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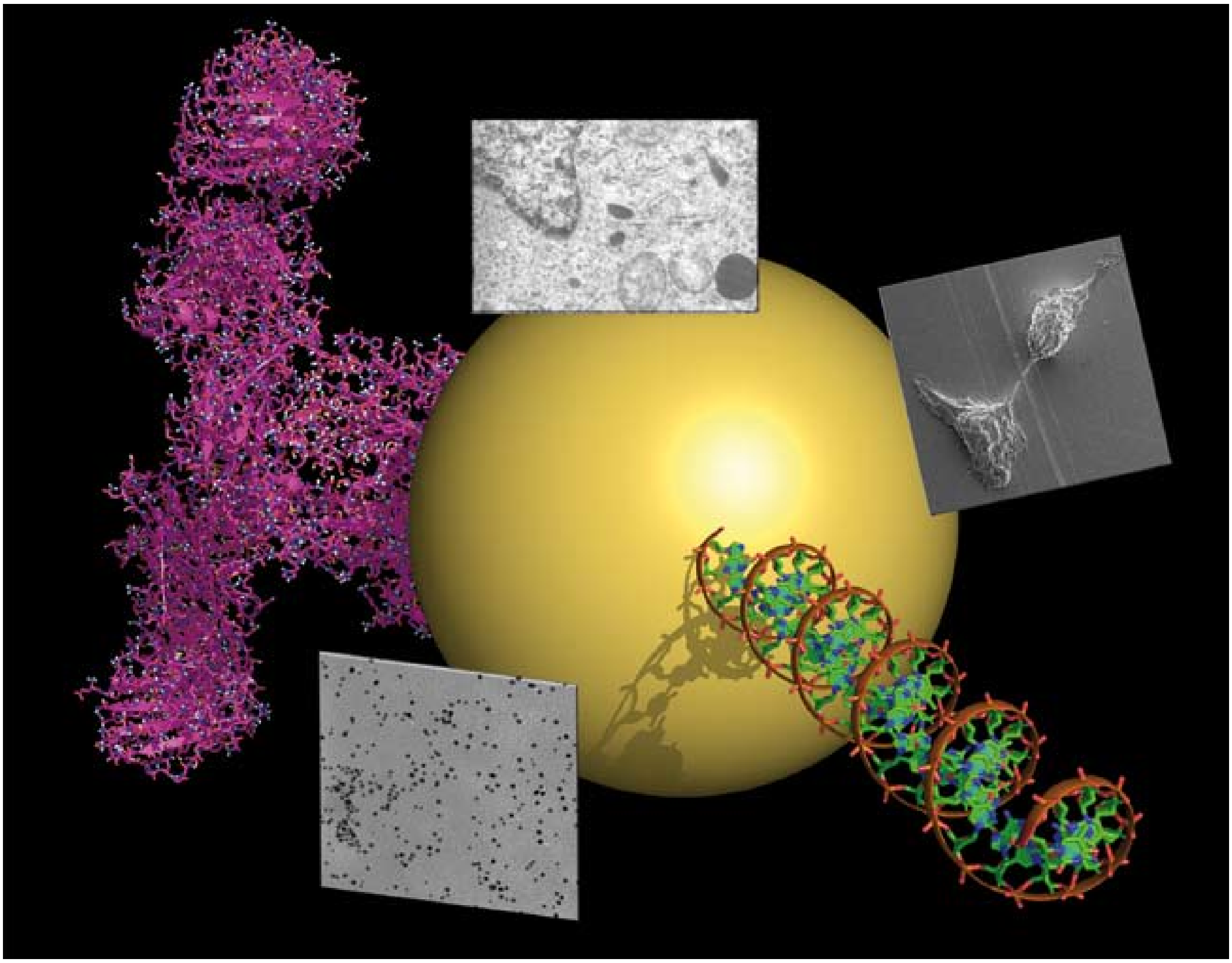

The use of aurophilic and other metal–metal interactions as crystal engineering design elements to increase structural dimensionality†

Michael J. Katz,[a] Ken Sakai[b] and Daniel B. Leznoff*[a]

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Research in the field of supramolecular chemistry has rapidly grown in recent years due to the generation of fascinating structural topologies and their associated physical properties. In order to rationally synthesize such high-dimensionality systems, several different classes of non-covalent intermolecular interactions in the crystal engineering toolbox can be utilized. Among these, attractive *metallophilic interactions*, such as those observed for d^{10} gold(I), have been increasingly harnessed as a design element to synthesize functional high-dimensional systems. This *tutorial review* will explore the methods by which gold(I) and other d^{10} and d^8 metal centres have been employed to increase structural dimensionality *via* the formation of metal–metal interactions. Physical and optical properties associated with metallophilicity-based supramolecular structures will also be highlighted.

Introduction

Supramolecular assemblies are polymeric systems in which molecular units, or building blocks, propagate infinitely in one-, two-, or three-dimensions.[1] The rational design and synthesis of these multidimensional compounds are driven by the demand for functional materials with tunable magnetic, conducting, vapochromic, optical, zeolitic or other properties.[2,3] This focus on supramolecular systems stems from the fact that the generation of many such properties is enhanced by, or depends on, the synthesis of high-dimensionality materials. Thus, one of the key requirements for generating functional materials by supramolecular self-assembly is the ability to rationally increase structural dimensionality.

In order to build supramolecular structures, the crystal engineering toolbox contains many types of interactions that can be harnessed, with hydrogen bonding, π–π stacking, and coordinate-bonding gaining perhaps the widest use.[1] For example, the addition of hydrogen-bonding groups into organic moieties to induce directional intermolecular interactions is a widespread technique for generating high-dimensionality systems.[4] Another dimensionality-increasing tool is based on the propensity of d^{10} metal ions such as gold(I) to be attracted to each other; in the case of gold(I), this effect has been termed "*aurophilicity*".[5,6] Aurophilic interactions arise from the overlap of the filled 5d orbitals with the empty 6s and 6p orbitals and is best described as a strong van der Waals attraction.[7] Thus, for a given d^{10}-metal complex, the presence of metal–metal distances that are shorter than the sum of the van der Waals radii is commonly used as a characteristic identifier for *metallophilic*


Daniel B. Leznoff

Daniel B. Leznoff (b. 1969, Toronto) received his PhD in 1997 from the University of British Columbia with Prof. M. D. Fryzuk and then moved to Bordeaux with Prof. O. Kahn as an NSERC Postdoctoral Fellow (1997–99). In 1999, he joined Simon Fraser University and is now Associate Professor of Chemistry. He was a JSPS Fellow during his 2007 sabbatical with Prof. K. Sakai (Kyushu). His interests include d^{10}-metal coordination polymers, paramagnetic organometallic and actinide chemistry.

Michael J. Katz (b. 1980, Haifa) received his BSc in chemistry from Simon Fraser University in 2004 and is currently an NSERC Doctoral Scholar there. His research with Prof. D. B. Leznoff targets $[Au(CN)_2]$-based heterometallic coordination polymers with vapochromic or birefringent properties.

Ken Sakai (b. 1962, Tokyo) received his BSc, MSc and PhD (1993) from Waseda University with Prof. K. Matsumoto. He became a Seikei University Research Associate, and moved in 1999 to the Tokyo University of Science. In 2004, he moved to Kyushu University as Professor of Chemistry. His interests focus on multinuclear metal complexes (especially Pt) as energy-conversion catalysts, metal–metal bonded systems and their conductivity and luminescence.

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[a] *Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, Canada V5A 1S6. E-mail: dleznoff@sfu.ca; Fax: 1-778-782-3765; Tel: 1-778-782-4887*
[b] *Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581, Japan*

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interactions in that material. Since attractive aurophilic interactions have an order-of-magnitude strength similar to hydrogen-bonding,[6] they should feature prominently in the crystal engineering toolbox as a design implement to increase structural dimensionality.

In addition, the photochemistry of compounds containing aurophilic interactions has been extensively studied in the solid state and in solution due to their interesting luminescence properties and the resulting applications.[8,9] Even dilute aqueous or methanolic solutions of $[Au(CN)_2]^-$ (and $[Ag(CN)_2]^-$) are luminescent, with concentration-dependent emission bands that shift depending on the degree of aggregation.[10]

Although the chemistry of gold has been extensively reviewed,[11] none have been specifically targeted to show how aurophilicity can be used as a crystal engineering design tool for increasing structural dimensionality. Thus, this tutorial review will focus on the design of and methods by which complexes containing d^{10} gold(I) can increase structural dimensionality *via* the formation of aurophilic interactions. For comparative purposes, the ability of the related d^{10} silver(I) and copper(I) metal centres, as well as d^8 systems such as platinum(II) and rhodium(I), to increase structural dimensionality will also be outlined. Metal-containing polymers in which the metal–metal bonds form part of a covalent backbone have been reviewed elsewhere and are beyond the scope of this article.[12]

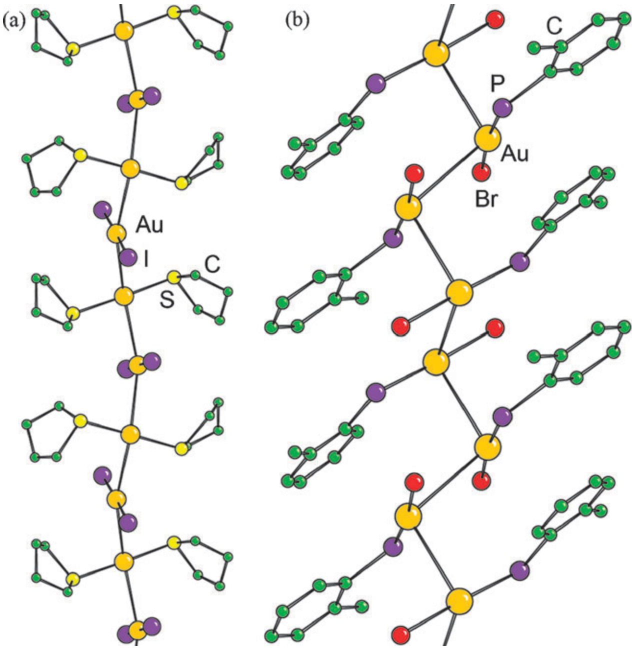


Fig. 1 (a) The 1-D chain of aurophilic interactions formed by the double salt [Au(tetrahydrothiophene)$_2$][AuI$_2$]. (b) The zig-zag 1-D chain of neutral [(2-methylphenylphosphine)AuBr] units.

