes, their optical properties and relevant applications. Herein, we attempt to highlight the important role of a diverse family of bridging phosphate ligands on the assembly and photophysical behavior of d- and polymeric aggregates containing d$^{10}$ ions of copper subgroup metals.

### 2. Phosphines with spatially separated P-donors: rigid spacers

#### 2.1 Cyclic and cage compounds based on bi-, tri- and tetratdentate rigid phosphines

Bi- and tridentate phosphines with rigid spacers separating the phosphate atoms (P1$^{1-3}$, P2$^1$, P3-P10, Fig. 2) have proved to be convenient blocks for the design of cyclic and 3D cage complexes of d$^{10}$ coinage metal ions. This strategy is predominantly applicable to gold(i) due to its linear two-coordinate geometry that facilitates the formation of discrete molecules, even without the use of ancillary ligands.

The simplest coordination complexes without metallophilic interactions have the stoichiometry [(Au(diphosphine))$_n$]$^{2n-}$ and contain from 2 ($n = 2$, P1$^{1-3}$ and P2$^1$) to 4 ($n = 4$, P3$^2$) metal atoms, depending on the stereochemical features of the ligand (i.e. directionality of P–metal bonding). Thus, acetylene-based P3 produces cyclic tetratetrigold species 1, but P4 and P5 stabilize trimetallaggregates 2$^3$ and 3, while bending the spacer in P6 further decreases the nuclearity to bimetallic gold complex 4 (Fig. 3).

Changing the metal ion from gold to copper and silver typically increases the phosphine to metal ratio or requires the
binding of ancillary ligands/counterions to saturate a higher coordination number of Cu(I)/Ag(I) centers, which diversifies possible structures. In combination with diphosphines P2 and P6, Cu(I) halides generate helicate and mesocate structures \([\text{Cu}_2X_2(\text{diphosphine})_3]\) (5a and b, Fig. 4).\(^{54,55}\) The luminescence of iodide 5a demonstrates a broad structured band \((\lambda_{\text{em}} = 500 \text{ nm})\), assigned to \((\text{CuI}) \rightarrow \pi^*(\text{phosphine})\) charge transfer (M, XLCT), and reveals interesting vapo- and solvatochromism with high sensitivity to tetrahydrofuran, which causes a dramatic enhancement of a negligibly small quantum yield \((\Phi_{\text{em}})\) to \(\Phi_{\text{em}} = 0.07\) with a very long lifetime of \(\tau_{\text{obs}} = 0.12 \text{ ms}\).

The reactions of AgX salts \((X^- = \text{ClO}_4^-, \text{PF}_6^-, \text{BF}_4^-)\) with P4 lead to three different crystalline modifications,\(^{56}\) tetranuclear \([\text{Ag}_4(\text{P4})_4 \supset \text{[ClO}_4]_2\text{[ClO}_4]_2\) (6a), dinuclear \([\text{Ag}_2(\text{P4})_2(\text{NCMe})_4]\) (PF6)2 (6b), and trinuclear \([\text{Ag}_3(\text{P4})_3 \supset (\text{BF}_4)](\text{BF}_4)\text{[BF}_4]_2\) metalloccyclic species (6c), the last of these is similar to gold analogue 2. The luminescence of such silver and gold compounds generally arises from intraligand \(\pi\pi^*\) transitions due to a lack of metal to ligand charge transfer (MLCT). Thus, complexes 2 and 6a-c display emissions of comparable wavelengths \((475-488 \text{ nm})\) despite their different structures and the metals.\(^{53,56}\) However, ligand emission can be substantially perturbed by metal atoms, and by subtle intra- and intermolecular interactions, which could be of particular importance in the solid state. The latter can be seen for compounds 1 with OTf\(^-\), PF6\(^-\) and ClO4\(^-\) counterions, which reveal a substantial alteration of the emission energy in frozen glass at 77 K.\(^{52}\)

Star-shaped tridentate phosphines have been utilized for the preparation of 3D tetrahedral coordination clusters. In earlier works by James, coordination clusters featuring a bowl-type motif \([\text{Ag}_4(\text{P7})_3]^{4+}\) (7) were constructed with the triazine-based P7 ligand.\(^{57,58}\) Expansion of the spacer in triphosphines P8 and P9 opened the way to closed tetrahedral cages \([\text{M}_4(\text{P8/ P9})_4]X_4\) (8/9; M = Cu(I), Ag(I), Au(I); \(X^- = \Gamma^-, \text{OTf}^-\)), which retain their structures in solution (Fig. 3).\(^{54,59}\)

Tetraphosphine P10 contains a tetraphenylene chromophore with an aggregation-induced emission (AIE) property. Embedding this ligand into a silver(i)-connected tetragonal cage \([\text{Ag}_4(\text{P10})_2]^{12+}\) (10) drastically increased the intraligand...
fluorescence ($\Phi_{em} = 0.02$ for P10, 0.45 for 10 in CHCl₃ solution) with a distinct blueshift from 550 nm (P10) to 490 nm (10) that was likely to be caused by the improved rigidity of the cage architecture.⁶³

In addition to compounds with a monometallic coordinating center, cluster units with metallophilic bonding also can be employed for the construction of cage-like molecules.⁴⁰,⁴¹ Different bridging groups, such as E²⁻ (E = S, Se), NR²⁻, and CR³⁻ were reported to assist in the stabilization of cluster cores. A tetragold cluster fragment, [Au₄CR]⁺ (R = COPh), is obtained via the transformation of σ-bound alkyne C₂Ph into the C-hypercoordinate μ₄-methylidyne ligand ³⁻C-(CO)-Ph. In the presence of diphosphines P11 (n = 1–3) and P6, two of these square pyramidal [Au₄C] cluster blocks are linked together and serve as “caps” for the helical cage species [(Au₄CR)₂(diphosphine)]⁺²⁻ (11, Fig. 6).⁶¹ The NR²⁻ and S²⁻ bridges generate trinuclear building blocks [Au₃NR]⁺ and [Au₃S]⁺, which can also be assembled with phosphines P11 (n = 1–4) into a series of homologous aggregates [(Au₃μ₃- X)]₄(diphosphine)₄⁺²⁻ (X = NBu 12,⁴² S 13,⁶³ Fig. 6), where complex 13 (n = 2) is isostructural to its Se analogue.⁶⁴ With triphosphine P9, it was possible to prepare a tetrahedral cage [(Au₃μ₃-NBu)]₄(P9)₄⁺²⁻ (12ᵀ). According to ¹H NMR spectroscopic studies, tubular compounds 11–13 undergo fast interconversion between two helical isomers ($P$ and $M$) at room temperature via an intramolecular twisting motion. Contrarily, the chiral tetrahedron of 12ᵀ does not demonstrate such molecular dynamics due to a considerably more rigid structure that prevents racemization in solution.

Among these cage-type complexes 11–13, only sulfide derivatives 13 exhibit appreciable luminescence, which predomnantly has an intraligand (phosphine) origin.⁶³ Due to the heavy atom effect of the {Au₃S}⁺ cores, aggregates 13 show multiple emissions, comprising of fluorescence (high energy) and phosphorescence (low energy) bands, the ratio of which depends on the length of the oligophenylene spacer of P1 (Fig. 6), i.e. the distance between the heavy atom and the chromophore. Remarkably, an unusual triple emission was observed for 13 (n = 2) in the solid state under ambient conditions. The fluorescence and dual phosphorescence were assigned to ¹ππ, ³(LM/LLCT) and ³ππ excited states with short (ns) and prolonged (ms) lifetimes, respectively.

2.2 Linear bidentate phosphines stabilizing heterometallic clusters

Combining phosphines with alkyanyl X ligands substantially increases the complexity of aggregates due to the formation of homo- and heterometallic cluster assemblies. Homoleptic alkyanyl compounds of copper subgroup metals range from simple anionic species [M(C≡CR)]⁻ to neutral polymeric and catenane aggregates (MC≡CR)₉₋₆⁶⁻⁶⁸, the structure of which is controlled by the metal and R group of the alkyne. However, the preparation of such compounds often suffers from poor predictability, which hampers the tunability of their structures and properties.⁶⁹–⁷⁷

One approach to vary the cluster size in a rational manner utilizes diphosphines with linear phenylene (P10) or alkyne-phenylene (P2⁶) spacers. This stereochemistry together with the two-coordinate linear geometry of gold(i) ions affords cationic triangles [Au(diphosphine)]⁺, which accommodate the heterometallic alkylnyl cores by means of Au(i)–Au(i) interactions in the series [Au₃₋₃M₉₋₉(C₂Ph)₂ₓ₋₉C[Au₄(diphosphine)]₃]⁺ (14–24), M = Cu(i), Ag(i).⁷₈–⁸₀ The clusters are efficiently self-organized from simple starting components (Fig. 7) due to the labile nature of M–P and M–C₃Ph bonds. The formation of larger oligo- and
polymeric alkynyl species is essentially prevented by the phosphine ligands, the rigid backbones of which define the shape and size of the confined space inside the external metallacyclic “belt”. Increasing the distance between phosphorus atoms in families P1n and P2m allows the central heterometallic framework to be enlarged and changes the overall nuclearity from eight (14, 15, 17) to 25 metal atoms in 22–24 (Fig. 7 and Table 1). 78–80 In addition to the geometric parameters of the P1n and P2m ligands, the assembly of aggregates depends on subtle electronic features of the constituting ligands. Whereas the structural topology of clusters 14–24 is accessible for tertiary diphosphines with aryl and electron accepting pyrrolyl (pyr) substituents (Fig. 7), no similar species were obtained for the electron richer ligand with i-Pr groups, 1,4-(i-Pr2P)2C6H4. 81

Fig. 7 Generalized self-assembly approach to the family of clusters 14–24, [AuMnΣx+2(C2Ph)σ+2C(Au3(diphosphine))3]n+. M = Cu(i), Ag(i).

