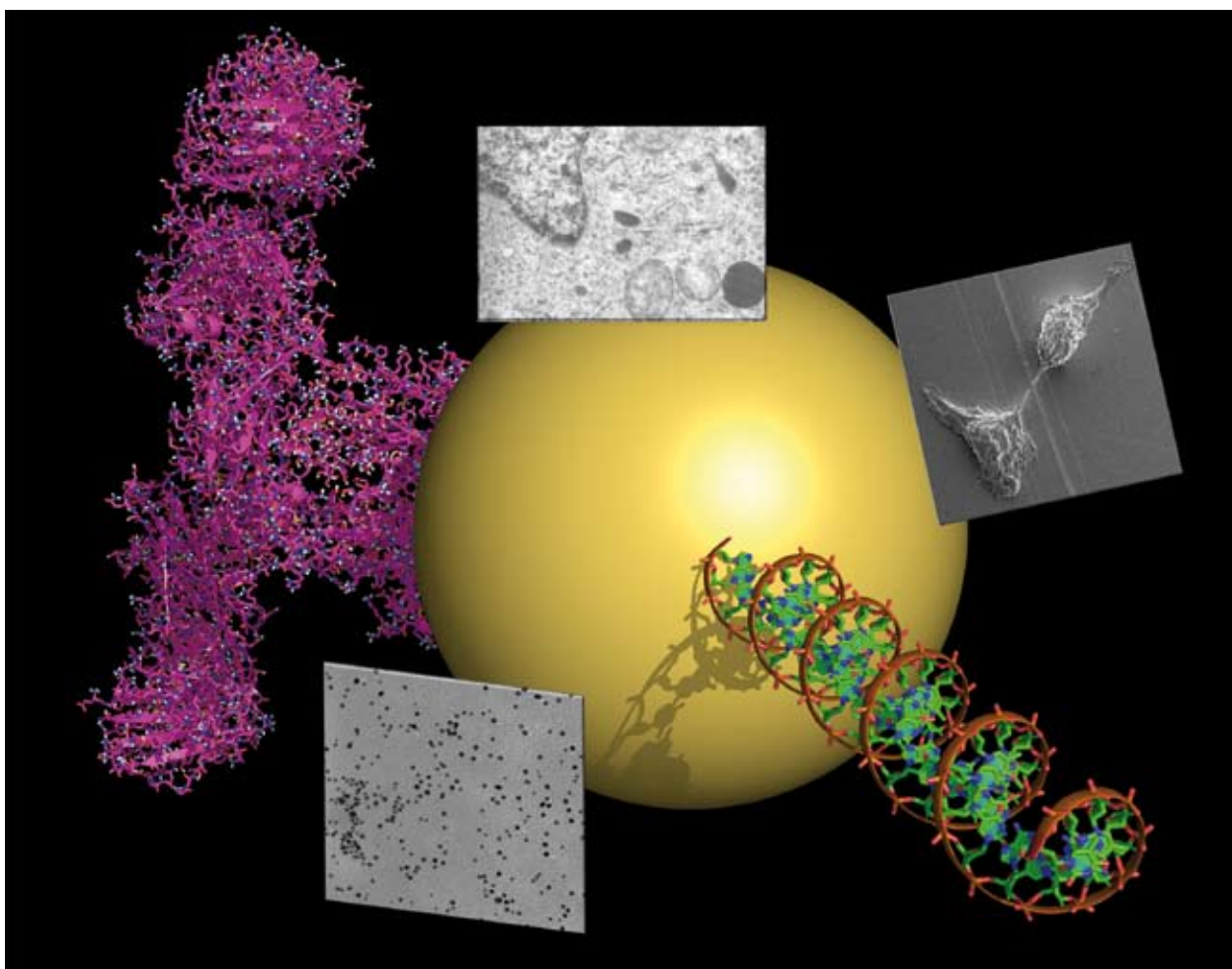


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Highlights on the recent advances in gold chemistry—a photophysical perspective†

Vivian Wing-Wah Yam* and Eddie Chung-Chin Cheng

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The presence of inter- and/or intra-molecular aurophilic interactions among the closed-shell gold(I) centres in various systems has been studied from various aspects, including synthetic, spectroscopic and theoretical approaches. The employment of different ligands can impose a significant influence on these factors and give rise to new complexes with interesting structural and photophysical properties. In this *tutorial review*, a number of recent examples are selected to illustrate the fascinating properties and chemistry, as well as versatility of gold(I) in these aspects and their potential applications to newcomers in this field. An emerging class of luminescent gold(III) complexes is also described.

1. Introduction

The chemistry of gold has attracted increasing attention in spite of the chemical inertness of metallic gold that makes gold a unique element and a measure of wealth. In particular, continuous efforts on the study of the coordination and organometallic chemistry have led to the discovery of a large number of novel gold metal complexes bearing oxidation states of +1, +2 and +3 with different coordination geometries. The strong relativistic effects possessed by gold also make itself unique.¹ Relativistic effects in chemistry refer to the associated phenomenon when high-speed electrons are moving close to a heavy atomic nucleus, causing an increase in the effective nuclear charge. The less-diffuse orbitals (such

as the s- and p-orbitals) will contract radially and be stabilized, whereas the more-diffuse orbitals (such as the d- and f-orbitals) will expand due to the enhanced shielding effect by the contracted s/p-orbitals. Gold exhibits a maximum relativistic effect among all other local neighbours in the periodic table, which means that the extent of contraction in the 6s and 6p orbitals, and at the same time the expansion of 5d orbitals, would be the most significant (Fig. 1). The observation of weak intermolecular attractive interactions present in between gold centres, especially in many mono- and polynuclear gold(I) systems, have attracted a growing attention and accelerated the development of gold(I) chemistry. Gold(I) has a closed-shell d^{10} electronic configuration and the tendency for weak metal-metal interaction involving affinity between same charges has been attributed to the sub-bonding interaction introduced through the stabilization of the filled 5d-orbital-based molecular orbitals with the empty molecular orbitals of appropriate symmetry derived from the 6s and 6p orbitals by configuration mixing. A simplified molecular orbital diagram explaining the configuration mixing in a tetranuclear gold(I) system was suggested by Vogler in 1988 (Fig. 2).² All these

Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research, Department of Chemistry, and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. E-mail: wwyam@hku.hk; Fax: +852 2857-1586; Tel: +852 2859-2153

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Vivian W.-W. Yam

Vivian W.-W. Yam obtained her BSc(Hons) and PhD from The University of Hong Kong. She is currently the Chair of Chemistry at her alma mater. She is a Member of the Chinese Academy of Sciences and a Fellow of TWAS, Academy of Sciences for the Developing World. Her research interests include the photophysics and photochemistry of metal complexes and clusters, and molecular functional materials.