Increasing structural dimensionality *via* Au(I)–Au(I) interactions

The simplest examples of gold(I) complexes that increase their structural dimensionality *via* the formation of Au(I)–Au(I) interactions can be found in molecular AuR_2 systems (R = ionic or neutral donors). This class of compounds can be separated into four categories: anionic gold(I) chains,[13] neutral gold(I) chains,[14,15] cationic chains,[14] and neutral chains formed *via* anionic & cationic Au(I) units, *i.e.*, double salts.[14,16] In all four cases, the structure of each molecule in the absence of aurophilic interactions resembles a rod or a cone, with a gold(I) atom at the centre. These gold(I) atoms link to one another *via* aurophilic interactions, increasing the dimensionality from an isolated molecule to a 1-D chain. Neutral gold(I) chains are particularly numerous: [(2-methylpyridine)AuCl] and [(2-methylphenylphosphine)AuBr] are two representative examples.[14,15] In general, gold(I)–gold(I) distances within the chains range from 2.967(2) and 2.979(2) Å for the double salt [Au(tetrahydrothiophene)$_2$][AuI$_2$] (Fig. 1a) to 3.4013(10) Å for cationic [Au(3-methylpyridine)$_2$](SbF$_6$).[14,16] However, rather than containing equally-spaced metal centres, many of these simple chains often have alternating gold–gold distances along the chain. For example, $(Me_4N)[Au(SCN)_2]$ has alternating distances of 3.1794(2) and 3.2654(2) Å. Cation substitution generated a series of (cation)$[Au(SCN)_2]$ chains for which the emission energy was observed to be inversely proportional to the Au(I)–Au(I) distance.[13] The angles between neighbouring gold centres in a chain range from 103 to 180° and, as with the distances, there is rarely only one angle present along the chain. Examining the torsion angles between R-groups on adjacent gold centres in the chains reveals a full range, from totally eclipsed (0 or 180°) to completely staggered (90°) linear units, but a more staggered arrangement is by far more common, as the steric effects of the ligands are minimized. A particularly unusual form of 1-D chain is found in the complex [(2-methylphenylphosphine)AuBr] (Fig. 1b), which contains pairs of [(2-methylphenylphosphine)AuBr] units bound at a distance of 3.097(1) Å with a torsion angle of 90°. These dimers link to the next pair at a longer distance of 3.380(1) Å, with a torsion angle of 180°, *i.e.* linking the dimers in a head-to-tail fashion. Unlike most chains, which are nearly linear, this system forms a zig-zag 1-D chain.[15]

In addition to influencing emission properties, generating aurophilic chains can also impact other physical properties of a material. The system (RNC)AuCl, where R is a C_2–C_{12} linear alkyl moiety, forms 1-D chains *via* aurophilic interactions in the solid-state. However, for the C_7–C_{11} systems, in addition to the solid and liquid phases, an intermediate mesogenic rotator phase was also observed.[17] This was attributed to the formation of bilayers with alternating aurophilicity-supported headgroups and hydrocarbon tails. This example clearly shows that aurophilic interactions can be used as a design element to induce the formation of mesomorphic phases in the absence of traditional mesogenic units such as aromatic rings, a result of the uniaxial gold(I)-based increase in structural dimensionality.

Although utilizing very bulky R-groups can yield isolated mononuclear AuR_2 systems, using very *non*-steric R-groups can induce the formation of 2-D arrays. For example, in [Au(*o*-xylylNC)CN] a typical 1-D chain is generated, with aurophilic interactions of 3.4615(6) and 3.4220(6) Å and torsion angles of 155° (Fig. 2). However, a second [Au(*o*-xylylNC)CN] unit bridges neighbouring chains to one another *via* shorter 3.1706(4) Å aurophilic interactions and a near-perpendicular torsion angle.[18] The propensity of shorter

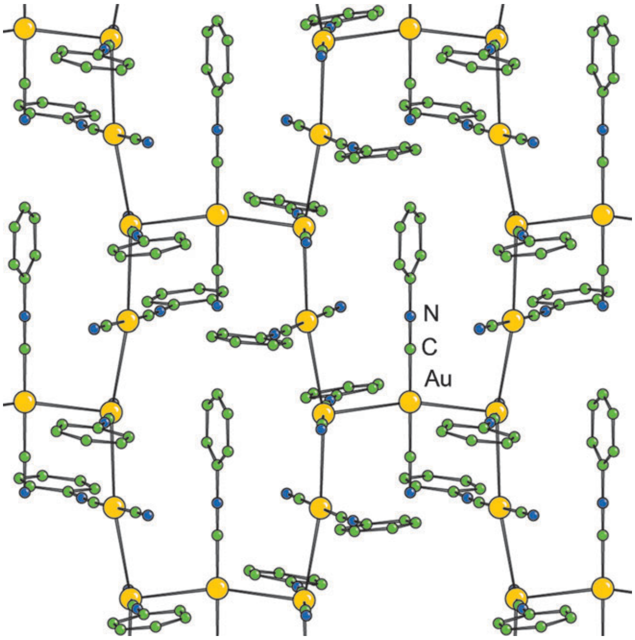


Fig. 2 2-D structure of [Au(*o*-xylylNC)CN] (xylyl methyl groups omitted for clarity).

bonds to form with perpendicular torsion angles is due to the steric repulsion of the R-groups on the gold(I).

The complexity of these 1-D chains can be increased by replacing the monodentate donors with small bite-angle, bidentate ligands; these enhance the formation of discrete Au(I) dimers or multimers, which contain intramolecular Au(I)–Au(I) bonding. These multinuclear complexes can further link to one another *via* the formation of intermolecular aurophilic interactions, once again increasing structural dimensionality. For example, using dithiophosphonate bridging ligands such as the asymmetric $[S_2PR(OR')]^-$, gold(I) dimers with intramolecular aurophilic interactions ranging from 2.954–3.235 Å (depending on the R-group) have been synthesized. These dimers form a 1-D chain *via* intermolecular aurophilic interactions (Fig. 3), with distances ranging from 2.926–3.082 Å and intermolecular torsion angles of *circa* 70°.[19] Note that although the gold(I) atoms within the dimer are held quite close together *via* the bridging ligand, the intermolecular aurophilic interactions are all shorter than the intramolecular ones. This trend, while common, is not universal: a hexamer of gold atoms in the *o*-methyldithiobenzoatogold(I) cluster $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$ contains intramolecular aurophilic interactions primarily below 3.0 Å, and intercluster ones of 3.195(1) Å.[20]

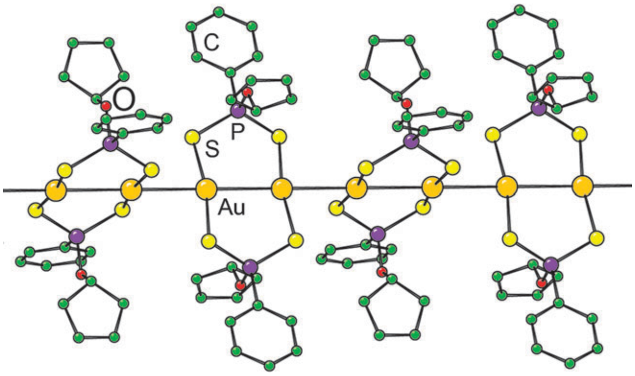
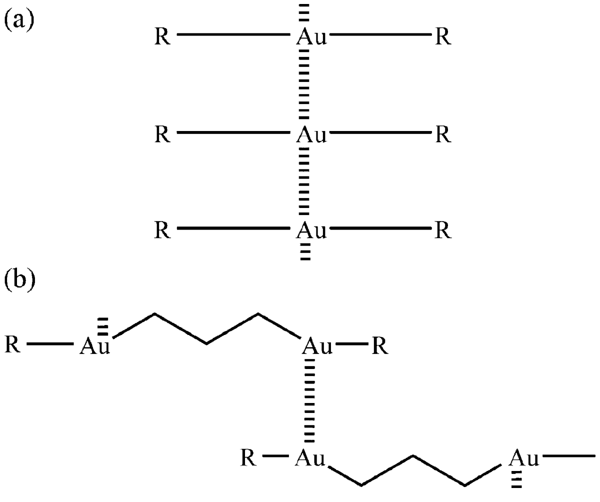


Fig. 3 1-D chain of dimers of $Au_2[S_2PPh(OC_5H_9)]_2$, formed from intra- and intermolecular aurophilic interactions.