A slight difference in the distance between phosphorus atoms due to variation of the spacer in P1n (phenylene) and P2m (alkynyl-phenylene) appeared to be useful in adjusting the size of the outer [Au(diphosphine)]3+ ring to the nature of the constituting metal. Thus, changing the Cu(i) ions in 14 for Ag (i) metal results in an expansion of the [Au3M2(C2Ph)6] framework due to the larger radius of silver (1.72 Å for copper). This gives a more sophisticated and less stable structure 16* with an open shell, [Au3Ag(C2Ph)(P1)3]5+ (Fig. 8). 79 For longer diphosphine P25, a “normal” architecture, [Au3Ag(C2Ph)6C[Au3(P2)3]]5+ (17), was observed. 80 Ligands with a larger spatial separation (P1n and P2m) induce a growing mismatch between the internal [Au10Cu12(C2Ph)20]2+ and external [Au(diphosphine)]3+ parts, which accounts for the failure to form the [Au10Cu12(C2Ph)20C[Au3(P2)3]]5+ cluster, analogous to 22. This reason, along with unfavorable electrostatics resulting from the increase in the positive charge of the central heterometallic alkynyl component, likely prevented further growth of the cluster core following the same strategy.

Modification of the synthetic protocol by using complementary halide ligands produced gold–silver complex [Au3Ag12Hal6(C2Ph)18C[Au3(P1)3]]5+ (25), 82 which contained a stabilized structural motif due to the substitution of the [Au

Fig. 8 Schematic representation of “open-shell” [Au3Ag(C2Ph)[P1]3]5+, 16*.

<table>
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<tr>
<th>Complex</th>
<th>λem, nm</th>
<th>τobs, μs</th>
<th>Φem</th>
<th>kτ, s⁻¹</th>
<th>knr, s⁻¹</th>
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<td>[Au3Cu2(C2Ph)6C[Au3(P1)3]]5+</td>
<td>594</td>
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<td>0.96</td>
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<tr>
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<td>[Au3Cu2(C2Ph)6C[Au3(P1pyr)3]]5+</td>
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<td>7.8</td>
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<td>15</td>
<td>[Au3Cu2(C2Ph)6C[Au3(P2)3]]5+</td>
<td>625</td>
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<td>0.08</td>
<td>1.0 × 10⁵</td>
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<tr>
<td>16*</td>
<td>[Au3Ag(C2Ph)6C[Au3Ag2(C2Ph)][P1]3]5+</td>
<td>507</td>
<td>0.5</td>
<td>0.29</td>
<td>5.8 × 10⁴</td>
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<tr>
<td>17</td>
<td>[Au3Ag(C2Ph)6C[Au3(P2)3]]5+</td>
<td>526</td>
<td>0.2 &lt;0.01</td>
<td>—</td>
<td>—</td>
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<td>9.5</td>
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<td>6.3 × 10⁴</td>
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Perspective

$(C_2Ph)_3^–$ unit for the $Hal_3^{3–}$ array. This method appeared to be applicable to the longest diphosphine within the oligophenylene-based series, $P1^+$, which yielded the nanoscale cluster $[Au_{14}Ag_{10}Hal_4(C_2Ph)_3c(Cu(P1^+))_{25}$ [26, Fig. 9].

The photoluminescence parameters for 14–26, most of which are intensely phosphorescent in solution, are summarized in Table 1. Several conclusions can be drawn on the basis of these experimental and accompanying theoretical data with respect to the phosphine constituents. First, aryl diphosphines $P1^+$ with phenylene spacers virtually do not participate in the frontier orbitals of the corresponding clusters (14, 16*, 18, 20, 22, 23), but the external “belt” enhances the rigidity and spin–orbit coupling within the emissive heterometallic central core. For example, 14 shows a dramatic improvement of the quantum yield ($\Phi_{em} = 0.96$, $\tau_{obs} = 5.9 \mu s$) compared with anionic species $[Au_3Cu_2(C_6H_4Me-p)_6]^–$ ($\Phi_{em} = 0.13$, $\tau_{obs} = 11.5 \mu s$) due to a significant increase in the radiative rate constant $k_r$ and suppression of non-radiative relaxation ($k_{nr}$). Simultaneously, steric protection of the emissive fragments by electronically innocent $[Au_3(P1^+)]^{3+}$ cycles leads to unusually low quenching of phosphorescence by molecular oxygen in contrast to conventional phosphorescent coordination complexes. Second, the more electron-withdrawing phosphines ($P1pyr$ and $P2$*) visibly contribute to the lowest excited triplet state, resulting in a smaller optical gap, faster non-radiative/slower radiative decay, and ultimately lower quantum efficiency.80,81 Third, the larger nuclearity of the heterometallic core stabilized by the longer diphosphine ligand causes a systematic bathochromic shift of the absorption and emission, expectedly accompanied by a decrease in $k_r$ and drop in the quantum yield (see e.g. the series 14, 18, 22 and 16*, 20, 23 in Table 1). Furthermore, the large cluster core has a detrimental effect on the nonlinear optical properties, namely, two-photon absorption (TPA). For gold–silver complexes 25 and 26, the TPA cross-section reached moderate values of 45 and 57 GM, respectively, at 800 nm.82 For the smallest gold–copper cluster 14, this parameter was 192 GM, which was additionally improved up to 387 GM by introducing an electron-accepting substituent into the alkyne ligands.84

Because templating phosphines mostly have a relatively small influence on the lowest energy electronic transition, the optical properties in these systems can be conveniently tuned by means of alkyne ligands, as shown for 14 and its congeners.81 This allows the overall structural motif to be retained and new functional groups to be introduced on the periphery of the ligand environment. Examples of $X$ substituents in $–C_2\equiv C_6H_4X–p$ fragments are acid-responsive amino groups,85 amino acid residues,86 receptors for sensing ions,87 groups suitable for covalent conjugation with biological species,88,89 and redox active terminal units.90,91

The architecture of the $d^{10}$ aggregates is regulated by the constituting metal ions due to their different connectivity. Unlike $Au(i)$–$Cu(i)$ aggregates, stabilization of a bimetallic Ag(i)–Cu(i) phenylalkynyl system with the $P1^+$ ligand yields an octanuclear $[Ag_4Cu_2(C_2Ph)_6]^2–$ core decorated with two tripod-like metallophosphine motifs $[Ag(P1^+)]^{\dagger}$ (Fig. 10).92 The resulting complex, $[\{Ag(P1^+)\}_2Ag_2Cu_2(C_2Ph)_6]^2–$ (27), is poorly luminous in solution, but exhibits moderate blue phosphorescence in the solid state ($\lambda_{em} = 453 \text{ nm}$, $\Phi_{em} = 0.26$, $\tau_{obs} = 11.5 \mu s$); this is assigned, to a large extent, to $\pi \rightarrow \pi^* (C\equiv C)$ intraligand transitions.

Another variation of the metal core in the $P1^+$ environment was observed for purely gold(i) cluster $[Au_4(C_2Bu)_4(P1^+)Au_4(C_2Bu)_4]^2–$ (28, Fig. 11).93 Due to a loose assembly, which reversibly dissociates in solution, 28 is strongly emissive in the crystalline state only ($\lambda_{em} = 585 \text{ nm}$, $\Phi_{em} = 0.69$). Shortening the spacer of the diphosphine from phenylene ($P1^+$) to the $–C\equiv C–$ linker ($P3$) in $[Au_4(C_2Bu)_4(P3)]^{2–}$ transforms the octanuclear framework (29, Fig. 11) into a more compact and rigid structure. This results in a dramatic increase of the phosphorescence quantum yield in solution ($\lambda_{em} = 570 \text{ nm}$, $\Phi_{em} = 0.92$, $k_r = 1.9 \times 10^5 \text{ s}^{-1}$), which is subject to minor quenching upon aeration ($\Phi_{em} = 0.82$).

![Fig. 9](image9) Schematic representation of halide–centered clusters 25 and 26.

![Fig. 10](image10) Structural motif of 27.

![Fig. 11](image11) Structural motifs of Au(i) clusters 28 and 29.
3. Phosphines with rigid and related ‘non-linear’ spacers

3.1 Complexes formed from bidentate phosphines

There are a variety of bidentate P-donor ligands that have suitable spacers and bite angles to support bimetallic units with short metal–metal contacts (for complexes with flexible diporphines refer to section 4.1). In the case of the Au(I) ion, its strong preference for linear coordination often forces even typically chelating ligands to adopt a bridging mode and hold the \{Au\_2\} fragment. Selected phosphines P12–P19, shown in Fig. 12, have been used for the synthesis of a range of luminescent digold complexes, which can generally be classified as heteroleptic neutral \([\text{Au}_2(\mu_2-\text{diphosphine})X_3]\) (30–37, except those containing anionic ligand P12, which have different compositions) and homoleptic cationic \([\text{Au}_2(\mu_2-\text{diphosphine})]^{+}\) (38–40) species (Fig. 13).

In the solid state, these compounds demonstrate diverse photophysical behavior (Table 2), which reflects the concerted influence of aurophilic bonding, the backbone of the phosphine, ancillary ligands, and packing effects. Due to these factors, the unambiguous interpretation of the excited state dynamics of molecular materials composed of such luminophores becomes a challenging task and can hardly be done solely based on the structure and orbital analysis of an individual molecule. The phosphine ligand has a major impact on the physical properties of the bulk material, albeit for the lower energy phosphorescence observed within the given series ($\lambda_{em} > 600$ nm) this effect could have little electronic nature because of the proposed domination of the (halide + metal)-centered (X + M) and halide-to-metal-to-metal charge transfer (XMMCT) excited states. Nevertheless, even minor variations in the structure of the bridging phosphine can offer substantial tuning of the emission parameters. Thus, iodide complex 31a with ligand P13 (1,2-bis(diphenylphosphino)benzene) is moderately luminescent ($\lambda_{em} = 551$ nm, $\Phi_{em} = 0.26$, $\tau_{obs} = 3.7$ ms, i.e. $k_r = 7.0 \times 10^4$ s\(^{-1}\)). Its analogue 31e, recently described by Osawa and co-workers, containing isopropyl-modified phosphine 13\(^{37}\) (1,2-bis[2-isopropylphenyl]phosphino)benzene), shows a quantum yield of up to 0.95 due to a nearly 6-fold increase of the radiative rate ($\lambda_{em} = 506$ nm, $\Phi_{em} = 0.95$, $\tau_{obs} = 2.3$ ms, i.e. $k_r = 4.1 \times 10^5$ s\(^{-1}\)), which is likely induced by more stERICally demanding 13\(^{37}\) and therefore a more rigid structure. Interestingly, 31e was isolated as two solvatomorphs, exhibiting orange ($\lambda_{em} = 597$ nm) and green ($\lambda_{em} = 506$ nm) phosphorescence. This pronounced alteration was explained by theoretical analysis, which suggested different stabilization of the T\(_1\) excited state in crystals on taking into account the crystallization solvent.