Eddie C.-C. Cheng

Eddie C.-C. Cheng received his BSc(Hons) from The University of Hong Kong and his PhD in 2001 from the same university under the supervision of Prof. V. W.-W. Yam. He was awarded the Croucher Foundation Scholarship in 1999. After the completion of his PhD, he was a post-doctoral fellow, and then a research officer at The University of Hong Kong. His research interests include the synthesis and luminescence behaviour of polynuclear coinage d^{10} metal complexes.

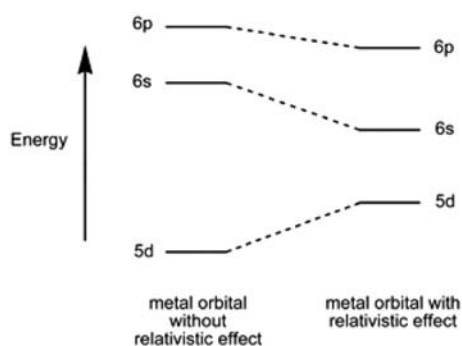


Fig. 1 Energy-level diagram showing the effect of relativistic effect on the energy of atomic orbitals.

effects would lower the energy differences between the filled-5d and empty-6s/6p orbitals, giving rise to a more effective overlap and stronger metal–metal interaction. The term “aurophilicity” describing this phenomenon has been introduced by Schmidbaur and is widely accepted nowadays.^{3,4} Its dispersion (van der Waals) nature according to theoretical studies suggested that the aurophilic attraction was caused by correlation effects and strengthened by relativistic effects rather than hybridization.⁵ In addition, the rich photophysical properties that gold complexes exhibit have no doubt made this class of complexes an important family of luminescent metal complexes.⁶ The presence of the heavy gold centre in these complexes would enhance the spin–orbit coupling of the system,

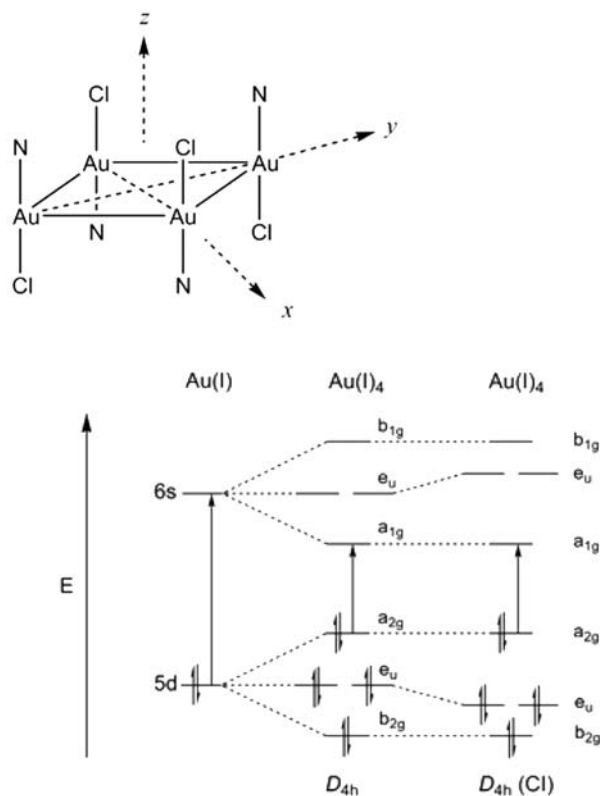


Fig. 2 Qualitative molecular orbital diagram of the Au_4^1 moiety including configuration mixing (CI = configuration interaction). Modified with permission from ref. 2. Copyright 1988, Elsevier Science B. V.

which in turn would facilitate the access to triplet excited states *via* intersystem crossing. Relaxation of the triplet excited state by radiative decay would usually result in phosphorescence with large Stokes shifts. Subsequently, the photophysical properties and the associated photochemical studies of some of these complexes have also been initiated.

In this article, selected recent examples of interesting luminescent gold systems will be discussed to highlight the fascinating luminescence properties of these systems and their potential applications.

2. Gold(I) alkynyls

There has been a growing interest in the exploration of novel alkynyl-bridged dinuclear complexes due to their potential application as molecular-scale electronics and NLO molecular materials.⁷ The alkynyl bridge, which is capable of connecting the two metal centres, provides a pathway for the two metal centres to communicate/couple electronically *via* its π -conjugated units. The spectroscopic and luminescence properties of this class of metal alkynyls involving triplet state of the alkynyl units, on the other hand, have received much less attention due to the presence of conjugated ancillary ligands that would hinder the direct observation of the π - π^* transition.^{8–10} Che and co-workers reported a series of alkynyl-bridged dinuclear gold(I) rigid-rod complexes bearing the optically transparent PCy_3 ligand ($\lambda \geq 250$ nm), $[(\text{Cy}_3\text{P})\text{Au}(\text{C}\equiv\text{C})_n\text{Au}(\text{PCy}_3)]$ ($n = 1–4$).^{11,12} The complexes with $n = 1$ and 2 showed a well-defined $[5d(\text{Au}) \rightarrow 6p(\text{Au})/\pi^*(\text{phosphine})]$ absorption band extending beyond 260 nm, whereas with $n = 4$ a highly vibronically structured electronic absorption at $\sim 274–290$ nm with vibrational progression of ~ 2010 cm^{-1} was observed and assigned as the dipole-allowed $[\pi \rightarrow \pi^*\{(\text{C}\equiv\text{C})_4\}]$ transition.