Scheme 1

The examples above illustrate how gold(I) molecules can aggregate *via* the formation of infinite 1-D chains or 2-D arrays of aurophilic interactions, thereby increasing structural dimensionality (Scheme 1a). However, multidimensional systems can also be formed where discrete molecules containing two or more *remotely situated* gold(I) atoms link *via* dimer-forming aurophilic interactions (Scheme 1b).

Many such systems contain two gold atoms at opposite ends of a diphosphine, dithiolate, diisocyanide or diacetylide donor bridging ligand or combinations thereof.[21–23] For example, each phosphine in the diphosphine ligand series $Ph_2P(CH_2)_n$-PPh_2 (n = 4–8) can independently bind an AuX (X = Cl, I) unit to yield a bis-monodentate digold molecule. Intermolecular gold–gold bonds of 3.130(1) Å link neighbouring molecules (X = I, n = 8) to form an overall 1-D chain (Fig. 4a).[21] Similarly, the reaction of a 1,3,5-triethynylbenzene framework with three ^{t}BuNC–Au fragments forms a triangular molecule which aggregates into 1-D chains *via* the use of two Au(I)–Au(I) interactions; inexplicably, the 3rd Au(I) centre does not participate in any aurophilic interaction (Fig. 4b).[22] Thus, depending on the distance between donor atoms, the bridge flexibility and secondary π–π or other bonding forces, these types of gold(I) systems can form chains, rings, catenanes or polymeric structures.[22] A more intricate example of this principle is illustrated in Cu(diethylenediamine)$[Au(CN)_2]_2$, where interdigitated molecular units link *via* 3.33–3.36 Å intermolecular aurophilic interactions rather than Cu–N-(cyano) coordinate bonds, to form a 1-D chain (Fig. 5).[24]

The two methods of employing infinite aurophilic chains and bridging ligands with remote gold(I) centres to increase dimensionality can be seen simultaneously in action. For example, in the case of the gold(I) complex with the tritopic bridging ligand $(Me_2P)_3CMe$, each phosphine donor binds to one gold(I) centre (Fig. 6). Two gold(I) centres are bridged by two phosphine groups, with aurophilic interactions of 3.084(2) Å. These gold

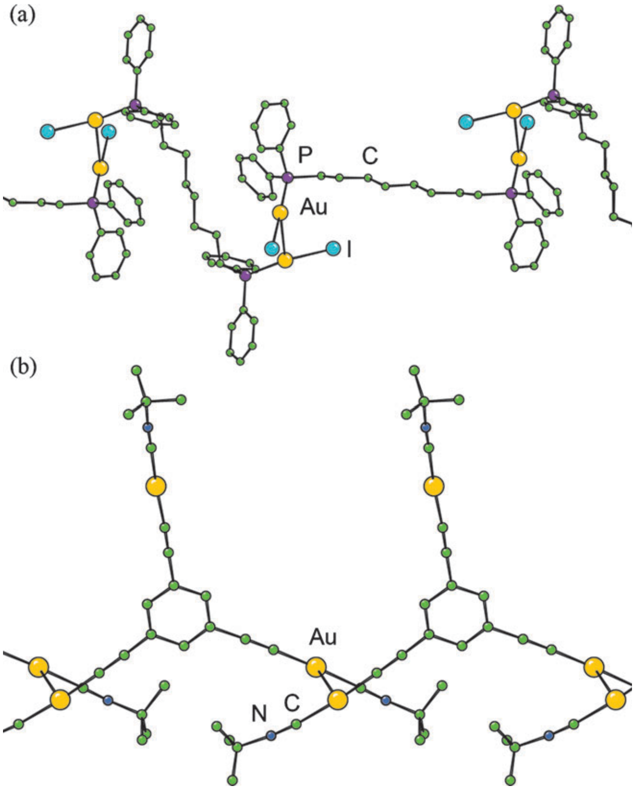


Fig. 4 (a) 1-D chains of $IAu(Ph_2P(CH_2)_8PPh_2)AuI$ formed *via* discrete gold–gold dimers at either end of the molecule. (b) The 1-D chain structure of $[1,3,5\text{-}(t\text{BuNC–Au–CC})_3C_6H_3]$, formed by discrete gold–gold dimers.

units link to one another to form a continuum of 3.077(2) Å intermolecular aurophilic interactions. The third gold(I) centre only forms dimers, linking neighbouring chains to one another through 3.179(3) Å aurophilic interactions.[25]

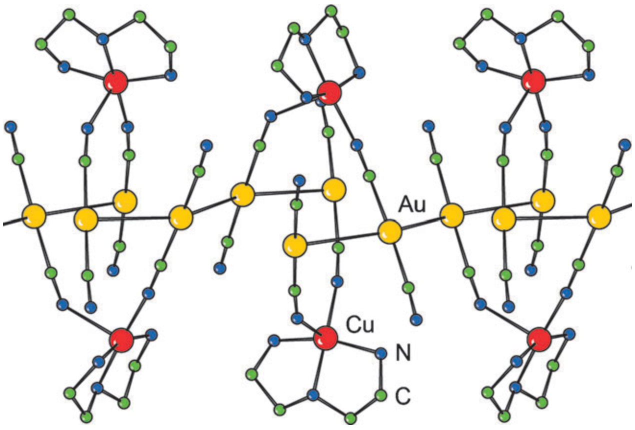


Fig. 5 The 1-D chain structure of $Cu(diethylenediamine)[Au(CN)_2]_2$, generated *via* a combination of aurophilic interactions and coordinate bonds.

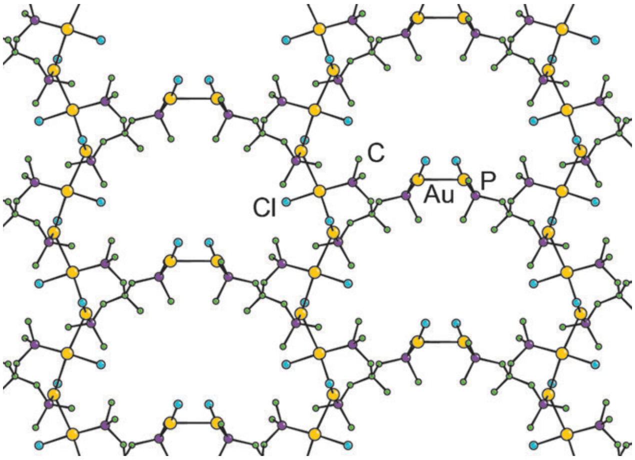


Fig. 6 2-D sheet of $MeC(PMe_2)_3AuCl$ generated *via* an aurophilic 1-D chain (vertical) linked through dimers of gold (horizontal).

Until fairly recently, and as exemplified by the cases above, compounds which increase their structural dimensionality *via* aurophilic interactions have been predominantly species in which the only metal present is the gold(I) centre itself; most of these systems are molecular if the Au(I)–Au(I) interactions are ignored. Our group has been among those pioneering the concept that aurophilic interactions could be used (like hydrogen-bonding) as a *tool* to increase dimensionality in systems containing *other metals* in addition to gold(I).[24,26–30] Thus, combining a gold(I) moiety into heterometallic compounds introduces a secondary building unit, which can further increase the structural dimensionality *via* the formation of aurophilic interactions. We considered the dicyanoaurate(I) ($[Au(CN)_2]^-$) building block to be an ideal unit with which to explore this principle of using aurophilicity as a supramolecular design element since (1) many other cyanometallates form a wide range of heterometallic coordination polymers, (2) the linear geometry of $[Au(CN)_2]^-$ favours the formation of aurophilic interactions and (3) compounds containing $[Au(CN)_2]^-$ are known to have luminescent properties both in the solid-state and in solution, and in principle materials incorporating the $[Au(CN)_2]^-$ unit could retain this useful property.[8,10] One of the first successful illustrations of this design principle in action was the synthesis of $Cu(tmeda)[Au(CN)_2]_2$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Its structure contains a zig-zag 1-D chain of Cu–N-CAuCN–Cu units, which exhibits ferromagnetic interactions along the chain mediated by the diamagnetic Au(I) centre.[26] A pendant $[Au(CN)_2]^-$ unit is also bound to the Cu(II) centre (Fig. 7a). In addition to this 1-D coordinately bonded framework, each gold centre participates in aurophilic interactions: the Au(I) atoms in the backbone of the 1-D chain form interchain 3.5378(8) Å interactions, yielding a 2-D array of alternating 1-D zig-zag chains in the *ab* plane (Fig. 7a), while the pendant Au units bind (3.345(1) Å) to their counterparts on adjacent chains in the *bc* plane (Fig. 7b), yielding a ladder-rung type motif running parallel to the 1-D chains. The complete 3-D picture of the structure is shown in Fig. 7b. The aurophilic interactions have increased the structural dimensionality from one to three.