There is no doubt that aurophilic contacts play an important role in the luminescence of gold(i) luminophores. For a single compound, variation of the Au(i)-Au(i) separation, e.g. performed under external pressure, can be directly correlated with the emission energy,\(^{96}\) but for complexes with different ligands and even for different crystalline modifications of the same compound (e.g., in addition to the above case of 31e, among three forms of 34a only the solvent-free one is luminescent),\(^{94,97}\) the crystallographic Au(i)-Au(i) distance loses its decisive character and can hardly be used for comparison.

One interesting feature that can be achieved for these easy to prepare digold luminophores is efficient low energy phosphorescence (red to NIR) with very large Stokes shifts exceeding 15 000 cm\(^{-1}\) (32a, 36).\(^{94}\) Other peculiar behavior is the high contrast luminescence thermochromism of complexes containing ligands P18 and P19. Upon cooling, iodide 36a and chloride 36b switch from low energy room temperature M/XM centered emissions ($\lambda_{em} = 562$ and 620 nm, respectively) to a long lived \(^{3}IL\) state at 77 K ($\lambda_{em} = 450$ and 447 nm).\(^{94,101}\) Similar to 36a,b, a temperature-dependent transition occurs for iodide 37, which exhibits a large hypsochromic shift of intense emission from 663 nm at 298 K ($\Phi_{em} = 0.54$) to 480 nm at 77 K (5750 cm\(^{-1}\), Fig. 14). Curiously, 36c, containing chlorinated phenyl X ligand, shows the opposite thermochromic change ($\lambda_{em} = 470$ nm at 298 K and 570 nm at 77 K).\(^{102}\)

The solid-state luminescence of some cationic diphosphine complexes remarkably depends on various stimuli and can be
demonstrated in the series of works by Deák and coauthors. The anion dependence of phosphorescence color in the crystalline complexes accompanied by an easily detectable optical response. Digold to external perturbation (mechanical stress, organic vapor) generates an anionic derivative of triazolyl-based phosphine X hydrogen e.

### Table 2: Photophysical properties of heteroleptic digold diphosphine complexes 30–37 in the solid state at 298 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \lambda_{em} ) nm (solution)</th>
<th>( r_{obs} ) ( \mu )</th>
<th>( \Phi_{em} )</th>
<th>Au–Au, Å/T, K</th>
<th>Proposed excited state</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>660 (485)</td>
<td>6</td>
<td>2.9885(8)/173</td>
<td>LMMCT</td>
<td>98</td>
</tr>
<tr>
<td>31</td>
<td>[Au2(C2F5)2][PPh2Me]</td>
<td>660 (485)</td>
<td>5</td>
<td>2.9286(6)/100</td>
<td>LMMCT</td>
<td>98</td>
</tr>
<tr>
<td>32</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>593</td>
<td>3.7</td>
<td>3.0166(5)/298</td>
<td>(X + M)/XLCCT</td>
<td>94</td>
</tr>
<tr>
<td>33</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>593</td>
<td>8.1</td>
<td>2.9521(5)/150</td>
<td>ML/LLCT</td>
<td>99</td>
</tr>
<tr>
<td>34</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>630</td>
<td>4.9</td>
<td>3.1189(4)/93</td>
<td>MC/MMCT</td>
<td>95</td>
</tr>
<tr>
<td>35</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>605</td>
<td>9.8</td>
<td>3.0953(4)/93</td>
<td>MC/MMCT</td>
<td>95</td>
</tr>
<tr>
<td>36</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>597</td>
<td>4.7</td>
<td>3.0791(4)/93</td>
<td>MC/MMCT</td>
<td>95</td>
</tr>
<tr>
<td>37</td>
<td>[Au2(C2F5)2][PPh2I]</td>
<td>506</td>
<td>2.3</td>
<td>2.9057(9)/93</td>
<td>MC/MMCT</td>
<td>95</td>
</tr>
<tr>
<td>b [Au2(C2F5)2][PPh2I]</td>
<td>506</td>
<td>5.0</td>
<td>0.12</td>
<td>3.2418(6)/298</td>
<td>(X + M)/XLCCT</td>
<td>94</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>580</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>MC</td>
<td>100</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>560</td>
<td>27</td>
<td>&lt;0.001</td>
<td>3.3156(5)/150</td>
<td>(X + M)/XLCCT</td>
<td>94</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>637</td>
<td>4.3</td>
<td>0.19</td>
<td>3.0682(2)/150</td>
<td>(X + M)/XLCCT</td>
<td>94 and 97</td>
</tr>
<tr>
<td>b [Au2(C2F5)2][PPh2I]</td>
<td>450sh, 620</td>
<td>12</td>
<td>—</td>
<td>3.0038(6)/150</td>
<td>MC/MMCT</td>
<td>101</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>472</td>
<td>54</td>
<td>&lt;0.001</td>
<td>2.89837(16)/150</td>
<td>IL</td>
<td>94</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>562</td>
<td>3.4</td>
<td>0.28</td>
<td>2.9835(13)/298</td>
<td>(X + M)/XLCCT</td>
<td>94</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>449sh, 620</td>
<td>76</td>
<td>—</td>
<td>2.9947(4)/173</td>
<td>IL (HE)</td>
<td>100 and 101</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>470, 490</td>
<td>—</td>
<td>—</td>
<td>2.9593(3)/297</td>
<td>IL</td>
<td>102</td>
</tr>
<tr>
<td>a [Au2(C2F5)2][PPh2I]</td>
<td>663</td>
<td>5.8</td>
<td>0.54</td>
<td>3.0354(2)/270</td>
<td>(X + M)/XLCCT</td>
<td>94</td>
</tr>
</tbody>
</table>

* Different solvatomorphs.

Further diversified by the nature of the counterions, which offer additional means of tunability and photofunctionality, as demonstrated in the series of works by Deák and coauthors. The optical behavior of dimers \([\text{Au2}][\text{PPh2}]_2\) (38, \( X = \text{CF}_3\text{SO}_3^-, \text{BF}_4^-, \text{PF}_6^-, \text{SbF}_6^- \)) can be altered by temperature, mechanical force, and volatile organic vapors. Moreover, the emissions of crystalline samples show an unusual excitation wavelength dependence, with maximum contrast observed for the \( \text{BF}_4^- \) salt \( (\lambda_{em} = 547/668 \text{ nm at } 365/312 \text{ nm at } 298 \text{ K}) \). Phosphine P17, which possesses a hydrogen donating N–H group, forms efficient N–H···X hydrogen bonding with counterions in compounds \([\text{Au2}][\text{PPh2}]_2\) (39, \( X = \text{NO}_3^-, \text{PF}_6^-, \text{SbF}_6^- \), \[\text{Au}([\text{CN}]_2)_2\], \( \text{BF}_4^- \)). As a result of different packing, the luminescence wavelengths for salts 39 range from 583 nm (yellow) to 623 nm (red). The relative weakness of intermolecular interactions determines their sensitivity to external perturbation (mechanical stress, organic vapor) accompanied by an easily detectable optical response. Digold complexes 40 bearing Xanthiphs P18 reveal an even higher anion dependence of phosphorescence color in the crystalline form, which changes from blue \( (X^- = \text{BF}_4^-, \lambda_{em} = 457 \text{ nm}) \) to red \( (X^- = \text{PF}_6^-, \lambda_{em} = 675 \text{ nm}) \) (Fig. 15).105

The heteroleptic cationic complex \([\text{Au}_4][\text{P}_2\text{O}_9][\text{bpe}]_4\) (41, \( \lambda_{em} = 515 \text{ nm and } 675 \text{ nm}) \). The emissions in the solid state \( (\lambda_{em} = 645 \text{ nm}) \) both in solution and in the solid state.

The click reaction of ligand P3 in a chlorogold(i) complex generates an anionic derivative of triazolyl-based phosphine P22, which is assembled into decanuclear cluster \([\text{Au}_{11}][\text{trans-P21}]_{\mu_1-\text{S}}]^{2+} \) (42a, Fig. 17A). Irradiation of 42a changes the cis-configuration of P21 into the trans-form, which results in a increase of the metal framework to octadecanuclear cluster \([\text{Au}_{18}][\text{trans-P21}]_{\mu_1-\text{S}}]^{2+} \) (43). Cluster 42a is a weakly red luminescence \( (\lambda_{em} = ca. 630 \text{ nm}) \), but the transition to 43 leads to the growth of the emission intensity and a bathochromic shift \( (\lambda_{em} = 645 \text{ nm}) \) both in solution and in the solid state.

The click reaction of ligand P3 in a chlorogold(i) complex generates an anionic derivative of triazolyl-based phosphine P22, which is assembled into decanuclear cluster \([\text{Au}_{10}][\text{P22}]_{\mu_1-\text{S}}]^{2+} \) (42b) containing the neutral protonated form \([\text{Au}_{10}][\text{P22}]_{\mu_1-\text{S}}]^{2+} \) (Fig. 17B). This aggregate is dually phosphorescent in the solid state \( (\lambda_{em} = 515 \text{ nm and } 675 \text{ nm}) \). The emissions are assigned to intraligand (HE band) and LMMCT \( (S \rightarrow \text{Au}^{10} \text{ LE band}) \) transitions. The ratio of these bands and the color of the observed luminescence is reversibly switched by soaking crystalline 42b in benzene and cyclohexane (Fig. 17B).