The ethynyl complex was non-emissive in dichloromethane at 298 K, while the butadiynyl counterpart showed a long-lived $^3[\pi \rightarrow \pi^*(\text{alkynyl})]$ emission at 417 nm. The ethynyl complex showed two dominant broad emissions centred at $\lambda_{\text{em}} = 415$ and 530 nm in both the solid state at 298 K and as alcoholic glass. The spin-forbidden nature of the lowest-energy $^3[\pi \rightarrow \pi^*(\text{alkynyl})]$ excited states was relaxed to a certain extent *via* spin–orbit coupling of the heavy gold centres for their prominence both in the electronic absorption and emission spectra. The hexatriynyl and octatetraynyl complexes exhibited sharp vibronically structured emission with the λ_{0-0} lines at 498 and 575 nm in dichloromethane, respectively, with vibrational progressions of ~ 2120 cm^{-1} , which could readily be assigned as the $^3[\pi \rightarrow \pi^*\{(\text{C}\equiv\text{C})_n\}]$ emission.

Subsequent studies on a series of mono- and dinuclear gold(I) complexes with arylalkynyl moieties coordinated to $[\text{Au}(\text{PCy}_3)]^+$ have been reported.¹³ Complexes with short arylalkynyl chains, including $[\text{Cy}_3\text{PAu}(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{Ph}, 4\text{-C}_6\text{H}_4\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Me}$), $\text{C}\equiv\text{CPh}$, py) and $[\text{Cy}_3\text{PAu}(\text{BL})\text{AuPCy}_3]$ ($\text{BL} = \text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$), showed emission bands at 408–488 nm in dichloromethane, whereas in the solid state a well-resolved vibronic-structured emission band at 420–493 nm with three types of progressional spacings ($\sim 1100, 1600$ and 2100 cm^{-1}) were assigned to the $^3[\pi \rightarrow \pi^*(\text{arylalkynyl})]$ emission. Complexes with more extensively conjugated arylalkynyl chains,

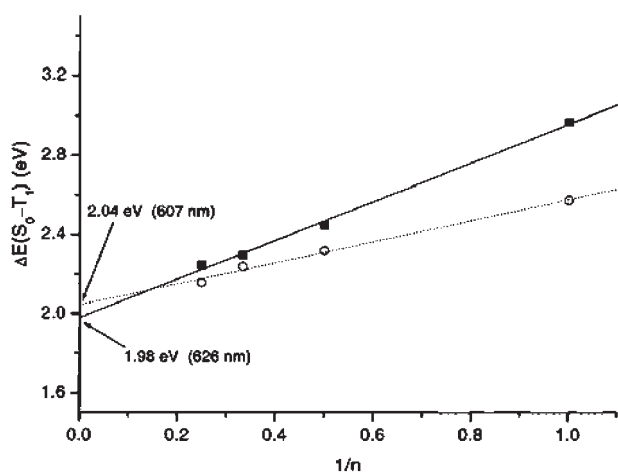


Fig. 3 Plot of $\Delta E(S_0-T_1)$ against $1/n$ in mononuclear $[(C_3P)Au\{(C\equiv CC_6H_4)_{n-1}C\equiv CPh\}]$ (■) and dinuclear $[(C_3P)Au\{(C\equiv CC_6H_4)_n C\equiv C\}Au(PCy_3)]$ (○) complexes. Reprinted with permission from ref. 13. Copyright 2002, American Chemical Society.

$[C_3PAu(C\equiv CR)]$ ($R = 4-C_6H_4Ph, C_6H_4(C\equiv CC_6H_4)_n C\equiv CPh$ ($n = 1, 2$)) and $[C_3PAu(LL)AuPCy_3]$ ($LL = (C\equiv CC_6H_4)_n C\equiv C$ ($n = 2-4$), $C\equiv C(C_6H_4)_2 C\equiv C$), displayed dual emissions at 330–407 and 495–558 nm. The high-energy emission was suggested to be the delayed fluorescence that occurred *via* a triplet–triplet annihilation mechanism. The phosphorescence energy was correlated linearly with the number (n) of $\{C\equiv C-C_6H_4\}$ units. Extrapolation from the linear plot of $\Delta E(S_0-T_1)$ vs. $1/n$ in the mononuclear $[(C_3P)Au\{(C\equiv C-C_6H_4)_{n-1}C\equiv CPh\}]$ and the dinuclear $[(C_3P)Au\{(C\equiv C-C_6H_4)_n C\equiv C\}Au(PCy_3)]$ ($n = 1-4$) complexes (Fig. 3) revealed an estimated $\Delta E(S_0-T_1)$ value for infinite repeating units (*i.e.* $[(C_3P)Au]$ -capped poly(*p*-phenyleneethynylene)s) of ~ 626 nm (1.98 eV) for the mononuclear species and ~ 607 nm (2.04 eV) for the dinuclear complexes.

$[(C_3P)Au(4-C\equiv CC_6H_4NO_2)]$ was found to exhibit polymorphism in the solid state.¹⁴ Two polymorphs (E- and N-forms) were structurally characterized, each with molecular dipoles in different orientations and with different dihedral angles between the neighboring nitrophenyl moieties (Fig. 4). The E-form showed ³IL phosphorescence maxima at 504 and 538 nm at 298 K, while the N-form showed an emission band at 486 nm at 77 K but was non-emissive at 298 K.