Systematic substitution of the metal cation, and the tmeda for a range of other nitrogen/oxygen containing capping ligands, generated a series of transition metal–Au(I) coordination polymers. Aurophilic interactions in many of these

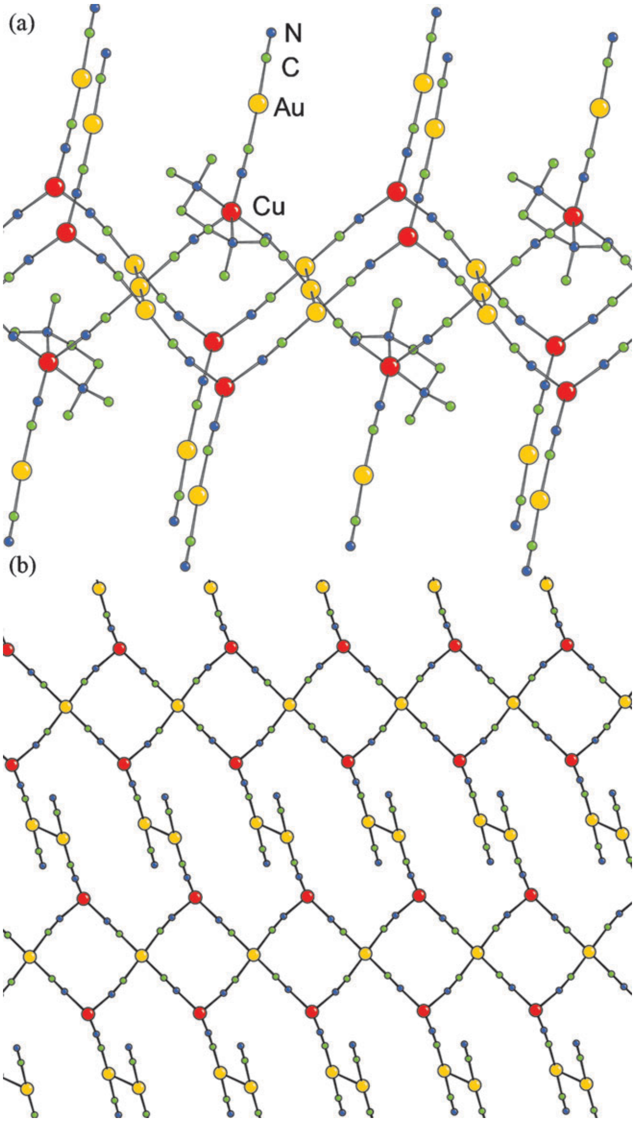


Fig. 7 (a) Coordinately bonded 1-D chains of Cu(tmeda)[Au(CN)$_2$]$_2$, linked *via* aurophilic interactions to form a 2-D sheet (tmeda omitted on 2 of the 3 chains for clarity). (b) 2-D sheets link together through the pendant [Au(CN)$_2$]$^-$-unit, forming the overall 3-D structure (tmeda omitted for clarity).

polymers also increased structural dimensionality, thereby illustrating the potential generality of the method.[24]

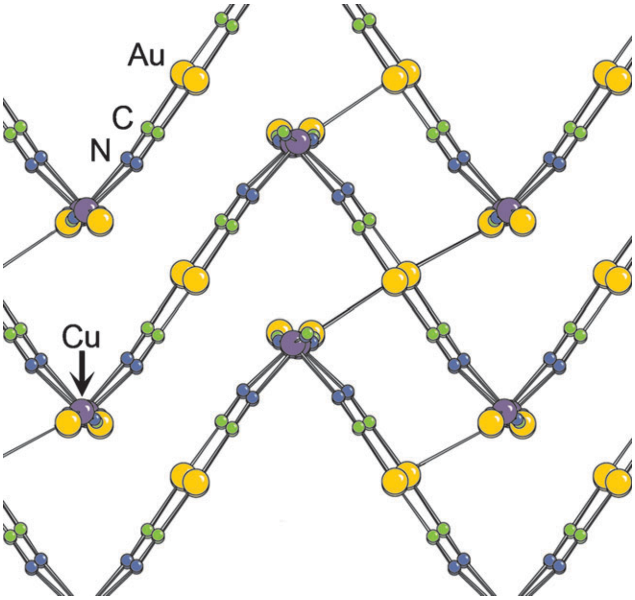


Fig. 8 2-D sheets of Cu(DMSO)$_2$[Au(CN)$_2$]$_2$ form a 3-D structure *via* intersheet aurophilic interactions.

Although most of the [Au(CN)$_2$]$^-$-based coordination polymers have been prepared with 1st row transition metals, the family can easily be expanded to include other metals, including main group cations. For example, the coordination polymer Pb(H$_2$O)[Au(CN)$_2$]$_2$ contains an 8-coordinate Pb(II) ion in a bicapped trigonal prismatic geometry.[28] A 2-D structure is formed *via* the cyanide and aqua bridging units; gold–gold interactions stack the sheets, generating an overall 3-D structure. A large birefringence (Δn), which corresponds to the non-zero difference in the refractive indices of a crystal in two perpendicular directions, was observed for this polymer: Δn = 0.070. The birefringence was attributed to the parallel alignment of the [Au(CN)$_2$]$^-$-units in this polymer along one of the crystal growth directions. Substituting the water unit with terpyridine, a very anisotropically polarizable chelate, produced a polymer with a remarkably large birefringence, Δn = 0.40.[29]

Utilizing monodentate ligands can also yield polymers with interesting physical/optical properties. In the case of Cu(DMSO)$_2$[Au(CN)$_2$]$_2$, neutral 2-D corrugated square grids of Cu[Au(CN)$_2$]$_2$ are linked *via* 3.419(3) Å aurophilic interactions, thereby converting the 2-D coordinately bonded-network into a 3-D array (Fig. 8)[27] This polymer readily substitutes the DMSO ligand with a wide range of other volatile donor atom-containing molecules, such as ammonia, pyridine, dimethylformamide, water and dioxane, in the vapour phase. Both the colour and ν_{CN} vibration of the Cu[Au(CN)$_2$]$_2$ polymer change depending on the identity of the donor molecule bound to the polymer framework. This polymer thus acts as a vapochromic sensor.

In some coordination polymers, aurophilic interactions do not increase structural dimensionality, but merely support it. This is observed in 3-D coordinately bonded structures such as the four polymorphic Zn[Au(CN)$_2$]$_2$ coordination polymers in which the (*n*-fold) interpenetrated networks are supported by 3.1–3.3 Å inter-network aurophilic interactions (Fig. 9).[30,31] Since the structure is already 3-D, the aurophilic interactions cannot further increase structural dimensionality, however they may play important roles in templating or stabilizing the material. These four polymorphs luminesce at different energies, corresponding to the average gold–gold distance in the polymer. Similar to the Cu(DMSO)$_2$[Au(CN)$_2$]$_2$ system described above, if these polymorphs are exposed to ammonia vapour, the structure of the Zn[Au(CN)$_2$]$_2$ framework changes to accommodate two zinc-bound ammonia units. This transformation leads to a concomitant shift in the emission energy of the polymer, attributed to the change in the distance between neighbouring gold-units and thus this material acts as a very sensitive (ppb-level) vapoluminescent sensor for NH$_3$.[30]

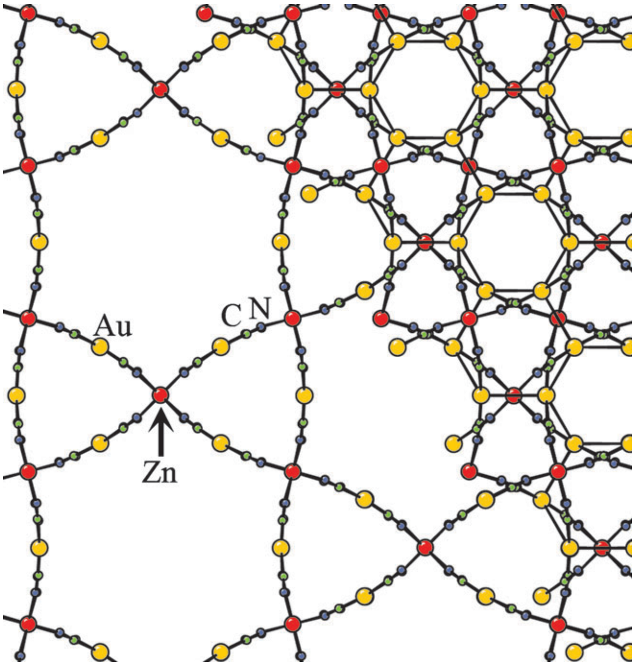


Fig. 9 (left) One 3-D quartz network of $Zn[Au(CN)_2]_2$. (right) All six interpenetrated networks of $Zn[Au(CN)_2]_2$, held together *via* inter-network aurophilic interactions.

While the $Zn[Au(CN)_2]_2$ example above illustrates how interpenetrated 3-D networks can be held together *via* gold–gold interactions, this phenomenon is not limited to dimensionally saturated structures. For example, in the 2-D $Cu(tmeda)[Au(CN)_2](ClO_4)$ polymer,[24] aurophilic interactions of 3.4018(7) Å link interpenetrated sheets to one another but, unlike in the aforementioned $Cu(DMSO)_2[Au(CN)_2]_2$ system, the polymer remains 2-D upon including the aurophilic interactions.