Phosphines of the family P12–P20 are also efficient in the synthesis of atomically precise partially reduced gold clusters. Ligands P16 and P18 allowed for the preparation of two \([\text{Au}_{11}][\text{diphosphine}][\text{Cl}]_5]^- \) compounds (44 and 45, Fig. 18) with

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*Fig. 14 Schematic structure of 37 [180–116 K].*
isomeric metal cores and different absorption characteristics due to a variation in the ligation of the diphosphines. The divalent \{Au_6\}^{2+} core decorated with P_2O ligands (46, Fig. 18) demonstrates markedly higher stability and a reduced optical band gap in comparison with its isostructural congeners; this has been attributed to an intramolecular Au⋯H–C interaction between the metal core and the phenylene spacer.

Chiral phosphines, such as widely used BINAP (P_23, Fig. 19), together with bridging ancillary ligands, provide a way to enantiomerically pure aggregates exhibiting circularly polarized luminescence; this topic has been recently reviewed. In addition to the optical properties at the molecular level, chiral clusters such as [Au_{10}(BINAP)_4S_4]^{2+} (47, Fig. 19) can be utilized for the fabrication of nanocrystalline materials of different morphologies when coupled with a chiral anion.

Silver and copper aggregates formed from this type of phosphine are rarer than their gold relatives. In most cases, the phosphines adopt a chelating coordination mode, and aggregation occurs via X-type anionic ligands (e.g. halides). For these compounds, the metal–metal interactions are frequently not operative or do not contribute to the frontier orbitals, and the photophysical behavior is mainly associated with intraligand transitions and variations of charge transfer between the metal ions, X and phosphate ligands. The structures and lability of Ag(I)/Cu(I) clusters are regulated by the bridging X groups, which include multidentate organic ligands. The non-phosphine linkers considerably increase the diversity of potential assemblies and consequently their optical characteristics. This alternative assembly pathway can be illustrated by a tetrasilver complex [Ag_4(μ-dmtp)]_{(P_{16})}^{3+} (dmtp = triazolylpyrimidine), which demonstrates intense green–yellow photoluminescence in the solid state (λ_\text{em} = 527 nm, \(\Phi_\text{em} = 0.76\) at 298 K). The emission, assigned to thermally activated delayed fluorescence, occurs with an impressively short lifetime of 0.65 s, providing a high radiative rate (\(k_r = 1.2 \times 10^6 \text{ s}^{-1}\)) that exceeds those of many noble metal phosphors.

3.2 Clusters supported by non-flexible tri- and tetradentate phosphines

The cluster chemistry of d^{10} metals employing ligands of higher denticity, which possess a rigid spacer, providing nonlinear configuration of P-donor functions, has been considerably less developed in comparison with that for the dipho-
sphines outlined above. The preparation of multimetallic aggregates is hampered by the limited number of suitable tri- and tetradeinate phosphines, and the tendency of these ligands for chelating coordination. Triphosphine P24 (Fig. 20) is the simplest capping ligand that is known to be a convenient template to favor metallophilic interactions and stabilize the \( \{M_3\} \) fragment.\(^{117,118}\) Together with alkynyl bridging ligands, the \( \{Au_3(C_2R)_3(P24)\} \) unit can efficiently trap the Cu(i) ion or CuX halides (\( X = Cl, Br \)) and form tetrametallic species \( \left[ Au_3Cu(C_2R)_3(P24) \right]^+ \) (48) and \( \left[ Au_3CuX(C_2R)_3(P24) \right]^+ \) (49), which adopt trigonal pyramidal and butterfly-shaped metal cores (Fig. 20).\(^{119,120}\) Complexes 48 are moderately phosphorescent in solution (\( \Phi_{em} = 0.006 \)–0.08); the emission wavelengths depend on the substituents of the alkynyl ligands and vary from yellow (550 nm) to red (680 nm). In the solid state, the emission is generally blueshifted and more intense, reaching a maximum value of 0.8 (\( \lambda_{em} = 501 \) nm, \( R = C(OH)Ph_2 \)). The hydroxyl groups of the alkynyl ligands diversify the luminescence behavior of 48 and 49. Complexes with \( R = C(OH)Ph_2 \) exhibit distinct luminescence vapochromism (Fig. 20) as a result of the phase transition between crystalline and amorphous states.\(^{120}\)

The supramolecular construction using the phosphino-cluster building block \( \{Au_2Cu(P24)\} \) is then realized with dialkynes. Self-assembly in the presence of latter star-shaped organic motif affords 3D cages of tetrahedral symmetry, \( \left[ \{Au_2Cu(C_2)R(P24)\}_4 \right]^+ \) (50, Fig. 21).\(^{121}\) The intense luminescence of complex 50a with a triphenylene–benzene moiety is assigned mainly to the MLCT character (\( \lambda_{em} = 565 \) nm, \( \Phi_{em} = 0.6, \tau = 59 \mu s \) in deaerated solution). Exchange of copper for silver ions retains the structural arrangement and switches the emission of 50a to an intraligand (alkyne) nature that is accompanied by a dramatic increase of the observed lifetime and sensitivity to molecular oxygen (\( \lambda_{em} = 508, 542 \) nm, \( \Phi_{em} = 0.12, \tau = 1430 \mu s \) in deaerated solution).

\[\text{Fig. 18} \quad \text{Partially reduced gold clusters 44–46 (Au--H--C hydrogen bonding is shown for 46).}\]

\[\text{Fig. 19} \quad \text{BINAP (P23) and sulfide cluster 47 of different crystal morphologies with chiral anions.}\]

\[\text{Fig. 20} \quad \text{Triphosphine P24 and its complexes 48 and 49; the photographs show the methanol vapor-induced emission color change (AM = amorphous and CR = crystalline).}\]
Phosphine P24 coordinates in a \( \mu_3 \)-capping mode also on silver and copper triangles, producing clusters of larger nuclearity and variability of structural motifs. Homometallic copper alkynyl complexes \([\text{Cu}_6(\text{C}_2\text{H}_4\text{X})_3(\text{P}24)]^2+)\) (51, Fig. 22) contain the Cu\(_6\) framework, composed of two \( \{\text{Cu}_3(\text{P}24)\} \) fragments, which are held together by cuprophilic bonding and bridging alkynyls.\(^{122}\) The cluster geometry in the solid state can be reversibly altered by weak binding of a coordinating solvent (acetone, acetonitrile), which alters the Cu(I)–Cu(I) connectivity. This transformation also affects the excited state and causes a distinct optical response, as the emission of 51 (X = H) changes from orange (\( \lambda_{\text{em}} = 615 \) nm) to blue (\( \lambda_{\text{em}} = 475 \) nm) upon interaction with acetonitrile.

In the case of a silver alkynyl system, P24 is also capable of assembling the hexametallic core in \([\text{Ag}_6(\text{C}_2\text{H}_4\text{X})_3(\text{P}24)]_2(\text{OTf})_3\) (52, Fig. 22), although with a somewhat different geometry due to bridging coordination of the counterions.\(^{123}\) Clusters 52 can be readily expanded to attain the heptanuclear core, \([\text{Ag}_7(\text{C}_2\text{H}_4\text{X})_3(\text{P}24)]_2(\text{OTf})_3\) (53a, Fig. 22), which improves their stability and rigidity, as indicated by a substantial growth of the emission quantum yield due to the faster radiative rate (e.g. \( \lambda_{\text{em}}/\Phi_{\text{em}}/k_r = 500 \text{ nm}/0.077/8.29 \times 10^3 \text{ s}^{-1} \) and 515 nm/0.176/6.33 \times 10^4 \text{ s}^{-1} for 52 and 53a X = OMe, respectively). The emission bands of structurally similar Ag(i)–Cu(i) compounds \([\text{Ag}_6\text{Cu}(\text{C}_2\text{H}_4\text{X})_3(\text{P}24)]_2(\text{O}_2\text{PPh}_2)_3\) (53b, Fig. 22) with diphenylphosphinic anions are bathochromically shifted compared with homometallic relatives 53a with quantum yields for the powder state reaching 0.78 thanks to a high \( k_r \) of \( 1.68 \times 10^5 \text{ s}^{-1} \). This performance allowed their utilization in the fabrication of solution-processed yellow OLEDs, which gave electroluminescence with a maximum external quantum efficiency (EQE) of 13.9% at a practically useful brightness of 184 cd m\(^{-2}\).\(^{124}\)

The rigid triphosphine with 1,2-phenylene spacers, bis(2-diphenylphosphinophenyl)phenylphosphine (P25), predominantly demonstrates chelating coordination and forms mononuclear complexes, except for a few early examples of trigold(I) chloride\(^{125}\) and cationic disilver/digold compounds. The tetraphosphine congener, tris(2-diphenylphosphinophenyl)phenylphosphine (P26), comprising an additional diphenylphosphine function, is an interesting example of a polydentate ligand that allows the combination of both chelating and bridging binding of d\(^{10}\) metal ions, which gives rise to dinuclear complexes \([\text{MM}′(\text{CN})(\text{P}26)]_4^+\) (54, Fig. 23).\(^{126}\) The cyanide bridges used instead of alkynyl ligands assemble the \( \{\text{MM}′(\text{P}26)\} \) bimetallic units into tetrametallic clusters \([\text{MM}′(\text{CN})(\text{P}26)]_4^+\) (55).\(^{127}\) For both families 54 and 55, an appreciable photoluminescence is observed in the solid state only, where cyanide complexes 55 exhibit thermally activated delayed fluorescence (TADF) and reach a quantum yield of up to 0.56 (\( M = M′ = \text{Cu}(i) \)). The emission parameters are sensitive to the nature of the metal ions and their interaction, particularly in the excited state, where metal–metal distances are significantly contracted, according to computational data.\(^{127}\)

4. Phosphines with flexible spacers

4.1 Complexes formed from flexible diphosphines

Conformational non-rigidity of the linker between phosphine groups brings additional degrees of freedom that often make it difficult to control the process of self-assembly of bi- and polymetallic complexes. Depending on the stereochemistry of the spacer, the formation of chelates could be a competing or even preferable coordinating pathway for these ligands, especially if coupled with Cu(i) and Ag(i) ions. Within this family, ligand P27\(^1\) (bis(diphenylphosphino)methane, dpdm), with a methylene spacer, and its N-bridged analogues P27\(^{1\text{NR}}\)
preferentially facilitate the formation of dinuclear units. As a stable and commercially available bridging diphosphine, P27 has been extensively used for decades for the synthesis of numerous bimetallic species and larger coinage metal clusters. The assembly of the latter compounds is mainly driven by bridging anionic ligands (alkynyls, thiolates, chalcogenides), which also have a strong impact on the optical properties. Because of the large number and diversity of species supported by P27 and similar ligands, in this section we highlight only selected examples.