A number of examples on gold(I) alkynyls that show interesting functional moieties such as calixarenes, have been demonstrated by Yam *et al.*¹⁵ A series of phosphine-free tetranuclear gold(I) alkynylcalixcrown complexes was prepared from the direct reaction between $[Au(tht)Cl]$ and the alkynylcalixcrown ligand under basic conditions.¹⁶ Formation of insoluble polymeric gold(I) alkynyls was circumvented by the conformationally controlled and sterically protected calixcrown moieties. Interestingly, two of the gold(I) centres in these discrete tetranuclear gold(I) alkynylcalixcrown complexes were σ -coordinated by two alkynyl units forming the linear $C\equiv C-Au-C\equiv C$ bridges, while the other two Au centres were π -coordinated by the two adjacent alkynyl units

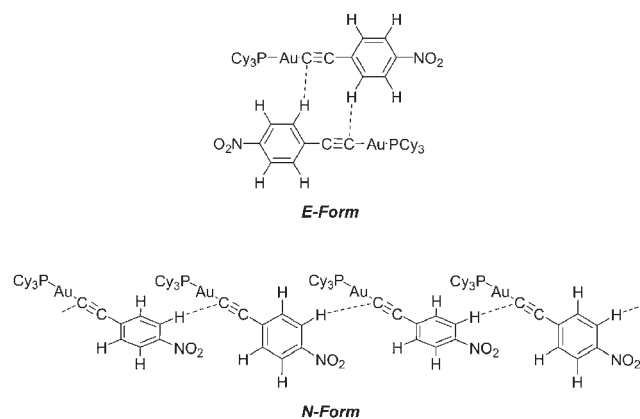


Fig. 4 The two polymorphic forms of $[(C_3P)Au(4-C\equiv CC_6H_4NO_2)]$.

in an unusual parallel η^2, η^2 bonding fashion (Fig. 5). Short $Au\cdots Au$ distances between adjacent gold atoms (3.1344(8), 3.2048(8) Å) were indicative of the presence of significant $Au\cdots Au$ interactions. The complexes displayed intense low-energy emission bands at ~ 590 – 620 nm, with the luminescence quantum yields of ~ 0.2 in chloroform at room temperature. Such emission was attributed to be derived from triplet states of metal-cluster-centred (ds/dp) character that were modified by $Au\cdots Au$ interactions, with some mixing of metal-perturbed intraligand $\pi-\pi^*(C\equiv C)$ states.

Azo-containing compounds are well-known to undergo reversible *trans-cis* isomerization reaction, and such properties have been utilized in the design and synthesis of molecular optical switches and logic gates.¹⁷ $[(dppm)Au_2(C\equiv CC_6H_4N=NC_6H_4C\equiv C)_2Au_2(dppm)]$, with an azo-containing alkynyl ligand,¹⁸ exhibited a $[\pi \rightarrow \pi^*(azo)]$ IL absorption band at ~ 380 – 390 nm and a $[n \rightarrow \pi^*(azo)]$ IL absorption tail at ~ 500 nm. The *trans-trans* to *trans-cis* photoisomerization process could be induced or reversed when irradiated at different wavelengths, inhibited when the alkynyl units were further π -coordinated to silver(I) centres, and restored upon removal of coordinated silver(I) ions by AgCl precipitation. As a result, the photoswitching process could be modulated *via* silver(I)-coordination/de-coordination, demonstrating a dual-input lockable molecular logic photoswitch (Fig. 6).

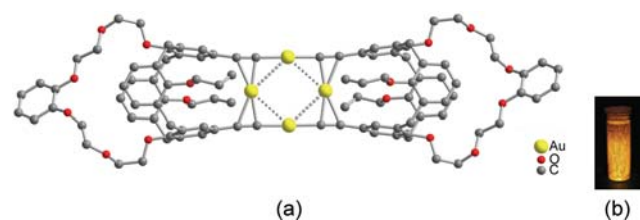


Fig. 5 (a) Structure of a tetranuclear gold(I) alkynylcalix[4]crown-6 complex. (b) Solid sample of the complex under UV irradiation at 298 K.

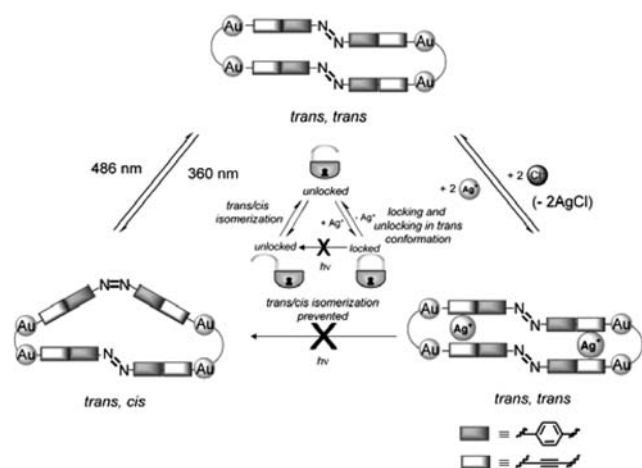


Fig. 6 Schematic diagram showing the “locking” and “unlocking” mechanism by the coordination and de-coordination of Ag^+ ions in $[(\text{dppm})\text{Au}_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{C})_2\text{Au}_2(\text{dppm})]$. Reprinted with permission from ref. 18. Copyright 2007, American Chemical Society.

3. Trinuclear gold(I) metallacycles

Trinuclear gold(I) isocyanide and pyrazolate complexes that possess intramolecular aurophilic contacts, were capable of displaying interesting luminescence associated with different extent of intermolecular stacking based on aurophilic interactions, which could be effectively perturbed by variation on the size and types of substituents on the ligands, pH, temperature, as well as the presence or absence of solvents, intercalating cations and aromatics.¹⁹ The solvent-stimulated luminescence (or solvoluminescence) of solid samples of $[\text{Au}_3(\text{MeN}=\text{COMe})_3]$ (Fig. 7(a)) was first reported by Balch.²⁰ $[\text{Au}_3(\text{MeN}=\text{COMe})_3]$ displayed a violet-blue photoluminescence in chloroform, whereas in the solid state it exhibited a dual luminescence behaviour with maxima at 446 and 552 nm. The crystal structure revealed indefinite columnar stacks of the triangular trinuclear units in both the eclipsed and staggered conformations, with the presence of weak intra- and intermolecular $\text{Au}\cdots\text{Au}$ interactions. When a polycrystalline