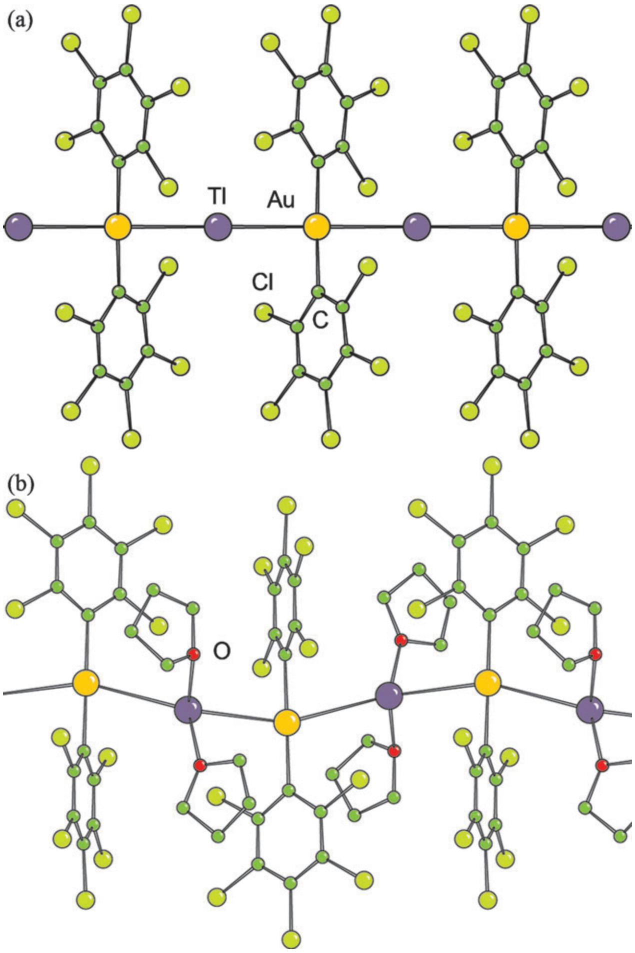


Fig. 10 (a) 1-D chain of $Tl[Au(C_6Cl_5)_2]$ formed by thallium(I)–gold(I) interactions; (b) Same 1-D chain after exposure to THF.

Increasing structural dimensionality *via* mixed Au(I)–metal interactions

With the expectation of generating interesting structures and photoluminescence, materials with mixed Au(I)–metal($d^{10}s^n$) interactions (n = 0, 2) have also received a great deal of attention; this subject has been recently reviewed.[32] Most notable are complexes with Au(I)–Tl(I) interactions. The use of bis(halophenyl)aurates such as $[Au(C_6X_5)_2]^-$ (X = Cl, F) in conjunction with $d^{10}s^2$ Tl(I)-cations has yielded a series of Au(I)–Tl(I)-chain materials (Fig. 10). For example, chains of alternating Tl^+ and $[Au(C_6Cl_5)_2]^-$, with Au(I)–Tl(I) bonds of 2.9726(5) and 3.0044(5) Å have been synthesized, and shown to be vapoluminescent at room temperature; the Tl–Au-based solid-state emission changes from 507 to 627 nm upon changing the solvent vapour (*e.g.* THF, THT, 2-fluoropyridine) above the material.[33] The assembly process here is essentially an acid–base double salt-forming reaction, with the metallophilic interaction supported by electrostatic attraction forces. This is a useful general methodology for enhancing metal-supported aggregation and increase of structural dimensionality between cations and anions. Variants that incorporate a range of terminal and bridging ligands (*e.g.* 4,4′-bipyridyl) on the Tl(I) centre have also been prepared and show strong emissive properties.[32]

Similarly, incorporating d^{10} Ag(I) cations with Au(I)-containing anions can increase structural dimensionality *via* the formation of mixed Au(I)–Ag(I) interactions. As in the Tl^+ double-salt example above, utilizing the $[Au(C_6F_5)_2]^-$ anion with a series of $[AgL]^+$ units (L = tetrahydrothiophene, benzene; other O-, N-, S- and P-donors have been used as well) generated 1-D chains *via* short Au(I)–Ag(I) distances of *circa* 2.7 Å and Au(I)–Au(I) distances of 2.9–3.2 Å.[32] Utilizing anionic gold(I) diacetylide species, a simple 1-D chain of the double salt $[Ag(Me_3P)_2][Au(CCPh)_2]$ was synthesized and found to contain alternating Au(I)–Ag(I) interactions of 3.206(2) and 3.224(2) Å, with a near-linear Ag–Au–Ag angle.[34]

A few Au(I)–Ag(I) chains that assemble based primarily on the closed-shell interaction (as in the homometallic Au-section) rather than utilizing the double-salt route have also been reported. The anionic MTP ligand, $[CH_2P(S)Ph_2]^-$, has been used to great effect in the preparation of a range of bridged dinuclear metal complexes with interesting emission properties.[35] In the case of $[AgAu(MTP)_2]_n$, an Au(I)–Ag(I) intramolecular bond of 2.9124(13) Å supports the dimer, which aggregates into 1-D chains *via* longer intermolecular Au(I)–Ag(I) contacts of 3.635 Å.[35] A comparison with the

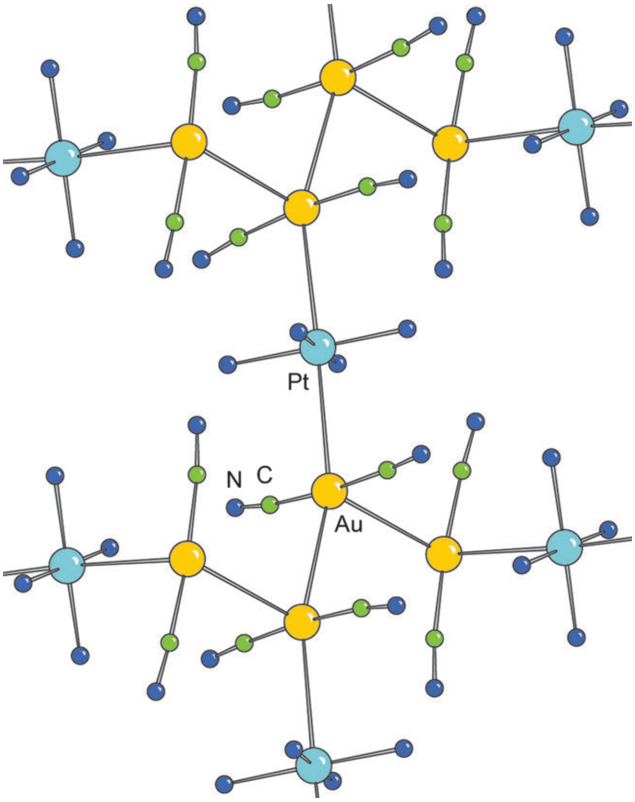


Fig. 11 3-D structure of $[Pt(NH_3)_4][Au(CN)_2]_2$ (interstitial water omitted for clarity).

analogous homometallic Ag(I) and Au(I) dimers illustrates a key feature of mixed Ag(I)–Au(I) systems: the heterometallic interaction distances are often shorter than either of the analogous homometallic systems, due to the presence of a dipole component in the mixed-metal system.[32,35]

In a different approach to mixed-metal systems, the 3-D coordination polymers $La(H_2O)_3[Au(CN)_2]_3$ were doped with $[Ag(CN)_2]^-$ in place of $[Au(CN)_2]^-$. These mixed $La(H_2O)_3[Ag_xAu_{1-x}(CN)_2]_3$ systems exhibit photoluminescent properties not observed in the pure gold(I) or silver(I) systems.[36]

The double-salt synthetic approach has also been harnessed to form d^{10}–d^8 Au(I)–Pt(II)-based chains. The general reaction of a judiciously chosen square-planar Pt(II) cation and a linear Au(I) anion has been shown to be a general metathesis route to metallophilic double-salt 1-D Pt(II)–Au(I) chains such as $[Pt(terpyridine)Cl][Au(CN)_2]$ and other metallophilic systems.[37] In another example that utilizes the same methodology, the reaction of $[Pt(NH_3)_4]^{2+}$ cations and $[Au(CN)_2]^-$ anions generates a rare 3-D array formed by a combination of Au(I)–Pt(II) interactions of 3.2794(4) Å in one direction and Au(I)–Au(I) interactions ranging from 3.1902(5) to 3.3312(5) Å in the other two dimensions (Fig. 11).[38] This Au(I)–Pt(II) coordination polymer is emissive at 443 nm when cooled.