The optical properties of phosphine-bridged complexes in the solid state are sensitive not only to the metal–metal separations, but also to the coordination number, which depends on the metal to ligand ratio and the nature of the phase. Crystals of digold complex [Au2(P27)2]Cl2 (56a) are brightly blue phosphorescent ($\lambda_{em} = 467$ nm; $\Phi_{em} = 0.65$). The addition of one more phosphine changes the coordination geometry of gold ions from linear to trigonal and redshifts the emission of the crystalline hydrate [Au2(P27)3]Cl2·8.5H2O (56b) to 513 nm ($\Phi_{em} = 0.95$). Removal of crystallization water by heating at 373 K converts 56b into an amorphous sample with yellow emission ($\lambda_{em} = 596$ nm, $\Phi_{em} = 0.52$), Fig. 24. Additional heating at 399 K gives rise to bright blue luminescence ($\lambda_{em} = 467$ nm, $\Phi_{em} = 0.55$), which is attributed to dissociation of one P27 ligand and the appearance of 56a. Grinding the latter mixture recovers the amorphous form of 56b, which is transformed into blue emissive crystalline 56b upon the addition of water.

The stable trigonal coordination environment of silver and copper ions in [M2(P27)2L2]2+ and an easy substitution of labile ligands L (e.g. acetonitrile) have offered a facile route to use these building blocks for engineering a range of clusters with bridging anionic ligands. An elegant series of cyanide-assembled luminescent supramolecular aggregates featuring the {Cu2(P27)2}2+ unit, termed “a molecular clip”, have been recently developed by the group of Lescop. Tetracopper metallocycle [{Cu2(P27)2(CN)2}]2+ (57, Fig. 25) formed from a ditopic CN− linear linker is an efficient blue TADF emitter in the solid state ($\lambda_{em} = 457$ nm, $\Phi_{em} = 0.72$ at 298 K). Treating cycle 57 with KCN transforms the tetrametallic discrete molecules into a helical polymer [{Cu2(P27)2(CN)2}]n (58) with moderately intense green–yellow emission at room temperature ($\lambda_{em} = 538$ nm, $\Phi_{em} = 0.2$), which is assigned to the phosphine-centered phosphorescence. Reacting 57 with CuCN extends the metallocycle to [{Cu2(P27)2{Cu(CN)2}}2]2+ (59), showing intense green TADF in the crystalline state ($\lambda_{em} = 490$ nm, $\Phi_{em} = 0.8$ at 298 K).

The utilization of a dicyanoaurate [Au(CN)2]− bridge instead of [Cu(CN)2]− however did not produce the gold analogue of 59 but afforded a more complicated aggregate [{Cu10Au2(P27)5(CN)10}]2+ (60, Fig. 25), as a result of certain flexibility of the {Cu2(P27)2}2+ constituents. The larger framework of 60 caused some decrease of the emission energy compared with 59 ($\lambda_{em} = 520$ nm, $\Phi_{em} = 0.7$) with excited state...
of the aliphatic R group in responded to 3MC/3LMMCT (S vs. LE bands was attributed to the formation of nanoaggregates in acetone/methanol/water mixtures. This behavior is likely to be governed by the long hydrophobic alkyl chains of P27\textsuperscript{INR} ligands and has not been observed for shorter substituents with R = propyl, octyl.

Complex 63, containing P27\textsuperscript{INR} functionalized with a methylpyridine group (R = CH\textsubscript{2}-o-py), which does not coordinate to the metal core, crystallizes in three different solvatomorphs.\textsuperscript{147} These modifications, which can be mutually interconverted upon grinding and treatment with certain solvents, exhibit blue, green and red luminescence (Fig. 26C) that points to the importance of molecular packing and subtle interactions on the photophysics of bulk materials. Interestingly, the stability of the decanuclear framework also can be affected by the amino R group of the bridging diphosphine. For small and sterically undemanding ethyl, methyl and H substituents, three clusters adopting \{Au\textsubscript{6}S\textsubscript{2}\}, \{Au\textsubscript{10}S\textsubscript{4}\}, and \{Au\textsubscript{12}S\textsubscript{4}\} motifs have been identified, with concentration-dependent cluster-to-cluster transformation observed for the P27\textsuperscript{INMe} ligand.\textsuperscript{148} Notably, the P27\textsuperscript{IN}-supported mixed-metal Au(I)-Cu(I) sulfide system, [Au\textsubscript{4}Cu\textsubscript{6}(P27\textsuperscript{IN})\textsubscript{4}S\textsubscript{4}] (64),\textsuperscript{149} indicates another possible direction for the development of this chemistry.

In comparison with P27\textsuperscript{I} and P27\textsuperscript{IN}-containing compounds with \{Au\textsubscript{4}\} and \{Au\textsubscript{6}\} cores, the nuclearity of sulfide gold clusters has been increased to 14 and 18 metal atoms \{[Au\textsubscript{14}S\textsubscript{6}(P27\textsuperscript{IN})\textsubscript{4}]\textsuperscript{2}\} \(65\text{a}\) and \{[Au\textsubscript{18}S\textsubscript{8}(P27\textsuperscript{IN})\textsubscript{6}]\textsuperscript{2}\} \(65\text{b}\) by introducing a longer spacer between phosphorus donors in diphosphine P27\textsuperscript{IN} (Fig. 27).\textsuperscript{150} The size of the metal–sulfur framework, regulated by the stoichiometry of the reactants \{[Au\textsubscript{4}Cl\textsubscript{2}(P27\textsuperscript{IN})]\} and Na\textsubscript{2}S, has a rather small effect on the emission. Both clusters are green phosphors in the solid state with somewhat hypsochromically shifted and more intense emission observed for the larger complex \(65\text{b}\) \(\lambda_{\text{em}}/\Phi_{\text{em}} = 540 \text{ nm}/0.21\) and 518 nm/0.27 for \(65\text{a},\text{b}\). Interestingly, these compounds are appreciably stable and luminescent in the DMSO/PBS buffer mixture, which, together with low cyto-
towards toxicity, makes them suitable for imaging HeLa cells, where 65a,b show specific lysosome localization.

The assembly of alkynyl clusters has been also realized with some flexible diphosphines. In earlier works by Chen, phosphine P27\(^+\) facilitated the formation of the Au(i)-Ag(i) aggregates \([\text{Au}_4\text{Ag}_8(\text{C}_2\text{R})_4]\)\((\text{P27}^+\))\(^3+\) (66) and \([\text{Au}_4\text{Ag}_4(\text{C}_2\text{R})_4]\)\((\text{P27}^+\))\(^3+\) (67),\(^{14,15}\) the latter has been photochemically converted into the cluster \([\text{Au}_3\text{Ag}_8(\text{C}_2\text{R})_4]\)\((\text{P27}^+\))\(^3+\) (68, Fig. 28A), comprising an aromatic ligand formed by alkynyl cyclotrimerization.\(^{132}\) Diphosphine P27\(^4\) with a longer butyl spacer produces a dynamic system, which adopts two molecular types – the “closed” cluster \([\text{Au}_4\text{Ag}_4(\text{C}_2\text{R})_4]\)\((\text{P27}^+\))\(^4\) (69a) structurally similar to 17, and the fluxional isomer \([\text{Au}_3\text{Ag}_6(\text{C}_2\text{R})_6]\)\((\text{P27}^+\))\(^4\) (69b) composed of two tetrametallic \([\text{Au}_4\text{Ag}]\) fragments linked by ligand P27\(^4\) (Fig. 28B).\(^{152}\)

Depending on the alkynyl group, the isomers of 69 can exist in temperature-dependent equilibrium. In contrast to poorly emissive Au(i)-Ag(i) congener 17 bearing the diphosphine with a butadiyne spacer \(\lambda_{\text{em}} = 526\) nm, \(\phi_{\text{em}} = 0.01\) (in solution), complexes 69a are blueshifted and much stronger phosphors \(\lambda_{\text{em}} = 471-490\) nm, \(\phi_{\text{em}} = 0.65-0.73\) with a radiative rate constant reaching \(5.9 \times 10^5\) s\(^{-1}\). Furthermore, a carbazole-based alkynyl was used to extend the Au(i)-Ag(i) cluster architecture to an octadecanuclear framework in \([\text{Au}_{10}\text{Ag}_8(\text{C}_2\text{R})_6]\)\((\text{P27}^+\))\(^4\) (70, \(\text{R} = 1,8\)-substituted 9H-carbazole, Fig. 28C).\(^{153}\) The cluster is a bright yellow emitter \(\lambda_{\text{em}} = 565\) nm, \(\phi_{\text{em}} = 0.77, k_r = 1.2 \times 10^5\) s\(^{-1}\) in solution; \(\lambda_{\text{em}} = 585\) nm, \(\phi_{\text{em}} = 0.21, k_r = 6.6 \times 10^4\) s\(^{-1}\) in the solid state) with a quantum yield reaching 0.96 for 5% doped polymer film. With such a performance, 70 has been employed in the light emitting layer of a solution-processed OLED, which exhibited a maximum EQE of 14.9% at a brightness of 662 cd m\(^{-2}\).

Even faster radiative rates were attained in the solid state for homometallic hexagold alkynyl clusters \([\text{Au}_6(\text{C}_2\text{R})_4]\)\((\text{diphosphine})\)\(^2+\) (71) assembled from ligands P27\(^2\)–\(^4\), P28–P30 (Fig. 29).\(^{154}\) Neat powders of compounds 71 are intense sky blue triplet emitters \(\lambda_{\text{em}} = 482-502\) nm, \(\phi_{\text{em}} = 0.61-1.0\) with \(k_r\) up to \(7.9 \times 10^5\) s\(^{-1}\) and nearly suppressed non-radiative decay.