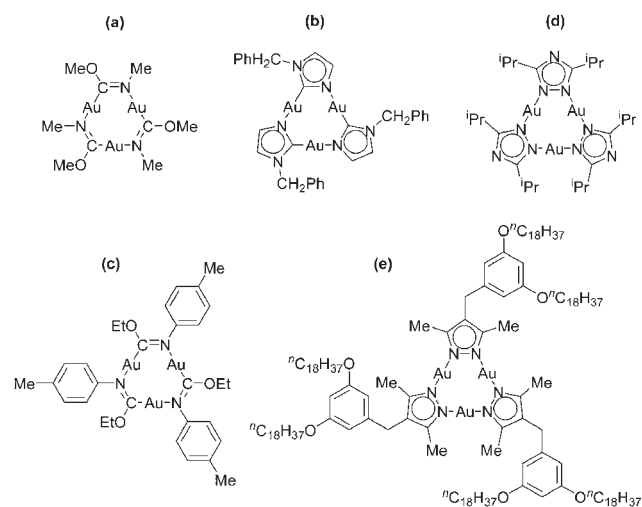


Fig. 7 Trinuclear gold(I) metallacycles.

sample of $[\text{Au}_3(\text{MeN}=\text{COMe})_3]$ that had been previously photo-irradiated at the near-UV wavelength was exposed to a drop of solvent in the dark, a spontaneous yellow emission, resembling the long-lived yellow emission in the dual luminescence of $[\text{Au}_3(\text{MeN}=\text{COMe})_3]$, could be observed. Such solvoluminescence behaviour was suggested to be related to the intermolecular aggregation present in the solid rather than to the discrete trinuclear monomers. Replacement of the N-methyl groups with the bulkier N-benzyl²¹ or N-isopropyl²² groups did not reproduce any intermolecular aurophilic interaction or any columnar stack in the crystal structure, and no solvoluminescence behaviour was observed.

The extensive intermolecular aurophilic Au_3 stacking was interrupted by intercalation using planar π -conjugated acids such as nitro-9-fluorenes and TCNQ, and the resultant crystalline adducts formed did not exhibit any luminescence nor solvoluminescence behaviour but low-energy charge-transfer absorptions were observed.^{23,24} Intercalation with perfluoronaphthalene resulted in phosphorescence of the perfluoronaphthalene due to the enhancement of the singlet-triplet intersystem crossing, whereas intercalation with perfluorobenzene quenched the blue Au_3 luminescence.²⁴ Intercalation with $[\text{Hg}_3(\mu\text{-C,C-C}_6\text{F}_4)_3]$ afforded a sandwiched complex that exhibited weak intermolecular $\text{Au}\cdots\text{Hg}$ interactions and a red shift in the emission energy,²⁵ while $[\text{Au}_3(\text{BzIm})_3]$ and $[\text{Au}_3(\text{MeC}_6\text{H}_4\text{N}=\text{COEt})_3]$ (Fig. 7(b) and (c)) could sandwich Ag^+ and Tl^+ ions to yield complexes bearing short intermolecular metallophilic contacts of $\sim 3 \text{ \AA}$ and exhibiting luminescence thermochromism. The Au_3 triazolate complex, $[\text{Au}_3(\text{C}_2\text{N}_3\text{-}^i\text{Pr}_2)_3]$ (Fig. 7(d)), was shown to exhibit multiple phosphorescence bands due to the different interconvertible effective symmetries that are governed by the temperature and concentration.²⁶ The quenching properties of $[\text{Au}_3(\text{C}_2\text{N}_3\text{-}^i\text{Pr}_2)_3]$ towards protonation by Bronsted acids and π -intercalation were also reported. Trinuclear gold(I) pyrazolate complexes with long alkyl chains were demonstrated to be capable of forming columnar mesophases based on the intermolecular aurophilic stacking interaction.^{27,28} Dendritic poly (benzyl ether) functionalized pyrazole ligands were recently employed in the synthesis of luminescent Au_3 complexes that formed superhelical fibres with extensive intermolecular Au_3 stacking and exhibited effective energy transfer from the dendritic wedge to the columnar $\{\text{Au}_3\}_n$ core (the antenna effect).²⁹ The gelation properties of the trinuclear gold complex (Fig. 7(e)) and its reversible RGB-colour switching could be achieved through the intervention of the Au_3 stacking by Ag^+ ions as illustrated in Fig. 8.³⁰ The red phosphorescence of the organogel was switched off upon the gel-to-sol process by heating, and restored upon cooling. Blue phosphorescence was achieved by doping a small amount of Ag^+ ions into the red-phosphorescent organogel and reverted by the addition of Cl^- ions that removed the Ag^+ ions as AgCl precipitates. The blue-phosphorescent Ag^+ -doped organogel was converted to the green-phosphorescent solution upon the gel-to-sol process by heating, and restored upon cooling. The green phosphorescence of this solution could be switched off by the addition of Cl^- ions that removed the Ag^+ ions as AgCl precipitates. These processes formed a reversible cycle with RGB-phosphorescence switching.

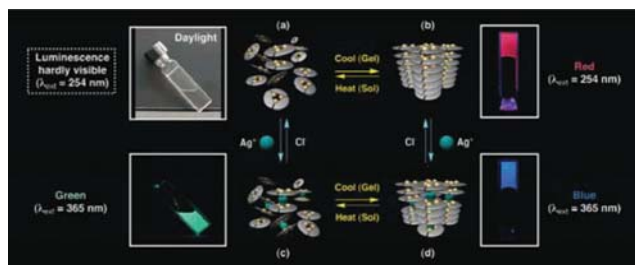


Fig. 8 Luminescence profiles of the Au₃ organogel in hexane. Pictures and schematic self-assembling structures of (a) sol, (b) gel, (c) sol containing AgOTf (0.01 equiv.), and (d) gel containing AgOTf (0.01 equiv.). Reprinted with permission from ref. 30. Copyright 2005, American Chemical Society.