Increasing structural dimensionality *via* Ag(I)–Ag(I) interactions

The field of silver(I) coordination complexes and polymers and their associated argentophilic interactions has been intensively studied and reviewed[39,40] relative to the gold(I) counterparts. However, the similarities and differences by which Ag(I) and Au(I) complexes increase structural dimensionality *via* the formation of metallophilic interactions are worth emphasizing here. The silver(I) ion is comparatively larger than that of gold(I), however argentophilic interactions are weaker than their gold(I) counterparts. Another significant difference is in the coordination chemistry of the two cations: while most gold(I) complexes are linear, silver(I) complexes show more diverse coordination numbers and geometries. Thus, although similar 1-D chains to the Au(I)-based systems described above have been observed for silver(I), such as dimeric $[Ag_2(MTP)_2]$ (which forms 1-D chains *via* inter-dimer argentophilic interactions of 3.227(2) Å),[35] more intricate chains can also be accessed. For example, reacting the carbene-type triazolium ligand 2,5,6,7-tetrahydro-2-phenyl-3*H*-pyrrolo[2,1-*c*]-1,2,4-triazol-3-ylidene·HCl (TPh) with Ag_2O produces three species in solution: anionic $[AgCl_2]^-$, cationic $[Ag(TPh)_2]^+$, and neutral Ag(TPh)Cl. In the solid-state, the neutral and anionic moieties combine *via* Cl-bridged dimers to form $[(TPh)Ag(\mu\text{-}Cl)_2AgCl]^-$ units, which contain 3-coordinate trigonal Ag(I) centres. The Ag(I) centres in this anionic moiety form argentophilic interactions of 3.0242(2) and 3.0752(2) Å to adjacent two-coordinate $[Ag(TPh)_2]^+$ cations, generating an overall 1-D zig-zag chain (Fig. 12).[41]

As with Au(I), coordination polymers containing Ag(I) centres which are already at least 1-D *via* metal–ligand bonding can further increase structural dimensionality *via* the formation of argentophilic interactions. In the simplest cases, homometallic Ag(I) complexes incorporating bridging ligands could yield polymeric arrays *via* the formation of Ag(I)–Ag(I) dimers, as per Scheme 1b. However, the ability of Ag(I) to readily alter its coordination number relative to Au(I) increases the flexibility of coordination polymer structural design. For example, the use of bridging bis-monodentate phenol groups of a di-Schiff base-type ligand with Ag(I) salts

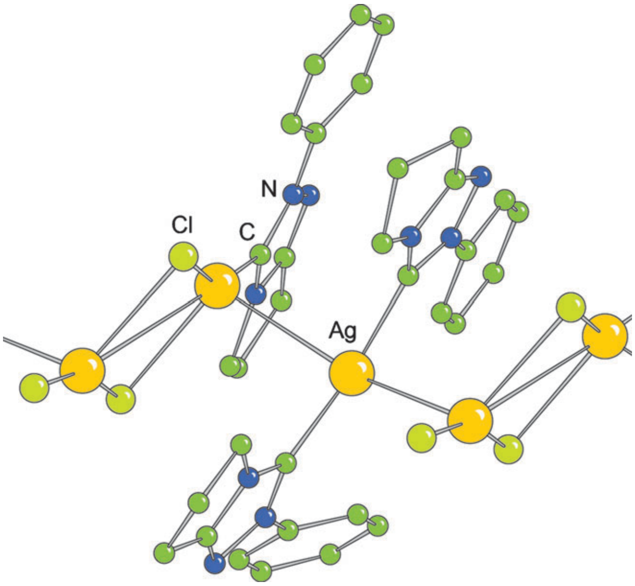


Fig. 12 1-D chain structure of $[Ag(TPh)_2][(TPh)Ag(\mu\text{-}Cl)_2AgCl]$ formed *via* argentophilic interactions.

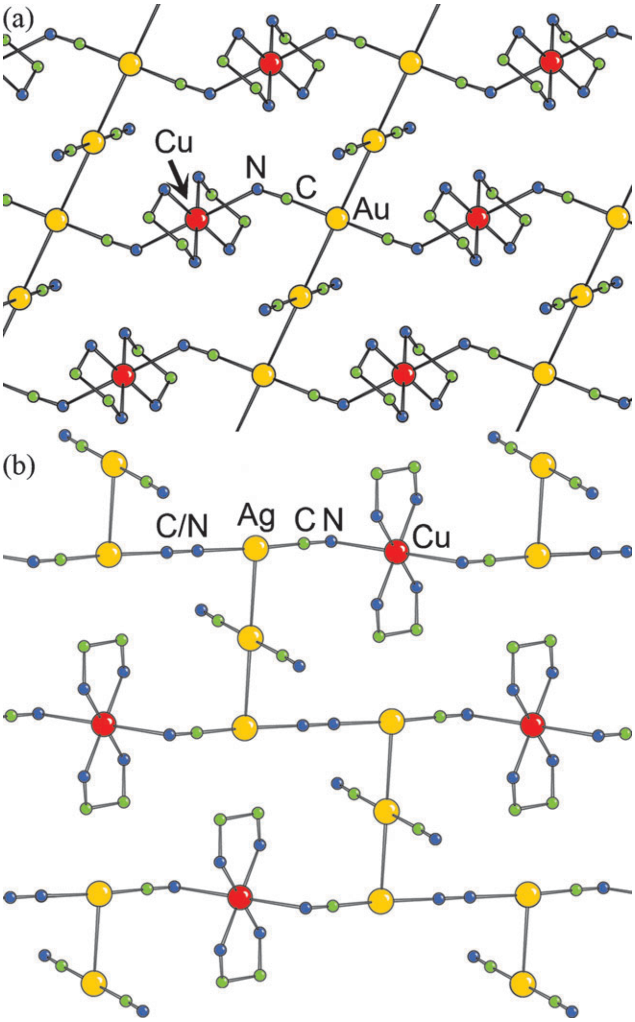


Fig. 13 (a) 1-D chains of $[Cu(en)_2M(CN)_2]^+$ linked *via* a free $[M(CN)_2]^-$-unit, forming a 2-D sheet (M = Au, Ag). (b) 1-D chains of $[Cu(en)_2Ag_2(CN)_3]^+$ linked *via* an $[Ag(CN)_2]^-$-unit into a 2-D sheet.

generates trigonal Ag(I) centres which form the nodes of a hexagonal 2-D sheet. These corrugated arrays, which can form due to the ability to access a trigonal geometry for Ag(I) *vs.* Au(I), link to one another *via* argentophilic interactions of 2.934(2) or 2.946(2) Å, thereby increasing the structural dimensionality to 3-D.[42]

Argentophilic interactions have also been exploited in heterobimetallic coordination polymers to increase structural dimensionality. The linear $[Ag(CN)_2]^-$ building block has been much more heavily utilized in polymer formation than its isostructural, isoelectronic $[Au(CN)_2]^-$ counterpart. However, as is the case with many Ag(I)-based systems, in comparison with Au(I), the chemistry is less controllable and predictable due to the flexibility of Ag(I) and also, in this particular case, due to the decreased stability of $[Ag(CN)_2]^-$ *vs.* $[Au(CN)_2]^-$ (β_2-formation constants are *circa* $10^{20.4}$ *vs.* 10^{37}, respectively). As a result, sometimes $[Ag(CN)_2]^-$ can act in an analogous fashion to $[Au(CN)_2]^-$, forming, for example, isostructural $\{Ni[tris(2\text{-aminoethyl})amine]M(CN)_2\}[M(CN)_2]$ (M = Au, Ag) polymers. These contain 1-D Ni–NC–M–CN–Ni chains connected into 2-D sheets by metallophilic bonds to free $[M(CN)_2]^-$ units between the chains.[43] On the other hand, $[Ag(CN)_2]^-$ is prone to dissociation and ligand redistribution to generate $[Ag_2(CN)_3]^-$ *in situ*, which is incorporated into the final polymer, such as in $[Cu(ethylenediamine)_2][Ag_2(CN)_3][Ag(CN)_2]$. This polymer contains a 1-D chain of cyanoargentate anions in which each Ag(I) centre in the $[Ag_2(CN)_3]^-$ unit forms 3.102(1) Å interactions with the adjacent $[Ag(CN)_2]^-$ moiety (Fig. 13b).[43] The analogous Au(I) system $[Cu(ethylenediamine)_2Au(CN)_2][Au(CN)_2]$ contains a 1-D Cu–NC–Au–CN–Cu chain bridged by $[Au(CN)_2]^-$ units, forming an overall 2-D sheet (Fig. 13a); no $[Au_2(CN)_3]^-$ type fragments have been observed to date.[24]

Complex 2- and 3-D structures in which argentophilic interactions support interpenetration are also known, such as the 2-D triply interpenetrated Borromean weave of $\{Ag_2[1,4\text{-bis}(2\text{-methylimidazol-1-ylmethyl})benzene]_3\}(BF_4)_2$ held together *via* 3.0619(4) Å Ag(I)–Ag(I) interactions.[44]

Thus, although argentophilic interactions are weaker than their gold(I) counterparts, they can nevertheless be used as a design element in coordination polymers to increase structural dimensionality, but with a reduced predictability factor. It is also worth noting that isoelectronic Hg(II), *e.g.* in linear, neutral $Hg(CN)_2$-based coordination polymers,[45] for the most part does not exhibit significant "mercurophilic" interactions, acting instead primarily as a soft Lewis acid.

Increasing structural dimensionality *via* mixed Ag(I)–metal interactions

Other than the Au(I)–Ag(I) cases discussed above, there are very few examples of materials which increase their structural dimensionality *via* mixed Ag(I)–M interactions. A Ag(I)–Cu(I) interaction of 3.1000(4) Å in $Cu(ethylenediamine)Cu(CN)_2Ag(CN)_2$ links a pair of 2-D interpenetrated nets to generate a 3-D system.[43] Only Cu(II) and Ag(I) salts were used in this synthesis, suggesting that a reduction process was necessary to generate the Cu(I) centre. The Cu(II) reduction was proposed to occur *via* the reaction with free CN^- (liberating cyanogen) with subsequent reaction of the resulting Cu(I) with additional CN^- to form $[Cu(CN)_2]^-$. The presence of free CN^- in the reaction was attributed to the lability of the $[Ag(CN)_2]^-$ unit.

A rare example of a chiral, helical 1-D chain of metallophilic metal units is $[cis\text{-}Pt(phpy)_2][Ag(acetone)](ClO_4)$ (Hphpy = 2-phenylpyridine), in which the chain is generated by dative Pt(II)–Ag(I) interactions of 2.6781(9) and 2.8121(9) Å (Fig. 14).[46] The units are also supported by inter-fragment Ag–C_π interactions. The helical structure originates from the π–π stacking of the phpy ligands.