The flexibility of digold halides \([\text{Au}_2(P27^2)^2\text{HAl}_2]\) (72, \(\text{HAl} = \text{Br, I}\)) determines their rich structural diversity in the solid state.\(^{155,156}\) Depending on the solvents, complexes 72 adopt different molecular arrangements with Au(i)-Au(i) separations ranging from a non-bonding distance to short aurophilic contacts. The structural transformations, which are induced by drying the crystals and exposure to solvent vapors, are responsible for a drastic change in the phosphorescence color from green to orange (Fig. 30).

Ligands P27\(^n\) have been used in the preparation of digold(i) complexes equipped with a secondary donor function (e.g., pyridine), which act as a metallogand in the supramolecular coordination self-assembly,\(^{37}\) for instance, of heterometallic macrocycles 73\(^{157}\) and helicates 74,\(^{158}\) Fig. 31. Homoleptic macrocycles \([\text{M}_4(P27^2)^2]^+\) (73) have been realized for phosphole alkynyl ligands with long aliphatic spacers containing an odd number of carbon atoms \(n = 3, 5, 7, 9; M = \text{Ag(i)}, \text{Au(i)});\(^{159,160}\) an even number of carbon atoms \(n = 4, 6, 8; M = \text{Au(i)}\) leads to the open chain structures.\(^{159}\) For copper(i), with its prefer-
ence for tetrahedral geometry, phospholane $\text{P}27^5$, depending on the reaction stoichiometry, yields either counterion ($\text{BF}_4^-$)-connected polymer $76$ composed of paddlewheel $\left[\text{Cu}_2(\text{P}27^5)\right]^{2+}$ blocks, or an unusual box-like aggregate $\left[\text{Cu}_4(\text{P}27^5)\right]^{4+}$ ($77$, Fig. 31).161 Alternatively, sulfide dianions give more sophisticated copper(I) clusters $\{\text{Cu}_{12}\text{S}_6\}$ framed by phosphines $\text{P}27^5$ and $\text{P}27^8$, which display red luminescence in the solid state with excellent quantum efficiencies of up to 0.65.162

Simultaneously, variable conformations of ligands $\text{P}27^n$ can affect the gold–gold distances, spin–orbit coupling, and therefore the photophysics of the corresponding digold complexes.163 The perturbation of metallophilic contacts in $\text{P}27^n$-bridged complexes $\left[\text{Au}_2(\text{P}27^n)(\text{XR})_2\right]$ ($78; X = S, C_2; n = 1, 2$), accompanied by an optical response, also occurs upon trapping the metal cations164-166 and anions167 with ancillary ligands.

Diazadiphosphacyclooctane ligand $\text{P}31$ (Fig. 32) is an interesting case of a bridge with limited conformational freedom. Its digold complexes $\left[\text{Au}_2(\text{P}31)\text{X}_2\right]$ ($X = \text{Cl} 79a, \text{C}_2\text{R} 79b$) exist in an “opened” basket-shaped configuration with long Au(I)–Au(I) separations (>5 Å), and a “closed” molecular conformation with metal–metal distances within a range of aurophilic contacts (ca. 3.3–3.5 Å).168,169 The preferable molecular shape depends on the crystallization solvents, which are involved in non-covalent interactions with X-ligands. The luminescence of 79 has been proposed to have an intraligand nature and is virtually insensitive to the presence or absence of Au(II)–Au(II) bonds. Nevertheless, intermolecular interactions and different packings of crystallosolvates dictate variations in the arrangements of the chromophore and cause an impressive alteration of the emission wavelengths, e.g. from 553 to 685 nm for 79b ($R = \text{Ph}$).169

4.2 Complexes formed from flexible polydentate phosphines

Tri- and tetradoentate phosphines with flexible backbones found in coinage metal assemblies are mainly represented by compounds $\text{P}32$–$\text{P}35$ (Fig. 33). Not surprisingly, several coordinating centers and non-rigid linkers lead to a wide variability in compositions and forms of polynuclear aggregates.

Ligands $\text{P}32$, $\text{P}34$ and $\text{P}35$ with methylene spacers are convenient templates for the synthesis of homoleptic cationic complexes of silver and gold (e.g. $\left[M_3(\text{P}32)\right]^{3+} 80$,170,171 $\left[M_4(\text{P}34)\right]^{4+} 81$,172 $\left[M_4(\text{P}35)\right]^{4+} 82$171) and supporting metallophilic contacts, which have a strong impact on the photophysical behavior, mainly associated with metal-centered electronic transitions. For instance, the emissions of gold(I) compounds with non-coordinating anions are shifted from deep blue ($80$)170,171 to the blue–green region upon increasing nuclearity of the Au$_4$ chain ($81$),172 but remain almost unchanged for the star-shaped Au$_4$ skeleton in $82$.171 Despite the bridging ligands and metal–metal interactions, heterometallic species $80$ and $82$ are labile in solution and give several components;
this makes them nearly non-luminescent in solution, in contrast to their intensely phosphorescent homometallic gold relatives 80 and 81.

The ethylene spacers between phosphorus atoms in P33 increase the variability of the gold(I)-based system. The complex \([\text{Au}_3(\text{P33})_2]^{3+}\) (83a) has a helicate structure (Fig. 34),173,174 which leads to box-like cationic aggregates \([\text{Au}_6(\text{P33})_4]^{5+}\) (83b) or halide-bridged helicates \([\text{Au}_3(\text{P33})_2(\mu-\text{X})]^{5+}\) (83c) upon interacting with halide anion(s).174,175 Mechanical force converts the “box” motif of 83b with blue luminescence into helicate 83c, which demonstrates yellow emission.

Introducing ancillary X-type bridging ligands (halides,176–178 sulfur-containing groups,179 hydrides180) and mixing different metals provides extremely wide-ranging possibilities for cluster assembly in the presence of flexible multidentate phosphines. For example, a peculiar case of combining all three coinage metals in a stepwise manner has been demonstrated for octanuclear metalloring \([\text{Au}_4\text{Ag}_2\text{Cu}_2(\text{P34})_4\text{Cl}_4]^{4+}\) (84, Fig. 35).181 Its conformation in the solid state is influenced by the counterions (\(\text{BF}_4^-\), \(\text{OTf}^-\), \(\text{Cl}^- + \text{PF}_6^-\)). Differences in packing and cluster–anion interactions are manifested by the luminescence properties of salts 84: the emission wavelength and the quantum efficiency change from 564 nm/0.07 (\(\text{BF}_4^-\)) to 586 nm/0.19 (\(\text{OTf}^-\)) and ultimately to 627 nm/0.10 for the mixture (\(\text{Cl}^- + \text{PF}_6^-\)).

Polynuclear alkynyl derivatives supported by ligands P32–P35 demonstrate interesting structural topologies and intriguing optical behavior. The silver–copper cluster \([\text{Ag}_{12}\text{Cu}_2(\text{P33})_3(\text{C}_2\text{C}_6\text{H}_4\text{Bu}^t)_3]^{2+}\) (85)182 is weakly luminescent in solution, but shows bright red to near-IR phosphorescence (\(\lambda_{\text{em}} = 675, 812 \text{ nm}\)) in the crystal. Tetraphosphine P35 stabilizes a smaller cluster core in compounds \([\text{Ag}_{16}\text{Cu}_9(\text{P35})_3(\text{C}_2\text{C}_6\text{H}_4\text{R})_20]^{5+}\) (86, R = \(\text{Bu}^t, \text{H}, \text{CF}_3\)), which emit in the yellow–orange region with a maximum quantum yield of 0.14 in the powder and 0.4 in the doped polymer (PMMA, 3 weight %).183 Impressively, complexes 86 demonstrate phosphorescence mechanochromism not only in the neat form, but also in the PMMA film. Grinding shifts the emission from 547 nm (R = \(\text{Bu}^t\)) to 592 nm (Fig. 36); the effect is assigned to the contraction of metal–metal separations and proposed as “intracluster phosphorescent mechanochromism”.

Gold–silver and –copper complexes of P33 with hydroxylphatic alkynes are dynamic in solution and crystallize predominantly in an octanuclear form \([\text{Au}_4\text{M}_2(\text{C}_2\text{R})_6(\text{P33})_2]^{2+}\) (M = Cu(1)87a, Ag(1)87b, Fig. 37) with blue (87a) to deep-blue (87b) emissions and moderate intensity (\(\Phi_{\text{em}} = 0.08–0.17\)).184 The aromatic substituents of the alkynyl ligands reduce the metal array to six atoms in \([\text{Au}_4\text{Ag}_2(\text{P33})_2(\text{C}_2\text{R})_4]^{2+}\) (88).185 Their moderate luminescence in solution (\(\Phi_{\text{em}}\) up to 0.1), which spans the range from 502 to 607 nm, depending on the electronic

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**Fig. 33** Homoleptic complexes 80–81 supported by flexible tri- and tetradeutate phosphines P32–P35.

**Fig. 34** Schematic representation of complexes 83a–c.

**Fig. 35** Trimetallic aggregate \([\text{Au}_4\text{Ag}_2\text{Cu}_2(\text{P34})_4\text{Cl}_4]^{4+}\) (84).

**Fig. 36** Phosphine–alkynyl cluster 86 showing luminescence mechanochromism.
features of the R groups, is significantly enhanced in the solid state ($\Phi_{em}$ up to 0.77) and in the film ($\Phi_{em}$ up to 0.63). The latter allowed appreciable green–yellow electrophosphorescence to be achieved with an EQE of 7.0%.

5. Phosphines with additional hetero-coordinating functionality (N, C, S)

The combination of electronically different coordination groups in the same ligating motif is a well explored strategy in heterometallic cluster chemistry in general. It is equally applicable to copper subgroup metals, for which the difference in binding of hard and soft donors is clearly seen for copper(i)/silver(i) and gold(i) ions. Heterodentate phosphines have been particularly useful in the selective assembly of heterometallic d\textsuperscript{10} complexes. Due to the wide variability of organic backbones, denticity and combinations of coordinating functions, many coinage metal compounds can be categorized as belonging to this family.