4. Polynuclear gold(i) chalcogenido and chalcogenolate complexes

The exploration of luminescent molecular gold(i) chalcogenido complexes was initiated since the report on the isolation of a dodecanuclear gold(i) sulfido complex, [Au₁₂(dppm)₆S₄](PF₆)₄, and the associated photophysical properties in 1999, followed by subsequent reports on the related luminescent hexanuclear and decanuclear complexes, [Au₆{Ph₂PN(C₆H₄-Me-*p*)PPh₂}₃S₂](ClO₄)₂ and [Au₁₀{Ph₂PN(“Pr”)PPh₂}₄S₄](PF₆)₂^{31–33} (Fig. 9). The ancillary diphosphine ligands act as a “protective coating” against the formation of any binary materials. The X-ray crystal structures of these complexes revealed short Au···Au contacts in the range of 2.939–3.3775 Å and were indicative of the presence of significant aurophilic interactions. In addition, all the complexes displayed an orange to red emission that was derived from states of a ³LMMCT [S → Au···Au] origin. An abnormally large Stokes shift of 15 052 cm⁻¹ (1.87 eV) was also observed for the hexanuclear complex, suggesting its highly distorted excited state structure. A series of gold(i) selenido complexes, [Au₁₈Se₈(dpppe)₆Br₂] and [Au₁₀Se₄(dpppe)₄Br₂] was reported, with the former possessing long-lived solid-state red phosphorescence and capability to photosensitize singlet oxygen in solution, whereas the latter showed a broad NIR phosphorescence.³⁴

On the other hand, the luminescence studies of the related gold(i) thiolate complexes were initiated at an earlier time^{35–37} and there has been a growing interest in such systems involving the fine-tuning of the Au···Au interactions and the

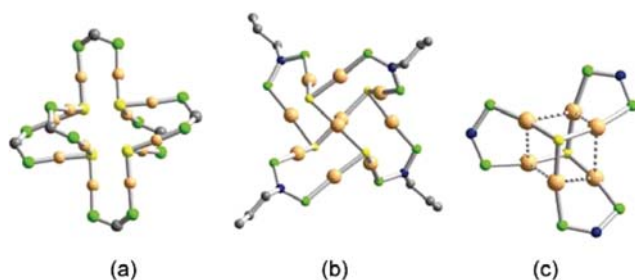


Fig. 9 Structure of (a) [Au₁₂(dppm)₆S₄](PF₆)₄, (b) [Au₁₀{Ph₂PN(“Pr”)PPh₂}₄S₄](PF₆)₂ and (c) [Au₆{Ph₂PN(C₆H₄-Me-*p*)PPh₂}₃S₂](ClO₄)₂.

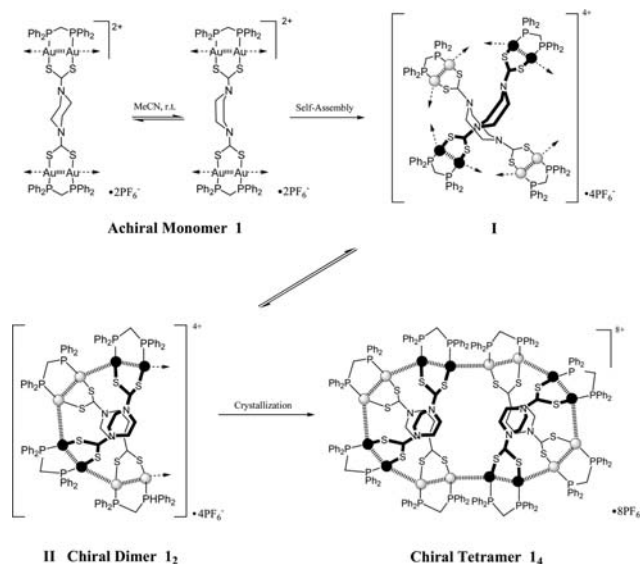


Fig. 10 Proposed chiral self-assembly process for the formation of a chiral macrocyclic Au₁₆ tetrameric complex from the achiral Au₄ monomer through Au(i)···Au(i) interactions. Reprinted with permission from ref. 40. Copyright 2005, American Chemical Society.

associated photophysical properties through different environmental perturbations. For instance, a series of diphosphine-bridged dinuclear gold(i) complexes with benzocrown-ether functionalized thiolate ligands were demonstrated to be capable of sensing alkali metal ions, with specificity depending on the size of the crown ether pendants.^{38,39} Upon encapsulation of alkali metal ions of appropriate size by intramolecularly sandwiching them between two crown ether pendants, *i.e.* K⁺ ion between two 15-crown-5 or Cs⁺ ion between two 18-crown-6 moieties, the intramolecular Au···Au interaction became “switched on” and the emission energy would be lowered according to the change of emission nature from a ³[RS → Au] LMCT to a ³[RS → Au···Au] LMMCT origin.

By using piperazine-1,4-dicarbodithiolate and dppm as bridging ligands, a tetranuclear gold(i) complex that crystallized as a tetramer (*i.e.* an Au₁₆ complex) by self-assembly, was reported. Upon the intermolecular aurophilic aggregation process, supramolecular chirality of the complex cation was induced (Fig. 10).⁴⁰ The Au₁₆ complex exhibited intense green solid-state photoluminescence that originated from ³[RS → Au] LMCT excited states that have been modified by the presence of weak Au···Au interactions, *i.e.* ³[RS → Au···Au] LMMCT excited states.

Eisenberg reported the vapochromism and VOC-induced luminescence behaviour of [Au₂{S₂CN(C₅H₁₁)₂}]₂.⁴¹ Intermolecular Au–Au distances of 2.9617(7) Å in the emissive solvated orange form and 8.135 Å in the non-emissive naked colourless form were observed in their crystal structures. Interestingly, when the colourless form was brought in contact with polar aprotic solvent vapors, luminescence could be restored. The formation of linear Au···Au chains induced by solvent triggered its orange colour and luminescence nature, even though there was no unusual complex–solvent interaction in the solid state.