Increasing structural dimensionality *via* Cu(I)–Cu(I) interactions

Considering that the strength of metallophilic interactions decreases from Au(I) to Ag(I), the existence of "cuprophilicity" has been subject to an ongoing debate. However, Cu(I)–Cu(I) interactions have been shown to be both theoretically and experimentally viable, and hence capable of being

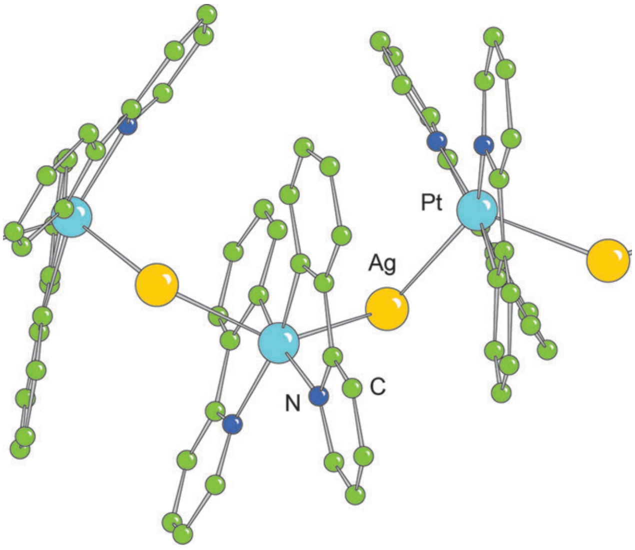


Fig. 14 Chiral 1-D chain of [*cis*-Pt(phpy)$_2$][Ag(acetone)](ClO$_4$) formed *via* metallophilic interactions between silver(I) and platinum(II) (acetone units and weak Ag–C interactions omitted for clarity).

used as a tool to increase structural dimensionality.[47] Copper(I) coordination chemistry is more similar to silver(I) than gold(I), adopting a flexible range of geometries and coordination numbers. The Cu(II) oxidation state is also readily accessible, allowing Cu(I) to be formed *in situ* from Cu(II) and an appropriate reducing agent (*e.g.* CN$^-$).[43] In light of this structural and chemical flexibility, the ability to controllably increase structural dimensionality *via* cuprophilic interactions is far more difficult than with gold(I). Nevertheless, a simple system such as the dimer [(terpyridine)$_2$Cu$_2$]$^{2+}$, in which each Cu(I) is bound by four pyridine units (two terminal and two bridging), links to a neighbouring dimer *via* 2.9951(9) Å Cu(I)–Cu(I) interactions to generate a 1-D chain (Fig. 15).[48] Intradimer, ligand supported, Cu(I)–Cu(I) bonding of 2.6371(9) Å is also observed. This 1-D chain is reminiscent of the previously described gold and silver MTP chains of dimers.[19,35]

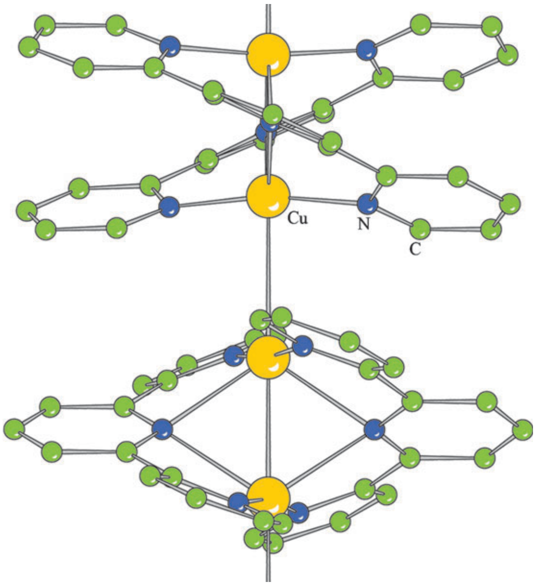


Fig. 15 1-D chain of [(terpyridine)$_2$Cu$_2$]$^{2+}$ dimers linked *via* Cu(I)–Cu(I) interactions.

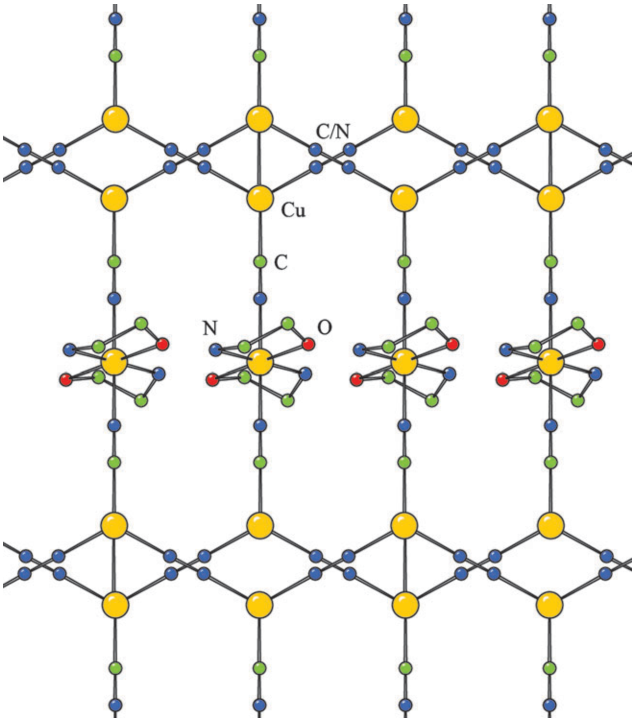


Fig. 16 2-D sheet of [Cu(ethanolamine)$_2$][Cu(CN)$_2$]$_2$ stacked *via* cuprophilic interactions, yielding an overall 3-D coordination polymer.

Cu(I)-containing coordination polymers can increase their structural dimensionality *via* Cu(I)–Cu(I) interactions. For example, by harnessing the *in situ* generation of Cu(I) from Cu(II), the reaction of CuCl$_2$ with ethanolamine and K$_3$Cr(CN)$_6$ (which acts as a source of CN$^-$) forms the mixed valent Cu(II)–Cu(I) system [Cu(ethanolamine)$_2$][Cu(CN)$_2$]$_2$. This polymer contains 1-D chains of trigonal planar [Cu(CN)$_2$]$^-$ units which are linked *via* [Cu(ethanolamine)$_2$]$^{2+}$ moieties, making a 2-D sheet *via* coordinate bonding (Fig. 16). Cu(I)–Cu(I) interactions of 2.7829(11) Å between the sheets increase the structural dimensionality to 3-D.[49]

Increasing structural dimensionality *via* d^8–d^8 interactions

The propensity of d^8 metal centres, particularly platinum(II) and rhodium(I), to form metallophilic interactions is well-recognized. These metal centres are predominantly found in a square-planar geometry, in which the empty d$_{x^2-y^2}$ orbital is much higher in energy than the remaining d orbitals, approximating a d^{10} closed-shell system like Au(I). The d^8 metal–metal bonding interactions arise from the overlap between filled nd$_{z^2}$ and empty (n + 1)p$_z$ orbitals on adjacent metal centres.[50,51]

One difference between metallophilic gold(I) and platinum(II) complexes is in their colours. While in the absence of coloured ligands, other metals, or counterions, gold complexes are generally colourless or yellow, the platinum(II) materials can be strongly coloured. The observed colours have been correlated to the Pt–Pt distances, which can also be tuned with the degree of hydration/solvation, making these compounds applicable as sensors.[52] Many of the Pt(II)–Pt(II) systems with an effective metal–metal interaction are also highly luminescent; similar tunability in Au(I)–Au(I) emissions have also been exploited.[8,9]

As with the simple Au(I) systems profiled in the first section, materials that show d^8–d^8 M–M (especially Pt–Pt) interactions can be classified into neutral, cationic, anionic and double-salt chain systems, based on the charge associated with the discrete building block in question. In all cases, chains in which the metal ions are linked *via* metal–metal interactions are the prevalent mode of aggregation: d^8–d^8 M–M interactions tend to increase structural dimensionality *via* the formation of 1-D chains from discrete units.