5.1 Complexes containing P–N ligands

Bridging phosphine ligands P\textsubscript{34} with 2-pyridine substituents, which incorporate one to three N-donor functions, are conventional building blocks to support a d\textsuperscript{10} bimetallic fragment (Fig. 38). For heteroleptic gold-based systems, the aggregation of a polymetallic cluster primarily depends on the properties of X-type ligands. It can be illustrated by a series of Au(i)–M(i) (M = Cu, Ag) species bearing P\textsubscript{34}\textsuperscript{1ppy} along with chalcogen-derived bridges\textsuperscript{186–188} and hypercoordinated carbon.\textsuperscript{28} Clearly, it is the bridging ability of the anionic ligand that largely determines the organization of the cluster core in 89–92 (Fig. 38); the photophysical behavior of 91, 92 and their relatives has been reviewed previously.\textsuperscript{28,186} Notably, although the emissive states for chalcogenide clusters 91 show little contribution from the phosphines, minor alterations in the structures of the phosphines (P\textsubscript{34}\textsuperscript{1ppy}, its pyridine-methylated analogue, P\textsubscript{34}\textsuperscript{1pm}) are accompanied by substantial modulation of the solid state luminescence of 91 (M = Ag) and its vapochromic response.\textsuperscript{188}

The pyridine groups are mainly involved in the binding of copper or silver ions, therefore increasing the number of N donors that can either influence the shape of the metal core and metallophilic bonding,\textsuperscript{187} or “trap” the additional metal ions, yielding a larger cluster framework.\textsuperscript{189} Thus, the gold octahedron {Au\textsubscript{6}C(phosphine)}\textsuperscript{2+} can be decorated with two silver atoms in the case of P\textsubscript{34} to give complex [Au\textsubscript{6}Ag\textsubscript{2}C(P\textsubscript{34}\textsuperscript{1ppy})\textsubscript{6}]\textsuperscript{4+} (92) with bright red phosphorescence in solution ($\lambda_{em} = 625$ nm, $\Phi_{em} = 0.29$) and green emission in the solid state.\textsuperscript{190} The congener cluster [Au\textsubscript{6}C(phosphine)]\textsuperscript{2+} containing the tridentate P\textsubscript{34}\textsuperscript{2py} ligand can accommodate four or six silver ions in [Au\textsubscript{6}Ag\textsubscript{4}C(P\textsubscript{34}\textsuperscript{2py})\textsubscript{6}]\textsuperscript{6+} (93; $\lambda_{em} = 603$ nm, $\Phi_{em} = 0.045$) and [Au\textsubscript{6}Ag\textsubscript{6}C(P\textsubscript{34}\textsuperscript{2py})\textsubscript{6}(CF\textsubscript{3}COO)\textsubscript{3}]\textsuperscript{5+} (94; $\lambda_{em} = 557$ nm, $\Phi_{em} = 0.92$), which reveal a gradual blueshift of the emission in solution and a dramatic increase of the quantum yield for 93.\textsuperscript{189} The growth of luminescence intensity in the latter cluster has been attributed to a more rigid structure and hindered nonradiative relaxation that is supported by a nearly two orders of magnitude decrease in the corresponding rate constant in 94 ($k_{nr} = 3.56 \times 10^{5}$ s\textsuperscript{−1}) vs. 92 ($k_{nr} = 1.25 \times 10^{5}$ s\textsuperscript{−1}).

With aryl and chloride ancillary ligands, phosphine P\textsubscript{34}\textsuperscript{1ppy} (and the methylated derivative) stabilizes trinuclear clusters
[\text{Au}_2\text{Cu}(\text{P}^{34}\text{py})_2\text{X}_2]^+ (X = \text{C}_6\text{Hal}_5 \text{95a}, X = \text{Cl} \text{95b})^{191,192} \text{ where the copper ion induces } ^3\text{MLCT states with a strong SOC found for 95b. Interestingly, the latter complex displays unusual temperature-dependent dual phosphorescence (} \lambda_{\text{em}} = 450 \text{ and } 550 \text{ nm}) \text{ that is assigned to two thermally non-equilibrated excited states with Cu } \rightarrow \text{ py and Au } \rightarrow \text{ py charge transfer character (Fig. 39).}

The P–N bridging phosphines with a similar bite angle to that of P\text{34}\text{, which contain a range of N-heterocycles, have been extensively used to generate a series of bimetallic species with fascinating photoluminescence properties.\text{193–196 In particular, dicopper compounds featuring the } \{\text{Cu}_2(\mu_2-P-N)\text{Hal}_2\}\text{ motif decorated with terminal auxiliary phosphines, as studied by Bräse, Yersin, Kato and others, often exhibit efficient TADF mixed with phosphorescence,\text{197 and therefore are appealing candidates for applications in electroluminescent devices.\text{198–207 Remarkable emission behavior has been realized for heteroleptic complexes } [\text{Cu}_2\text{X}_2(\mu_2-\text{P}^{34}\text{py})] \text{96, } X = \text{ heterocycle, Table 3}. \text{ The electronic transitions responsible for population of the emissive excited states have } (M + X)\text{LCT character, with the LUMO localized on the N-heteroatom of the bridging ligand. Thus, accessible variation of this component of the phosphine allows for broad tuning of the luminescence color, whereas solubility can be dramatically improved by using branched aliphatic fluorinated substituents of the constituting ligands.\text{205}}

Tetracopper halide clusters [\text{Cu}_4\text{X}_4(P-N)_2] \text{(97) are readily formed by reacting CuX salts with the P\text{34}\text{py}-type and congner phosphine–pyridine P\text{35}\text{py} \text{213 ligand in 2:1 ratio (Fig. 40). The solid state luminescence of 97, assigned to the } (M + X)\text{LCT excited state, depends inter alia on the shape of the } \{\text{Cu}_4\text{X}_4\} \text{ framework. The cluster core is relatively dynamic and its structure can be modulated, for instance, by the crystallization solvent, which affects the packing and intermolecular interactions. Thus, the dichloromethane solvate of iodide 97 (P-N = P\text{34}\text{py}) \text{ emits at 576 nm (yellow), but its solvent-free form displays a band maximized at 527 nm (green).\text{209 By changing the position of the methyl substituent in the pyridine ring, it was possible to distort the geometry of the}}

### Table 3 Photophysical properties of selected heteroleptic dicopper complexes 96 in the solid state at 298 K

<table>
<thead>
<tr>
<th>Bridging ligand/L</th>
<th>(\lambda_{\text{em}}) nm</th>
<th>(\tau_{\text{av}}) (\mu\text{s})</th>
<th>(\Phi_{\text{em}})</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>I/Ph\text{3}</td>
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<td>1.09</td>
<td>0.36</td>
<td>198</td>
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<tr>
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<td>488</td>
<td>7.0</td>
<td>0.85</td>
<td>203</td>
</tr>
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<td>2.85</td>
<td>0.99</td>
<td>198</td>
</tr>
<tr>
<td>IV/Ph(C_6H_4F)_3</td>
<td>524</td>
<td>5.5</td>
<td>0.90</td>
<td>205</td>
</tr>
<tr>
<td>V/Ph\text{3}</td>
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<td>3.67</td>
<td>0.86</td>
<td>198</td>
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<tr>
<td>VII/VII</td>
<td>713</td>
<td>—</td>
<td>0.03</td>
<td>208</td>
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</table>

Fig. 39 Gold–copper clusters 95 and the dual emission of chloride 95b.

Fig. 40 Phosphine pyridine ligands stabilizing [\text{Cu}_4\text{X}_4(P-N)_2] clusters 97 capable of thermochromic luminescence.
the [Cu4I4] core and redshift the emission from 529 nm (P–N = P341py4me) to 593 nm (P–N = P341py6me).212 Furthermore, the complex bearing phosphine P341py6me reveals thermochromic luminescence (Fig. 40) associated with (M + X)LCT (high energy) and cluster-centered (CC, low energy) excited states; similar behavior was observed for compounds with phospholane ligands.210 However, analogous complexes with P341py4me212 and tolyl-substituted P341py6me211 ligands do not show such a phenomenon. A somewhat similar tunability has been demonstrated for compounds [Cu4I4(P3530p)]2 with different R substituents at the phosphorus atom, for which only the ligand with R = Ph produces the complex with distinct dual emission at room temperature (λem = 460/580 nm), whereas a blue band dominates for its congeners.213

Dual and temperature responsive phosphorescence in the crystalline state has also been attained for aggregates, which comprise two [Cu4I4] units held together with a tetradentate N–P ~ P–N ligand structurally similar to P31 ([Cu4I4(P31a)]98,214 Under ambient conditions, the low and high energy bands (λem = 466/615 nm) of comparable intensity generate nearly white emission with up to 0.2 quantum yield, which is rare behavior for Cu(II) clusters.

As for homodentate phosphines, cluster growth is conventionally achieved by adding coordinating groups to the parent heterobidentate motif. Two equivalents of the [PNP] diphenosphine (6,6-bis(diphenylphosphino)-2,2′-bipyridyl, P36), which can be seen as a “dimer” of P341py99, accommodate four silver ions in light-blue luminescent complex [Ag4(P36)]2+ (99).215 An interesting case of silver cluster aggregation assisted by a tetradentate [P–N–I] ligand gives pentanuclear [Ag@Ag4(P34)5]n (100), the blue–green luminescence of which is modulated by counterions and weakly coordinated solvent molecules.216 On the other hand, decoration of the pyridine motif with phosphine groups offers a [PNP] bridging system in P37 (Fig. 41) suitable for supporting a tetravigold linear chain in [Au4Cl2(P36)]2+ (101).217 The interaction of P37 with silver trifluoroacetate gives hexanuclear complex [Ag6(P37)2(CF3COO)]3+ (102).218 The acetate-stabilized cluster core induces a strong SOC, resulting in bright blue phosphorescence (λem = 453 nm, Φem = 0.22), which has been proposed to originate from an O/Ag → P37 electronic transition termed inter-ligand trans-metallic charge-transfer (ITCT). However, it should be noted that, despite different ligands and the structures of silver(i) complexes 99, 100 and 102, there is little variation in the emission energy between these species. On the other hand, heterometallic tetraneuronal clusters [Au2M2(P37)(X)n]4+−n (M = Cu(i), X = OH, n = 1 103a; M = Ag(i), X = O2PF2, n = 2 103b) demonstrate more diverse photo-luminescence behavior. The emission of 103a shows a distinct vapochromic response to certain solvents (pyridine, methanol, dichloromethane, tetrahydrofuran) with the maximum shifted from 480 to 600 nm, related to hydrogen-bond interactions.219 Complex 103b is a rare example of a dual temperature-dependent phosphor with a broad warm white luminescence in the powder at room temperature, although with a weak quantum yield of 0.03.220