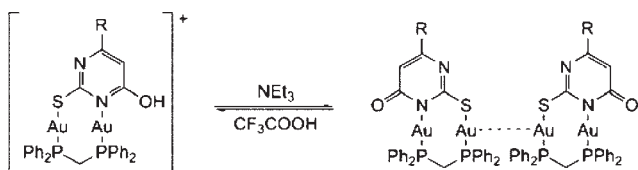


Fig. 11 Acid-base controlled interconversion of dinuclear gold(I) thiouracilate complexes.

Luminescence tribochromism, which refers to a sustained change in the photoluminescence spectrum upon the initial application of a pressure, was demonstrated in a series of dinuclear gold(I) thiouracilate complexes (Fig. 11).⁴² Interconversion of the weakly emissive complexes that possessed the singly deprotonated thiouracilate ligand, and the intensely blue-to-cyan photoluminescent counterparts with the doubly deprotonated ligand, could be achieved by pressure application and recrystallization, as well as through pH control, and monitored by the turning on-and-off of the emission. It was suggested that the observation of the intense emission is a consequence of the presence of strong intermolecular Au...Au interactions.

5. Heterometallic gold(I) complexes

The tendency for gold centres to aggregate is not limited to gold itself but also with other heavy metal centres such as silver, platinum, mercury and thallium in many mixed metal complexes, which often results in many interesting optical properties.⁴³ $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4\text{L}_2]_n$ ($\text{L} = \text{MeCN}$,⁴⁴ Me_2CO ⁴⁵) (Fig. 12) were prepared by the reaction of $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$ with silver salts, followed by crystallization in the respective solvent. The complexes possessed an extended polymeric chain structure in the solid state, with each tetranuclear $\{\text{Au}_2\text{Ag}_2\}$ unit exhibiting short Au...Ag and Ag...Ag contacts of *ca.* ~ 2.7 – 2.9 and 3.1 – 3.2 Å, respectively, and were linked together by short intermolecular Au...Au contacts ($2.8807(4)$ Å for $\text{L} = \text{MeCN}$; $3.1674(11)$ Å for $\text{L} = \text{Me}_2\text{CO}$).

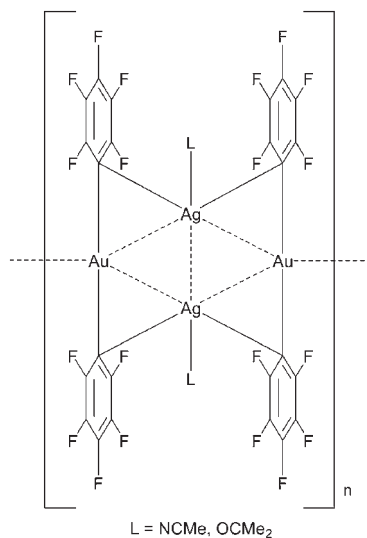


Fig. 12 Polymeric gold(I)–silver(I) complexes with concentration dependent luminescent properties.

Photoexcitation of the complexes in the solid state resulted in an intense yellowish green luminescence that has been attributed to originate from the metal-centred $(d\sigma^*)^1(p\sigma)^1$ or $(d\delta^*)^1(p\sigma)^1$ excited states. In dilute solutions, where intermolecular Au...Au interactions are insignificant, the complexes exhibited high-energy blue/green photoluminescence that might be attributed to excited states derived from the IL $[\pi \rightarrow \pi^*(\text{C}_6\text{F}_5)]$ or LMMCT $[\pi(\text{C}_6\text{F}_5) \rightarrow p\sigma(\text{Ag}/\text{Au})]$ transition. Upon increasing the complex concentration in solution, a significant red-shift in emission energy was observed, which was in line with the increase in the extent of $d\sigma$, $d\delta$ and $p\sigma$ overlaps associated with the intermolecular Au...Au interactions, and hence a decrease in the $d\sigma^*/d\delta^*-p\sigma$ energy gap. Interesting linear relationships for the emission energy ($\text{L} = \text{Me}_2\text{CO}$) and excitation energy ($\text{L} = \text{MeCN}$) against the reciprocal of the metal complex concentration were determined.

The vapochromic properties of a chain polymeric complex, $\{\text{Tl}[\text{Au}(\text{C}_6\text{Cl}_5)_2]\}_n$, subjected to a series of VOCs were reported by Laguna and Fackler.⁴⁶ The crystal structure of $\{\text{Tl}[\text{Au}(\text{C}_6\text{Cl}_5)_2]\}_n$ was composed of perfectly linear, continuous and unsupported Au(I)–Tl(I) interactions with Au(I)–Tl(I) separation of *ca.* 3 Å (Fig. 13). The thallium(I) ions were not bonded to any ancillary ligand but only weakly stabilized by the *ortho*-chloro groups in the adjacent $\{\text{Au}(\text{C}_6\text{Cl}_5)_2\}$ moieties. This, together with the presence of cavities of *ca.* 10 Å in diameter in the crystal lattice, rendered this system capable of interacting with other gaseous basic molecules to perturb the intermetallic separation and its associated photophysical properties. The colour of the complex, as well as its emission energy upon photo-excitation, could be perturbed significantly upon exposure to VOC vapour and reversed upon heating. For instance, the room-temperature solid-state emission energy of the complex was found to shift from 531 nm to 507 (thf), 511 (NEt_3), 513 (MeCN), 532 (Me_2CO), 567 (tht), 627 (2-F-py), 646 (py) and 650 (H-acac) nm upon exposure to the respective vapour. Related complexes of the type $\{\text{Tl}(\text{L})_2[\text{Au}(\text{C}_6\text{Cl}_5)_2]\}_n$ ($\text{L} = \text{solvent}$) were prepared and their photophysical properties were reported. Their solid-state emission energies at room temperature had an energy trend of $479 (\text{L} = \text{thf}) > 525 (\text{MeCN}) > 531 (\text{none}) > 554 (\text{NEt}_3) > 556 (\text{Me}_2\text{CO}) > 560 (\text{tht}) > 599 (2\text{-F-py}) > 644 (\text{H-acac}) > 665 (\text{py})$ nm, more or less in line with that observed in the vapoluminescent studies on $\{\text{Tl}_2[\text{Au}(\text{C}_6\text{Cl}_5)_2]\}_n$ for the respective vapour L. The discrepancy among the two trends was attributed to the difference in composition between the solvated complexes in the former trend where not all the Tl(I) centres were completely