More complex aggregates using phosphine P37 have been assembled with the assistance of alkynyl groups. In the presence of monoalkynyl ligands, gold(i) and silver(i) ions form tetraneuronal clusters [Au2Ag2(C2C6H4R)6(P37)]3+ (104), in which the pyridine spacer of the diphosphine is not involved in coordination to the metal centers.221 Complexes 103 display moderate blue luminescence both in the solid and solution states (Φem ~ 0.02–0.03 in dichloromethane) with little effect of the R group (H, Me, CO2Me, CHO) on the emission. In the same ligand environment, the combination of Ag(i)/Cu(i) produces compounds [Ag5Cu5(C2C6H4R)6(P37)]3+ (105) with a compact octametallic core, where P and N donor atoms selectively coordinate to silver and copper ions, respectively (Fig. 42).222 These species demonstrate an AIE property as the quantum yield of the orange phosphorescence increases ca. 10-fold in the CH3CN-water (1 : 9 v/v) mixture vs. pure CH3CN. Besides, complexes 105 were the first examples of coinage metal alkynyl clusters capable of electrochemiluminescence. For dialkynyl–carbazole (H2decz), which can act as a di- (C–C) or trionic (C–N–C) ligand, silver clusters featuring {Ag6(P37)i}, {Ag6(P37)ii} and {Ag6(P37)iii} frameworks have been prepared by careful modification of the reaction stoichiometry.223 The stepwise growth of the metal core gradually decreased the emission energy to the near-IR region, reaching a maximum of 918 nm in the powder form for [Ag20(Hdecz)2(decz)8(P37)h] (106, Fig. 42).

It should be mentioned that the P–N ligands are not limited to compounds for chelating coordination or supporting bimetallic units with short metal–metal contacts. Ligands with the spatial separation of binding functions (P38, P39, Fig. 43) have been successfully used for the assembly of tubular discrete structure [Ag6n(P38)i]n (107)224 and luminescent gels formed from coordination polymers [Ag(OTf)2(P39)h]n (108).225

5.2 Complexes containing P–C ligands

In contrast to relatively labile pyridine and phosphine groups, the NHC carbene function is an attractive alternative that offers more robust coordination along with a greater electron donating ability. Several phospha–carbene ligands of P40–P44...
Alkynyl heterometallic complexes 105 and 106 formed from phosphine P37, and NIR emission for 106.

Surprisingly, rather limited studies of the photophysical properties have been performed, to date, on phosphacarbene compounds of coinage metals. After the initial report on cluster 108, it was later characterized as a dual emitter.\textsuperscript{235} Under 300 nm excitation in CH\textsubscript{2}Cl\textsubscript{2} solution, it exhibits two distinct bands, \(\lambda_{\text{em}} = 512\) and 694 nm, assigned to singlet (HE fluorescence) and triplet (LE phosphorescence) excited states. The triflate salt of cationic complex [Au\textsubscript{3}(P44\textsubscript{bu})\textsubscript{2}]\textsuperscript{+} (n = 0, 109)\textsuperscript{236} with an linear arrangement of the trigold core is intensely deep-blue phosphorescent, demonstrating a quantum yield of 0.82 in acetonitrile solution (\(\lambda_{\text{em}} = 446\) nm, \(k_\text{r} = 2.1 \times 10^5\) s\textsuperscript{-1}) and 0.8 in the solid state (\(\lambda_{\text{em}} = 442\) nm), where the radiative rate constant is even higher and reaches an excellent magnitude of 3.0 \(\times\) 10\textsuperscript{5} s\textsuperscript{-1} and is comparable to that of [Au\textsubscript{3}(P32)\textsubscript{2}]\textsuperscript{3+} (80, \(\lambda_{\text{em}} = 460\) nm, \(k_\text{r} = 4.2 \times 10^5\) s\textsuperscript{-1}).\textsuperscript{170,171} Interesting behavior was disclosed for [Cu\textsubscript{6}I\textsubscript{5}(P44\textsubscript{bu})\textsubscript{2}]\textsuperscript{+} (n = 0, 110) and [Au\textsubscript{5}Cl\textsubscript{4}(P44\textsubscript{bu})\textsubscript{2}]\textsuperscript{+} (n = 0, 111), Fig. 46, the neat powders of which show emission maxima in the deep-red to
NIR region at $\lambda_{em} = 676$ nm ($\Phi_{em} = 0.29$) and 749 nm ($\Phi_{em} = 0.06$), respectively.237

Contrary to phosphorescent clusters derived from ligand P44, the complexes obtained from rigid diphosphine P45 predominantly emit ligand-centered fluorescence in solution ($\lambda_{em} \sim 500$ nm) under ambient conditions, despite possessing dinuclear and $\{\text{Au}_4\}, \{\text{Cu}_4\}, \{\text{Cu}_4\text{Br}_4\}$, and $\{\text{Cu}_5\text{Br}_3\}$ cores.238,239

A prospective direction for the development of bifunctional heterodentate phosphines to generate new luminescent d10-based molecular materials was recently suggested by Beckmann and coauthors, who introduced a carbanionic group into the ligand backbone. The P–C–P diphosphine P46 supports the tetragold string-like arrangement in $\{\text{Au}_4\text{Cl}_2(P46)\}_2$ (112) with short metal–metal contacts, which emits yellow–green light ($\lambda_{em} = 539$ nm) with $\Phi_{em}$ of 0.17 in the solid state.240 A more prominent result was obtained for copper(i), which reacted with the neutral silyl precursor Me3Si–C the solid state.240 A more prominent result was obtained for thione-containing diphosphine P47 to yield tetrannuclear complex $\{\text{Cu}_4(P46)\}_3^+$ (113, Fig. 47), having a distorted rhomboidal geometry of the metal core with Cu(i)–Cu(i) contacts of 2.316–2.725 Å.241 Cation 113 with the $\text{BArF}_4$ counterion displays bright green luminescence ($\Phi_{em} = 0.50/0.79$ in the solid state/THF solution), assigned to TADF. Although the radiative rate is not exceptional ($k_r = 5.0 \times 10^4/7.2 \times 10^3$ s$^{-1}$ in solid/solution), a high quantum efficiency is achieved due to suppressed non-radiative relaxation, apparently arising from the compact and rigid molecular structure. A solution-processed green OLED, fabricated with 113 as a dopant emitter, showed a maximum EQE of 11.2% at a brightness of 42 cd m$^{-2}$.

5.3 Complexes containing P–E ligands (E = chalcogen)

In view of the large number of d10 complexes formed from sulfur-containing ligands, there are remarkably few luminescent multinuclear compounds constructed from heterodentate phosphines with additional chalcogen donors. One example of a such ligand is thione-containing diphosphine P47 (Fig. 48), which is prepared from 4-phenylthiosemicarbazide. It binds to the gold(i) ion to form dimeric complex $\{\text{Au}_2(P47)\}_2^{2+}$ (114), in which sulfur atoms occupy bridging positions between the metal centers.242 Non-emissive in the solid state at 300 K, upon cooling, 114 demonstrates a gradual increase of the emission intensity maximized at 475 nm, which linearly depends on the temperature and has been correlated with the Au–S distance, as determined by variable-temperature structural studies. Room temperature luminescence was induced by co-crystallizing with protic solvents, resulting in a quantum yield of 0.06 and the shortest Au–S contact for the hydrate of 114.

6. Conclusions

The marriage of phosphine ligands with d10 coinage metal ions has a long and fruitful history. Progress in the synthetic and structural chemistry of polynuclear complexes of copper, silver and especially gold has been primarily associated with metallophilic interactions, framed by the ligand environment, which comprises a diverse family of organophosphorus P-donor compounds often combined with X-type bridging anionic ligands (alkynes, chalcogen derivatives, halides). Due to the cooperative effect of metal–metal and metal–ligand bonding, it is not easy to segregate the role of the phosphines on the assembly and photophysical properties of the described clusters. Nevertheless, it is clear that these ligands are very useful components to stabilize discrete multimetallic aggregates and govern their molecular architecture. The success of the phosphine-assisted self-assembly approach likely stems from the relative lability of the phosphorus–d10 metal bond, which allows for the utilization of simple starting components due to easy reorganization of the ligand sphere. Bridging phosphines have nearly unlimited potential for the variation of organic backbones, and they offer rich opportunities to alter the composition and topologies of the metal–ligand or cluster frameworks.

In relation to photoluminescence behavior, multinuclear phosphine complexes of coinage metals, as a wide class of compounds, undergo a number of electronic transitions, resulting in the formation of emissive excited states that provide substantial freedom in tuning of the photophysical characteristics through ligand design. Silver(i) and gold(i) phosphine assemblies without metal–metal interactions typically display intraligand ($\pi\pi^*$) emission of singlet or triplet multiplicities. Metallophilic bonding introduces metal (or cluster)-centered ($^1\text{MC}, ^3\text{CC}$ or $^3\text{XM}$) transitions responsible for lower energy phosphorescence. Although in many gold-based cluster compounds P-ligands contribute little to the frontier orbitals, they define the size and nuclearity of the cluster core, which has a decisive impact on the optical characteristics. On
the other hand, for complexes of smaller nuclearity and comprising lighter metals (Ag(I), Cu(I)), the aromatic system of the phosphines is generally involved in charge transfer excited states, such as metal to metal charge transfer (MMLCT), often mixed with X to ligand (phosphine) charge transfer (XLCT) for halide species.

Many bridging phosphorus-containing ligands and their coinage metal derivatives with fascinating luminescent features have been utilized in the cluster chemistry of these metals to a rather limited extent. In particular, merging classical anionic groups with soft phosphine donors and applying as-yet unexplored combinations in the coordination chemistry of copper subgroup metal ions could be a promising way to generate new structures and properties.

Conflicts of interest

There are no conflicts to declare.

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