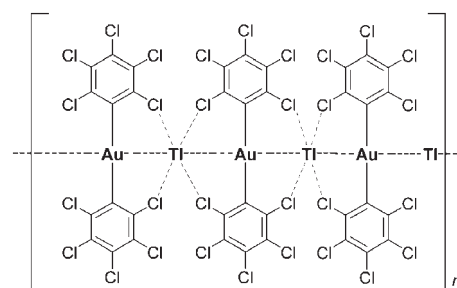


Fig. 13 Vapochromic gold(I)–thallium(I) complex.

ligated as two-coordinate Tl(I) centres, and that with complete ligation in the latter.

6. Gold(III) alkynyls

In contrast to the interesting luminescent gold(I) alkynyl system that has been supported by ample examples, reports on luminescent gold(III) alkynyl complexes are very scarce. Very recently, Yam and co-workers employed the dianionic bis-cyclometallated diarylpyridine ligands as the electron-rich and rigid skeleton in stabilizing the gold(III) metal centre in gold(III) alkynyls, and reported the successful isolation of a series of luminescent bis-cyclometallated gold(III) alkynyl complexes, $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CC}_6\text{H}_4\text{-R-}p)]$ ($\text{HC}^{\wedge}\text{N}^{\wedge}\text{CH} = 2,6$ -diphenylpyridyl; $\text{R} = \text{H}, \text{Cl}, \text{OMe}, \text{NH}_2, \text{NPh}_2$).^{47–49} The complexes were stabilized against thermal and photodecomposition through the strong σ - coordinations of the diarylpyridyl and alkynyl ligands. These strong σ -donor ligands could effectively raise the low-lying non-emissive d–d ligand field state energy, and hence disfavour any quenching mechanisms associated with thermal equilibration or energy transfer, as well as making the gold(III) centre less susceptible to undergo further reductive elimination reactions.

The alkynylgold(III) complexes were found to exhibit intense luminescence in various media at both low and ambient temperature. $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CC}_6\text{H}_4\text{-R-}p)]$ ($\text{R} = \text{H}, \text{Cl}, \text{OMe}$) exhibited characteristic metal-perturbed $[\pi \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ IL absorptions and phosphorescence, with their vibronically structured absorption bands at 362–402 nm and emission maxima at 474–476 nm in dichloromethane at 298 K, respectively. An additional low-energy absorption tail ascribed to an admixture of $[\pi \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ IL and $[\pi(\text{C}\equiv\text{CC}_6\text{H}_4\text{NR}_2) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ LLCT transitions was noted for complexes with $\text{R} = \text{NH}_2$ (~ 415 nm) and NPh_2 (~ 460 nm), because of the presence of the good electron-donating amino group on the phenyl alkynyl ligands. The emission energies of the complexes with $\text{R} = \text{NH}_2$ (611 nm) and NPh_2 (620 nm) in dilute solutions were significantly red-shifted, and the structureless feature of the emission band supports an assignment of a ${}^3[\pi(\text{C}\equiv\text{CC}_6\text{H}_4\text{NR}_2) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ LLCT origin. The intermolecular interaction were found to play a fairly significant role in determining the photophysical properties of this class of planar complexes. The organogold(III) complexes displayed a low-energy structureless emission band at 550–588 nm in the solid state, and such a red shift was attributed to dimeric or excimeric emission arising from the intermolecular π – π stacking of the planar $\{\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\}$ units. These assignments were further supported by the elucidation of the characters of the frontier orbitals using theoretical calculations and electrochemical studies.

The neutral nature of these gold(III) alkynyl complexes, their rich photophysical properties, the ease of fine-tuning on the emission energy *via* the use of substituent groups on the ligands with different electronic and steric effects, and the ease of incorporating functional units to enhance hole- and/or electron-transporting properties have suggested the inherent potential of using this class of complexes as both electrophosphorescent emitters and dopants in the fabrication of

multilayer organic-light-emitting devices (OLEDs) using vacuum deposition methods.⁴⁸ $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CC}_6\text{H}_4\text{-R-}p)]$ ($\text{R} = \text{H}, \text{NPh}_2$) were demonstrated to possess interesting electroluminescence properties and were employed in the fabrication of multilayer OLEDs. Dopant concentration- and voltage-dependent tunable OLEDs were fabricated and a maximum external quantum efficiency of 5.5%, corresponding to a current efficiency of 17.6 cd A⁻¹ and luminance power efficiency of 14.5 lm W⁻¹ were achieved in one of the multilayer OLEDs, indicative of the promising nature of using such type of complexes in OLED developments.

Conclusions

Gold complexes usually display interesting luminescence properties. The heavy gold metal centres are capable of enhancing intersystem crossing and providing an effective means for the access of the spin-forbidden triplet states upon photoexcitation to the singlet excited states. The less-explored luminescent gold(III) complexes, in general, could be obtained by raising the d–d LF excited state energy *via* the coordination of good σ -donor ligands. Homo- and heterometallic gold(I) complexes that are not sterically hindered in structures often display weak intra/intermolecular Au–M interactions ($\text{M} = \text{heavy atoms}$ including gold itself). Such kind of weak interactions usually play a crucial role in governing the interesting photophysical properties, especially when the metal-based orbitals contribute significantly to the character of the frontier molecular orbitals.

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