Thus, neutral Pt(1,10-phenanthroline)(CN)$_2$ and Pt(2,2′-bipyridine)(NCS)$_2$,[51] form 1-D chains *via* Pt(II)–Pt(II) interactions of 3.338(1) and 3.299(2) Å, respectively. A rare example of a Ru(0) complex increasing structural dimensionality is neutral, square-planar d^8 Ru(CO)$_4$ which forms 1-D chains *via* short 2.860(1) Å Ru–Ru bonding (Fig. 17).[53] An example of cationic chains, [Pt(2,2′:6′,2″-terpyridine)(C≡C–C≡CH)](OTf) aggregates in two different forms: recrystallization from diethyl ether–acetonitrile yields a dark green material with a linear 1-D cationic chain *via* 3.388 Å Pt–Pt interactions, while isolation from diethyl ether–acetone generates a red compound containing interacting dimers with alternating Pt–Pt distances of 3.394 and 3.648 Å in a zig-zag arrangement. Remarkably, these systems also aggregate in solution, exhibiting a strong solvatochromism as well as a large change in emission intensity, depending on the relative diethyl ether concentration.[54] A series of dinuclear Pt(II) complexes of the form [Pt$_2$(NH$_3$)$_4$(μ-carboxylato)$_2$]$^{2+}$ (carboxylate = acetate or glycolate) also afford 1-D chains in the solid-state, with intra- and intermolecular Pt(II)–Pt(II) interactions of 2.9892(9) and 3.2735(9) Å, respectively for the glycolate analogue; this subject has been recently reviewed.[55]

Anionic [Pt(CN)$_4$]$^{2-}$ units have been extensively investigated with a diverse range of organic and inorganic cations due to their propensity to form Pt–Pt stacks; many of these 1-D chain systems are luminescent.[50] As a result, many double-salt systems incorporate [Pt(CN)$_4$]$^{2-}$ units as the anion. For example, the [Pt(CN-*i*-C$_3$H$_7$)$_4$][Pt(CN)$_4$]·16H$_2$O system, which forms a 1-D chain *via* 3.1425(3) and 3.1617(3) Å Pt–Pt interactions, is highly luminescent and vapochromic, both properties of which can be directly related to the Pt–Pt chain structure.[52] Many similar species have been studied with respect to their ability to act as vapochromic sensors for a range of volatile organic compounds.[52]

One hallmark of d^8 metal–metal chain systems that is not featured in the analogous d^{10} systems is the ability to undergo partial oxidation to generate mixed-valent 1-D chain materials. These are exemplified by the ''Platinum-Blue'' class of intensely blue/purple Pt(2.25+)$_n$ or Pt(2.5+)$_n$ polymeric complexes, which have been recently reviewed.[55] Dinuclear Pt(II) cationic complexes can also be utilized to generate partially oxidized 1-D systems: slow electrochemical oxidation of the aforementioned [Pt$_2$(NH$_3$)$_4$(μ-acetato)$_2$]$^{2+}$ complex yields 1-D chains with intra- and intermolecular Pt–Pt distances of 2.8517(11) and 3.0107(14)/3.0148(13) Å, respectively, as well as supporting intermolecular hydrogen-bonding (Fig. 18).[56] Note that partial oxidation efficiently reinforces the metal–metal interaction, which is shorter relative to the un-oxidized counterpart, hence the generation of delocalized, mixed-valent metal units can promote the increase in structural dimensionality. The average oxidation state in the [Pt(II)$_4$Pt(III)] chain is Pt(2.2+) and the deeply coloured, almost black material absorbs a wide range of visible and near-infrared light and is semiconducting.

Electrocrystallization is a valuable, under-appreciated technique by which such mixed-valent 1-D chain materials can be generated.[57] In addition to many Pt-based systems as described above, rhodium(I) complexes are also amenable to a similar treatment. For example, slow one-electron galvanostatic *reduction* of the Rh(II/II) dimer [Rh$_2$(MeCN)$_{10}$][BF$_4$]$_4$ yields crystals of the mixed-valent [Rh$^{\text{I,II}}$(MeCN)$_4$(BF$_4$)$_{1.5}$]$_n$ 1-D chain, which contains 2.8442(8) and 2.9277(8) Å Rh–Rh interactions (Fig. 19); like the Platinum-Blue materials, this mixed-valent rhodium 1-D chain material is also a semiconductor.[58] Using chemical redox instead of electrochemistry, the reaction of [Rh$_4$(CO)$_{12}$] with 3,6-^{t}Bu$_2$-4,5-dichloro-1,2-benzoquinone (dbdiox) generates a 1-D chain of [Rh(dbdiox)(CO)$_2$] (with Rh–Rh distances around 2.88 Å) in which the mixed-valent Rh(I/II) nature is created *via* a semiquinonato–catecholato valence-tautomerization; this material, although a neutral chain, is also a good conductor at room temperature, consistent with the mixed-valency.[59]

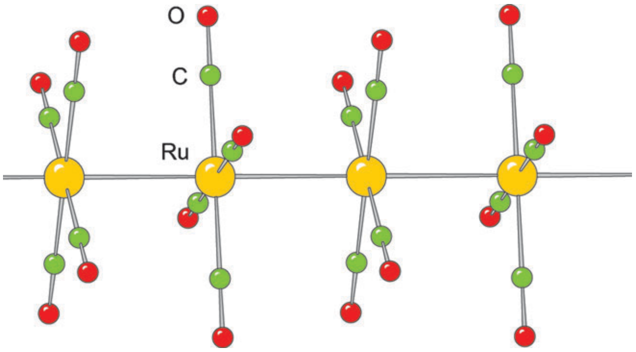


Fig. 17 1-D chain of Ru(CO)$_4$ units linked *via* homometallic ruthenium(0) interactions.

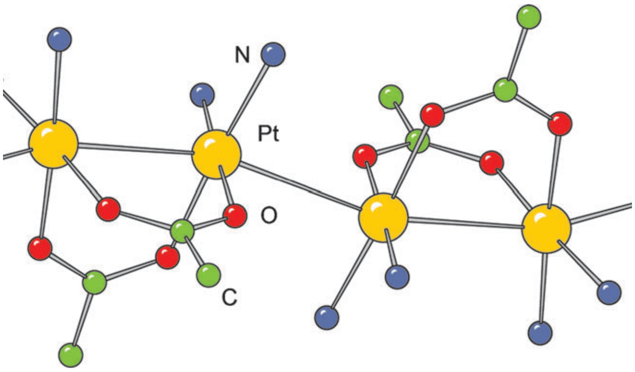


Fig. 18 The 1-D chain structure of [Pt$_2$(NH$_3$)$_4$(μ-acetato)$_2$]$^{2+}$ dimer units.

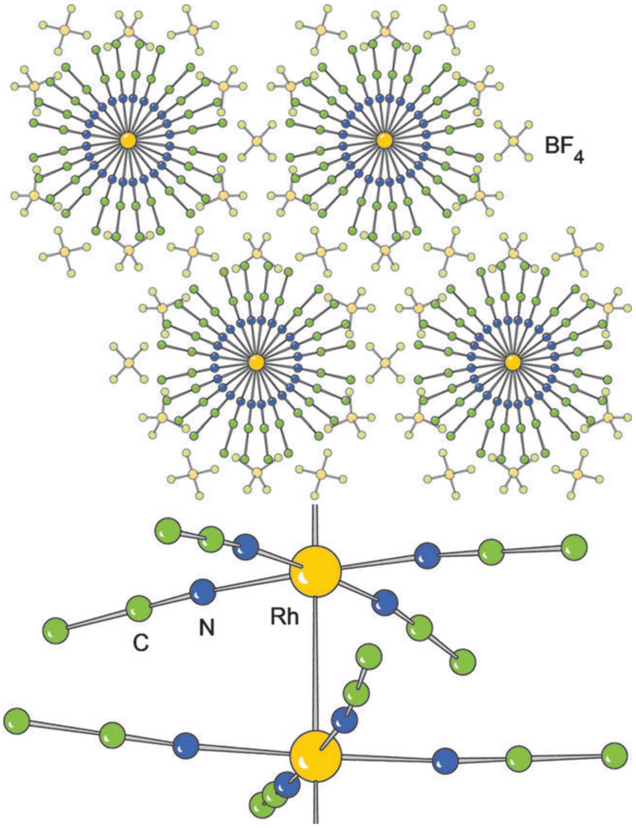


Fig. 19 (a) Packing diagram of 1-D chains in $[Rh^{I,II}(MeCN)_4(BF_4)_{1.5}]_n$. (b) Close-up of the 1-D chain structure.

While the propensity of linear d^{10} gold(I) and square-planar d^8 platinum(II) complexes to form attractive metal–metal interactions has been clearly delineated, related d^8 square-planar Au(III) systems such as $[Au(CN)_4]^-$ show practically no affinity for formation of Au(III)–Au(III) interactions; if there is any bonding participation by the Au(III) centre, it tends to act as a weak Lewis acid instead. A series of Cu(ligand)-$[Au(CN)_4]_2$ coordination polymers (ligand = multidentate amines and heterocyclic amines) exhibited no Au(III) metallophilicity at all.[60]

Conclusions

The above examples illustrate the design principle that metallophilic interactions, particularly with d^{10} gold(I) and d^8 platinum(II), can be actively utilized as a tool in crystal engineering to increase structural dimensionality. By harnessing aurophilicity in particular, isolated molecules can be linked by gold(I)–gold(I) interactions to form simple dimers, infinite bands or sheets of gold(I), or in some cases, complex 3-D arrays.

High dimensionality can also be generated by combining multidentate ligands with long flexible bridges and strategically placed gold(I) centres. This methodology opens the door to forming discrete supramolecular objects (*e.g.* catenanes), aurophilicity-supported chains or closed rings. This particularly rich, ligand-sensitive assembly of supramolecular systems has been exploited primarily with d^{10} metals rather than the d^8 congeners. Similarly, the use of metallophilic interactions as a structure-directing unit in heterobimetallic coordination polymers is much more prevalent for d^{10}-metals, with the greatest level of control and strength found for gold(I). On the other hand, the synthesis of conducting, emissive, mixed-valent metallophilicity-based multidimensional materials is the purview of the d^8-metals; there are virtually no d^{10}-based examples of this type to date.

The synthesis of double salts is a particularly powerful strategy to generate metallophilicity-based increases in structural dimensionality, due to the additional supporting electrostatic bonding component. This route to mixed Au(I)–M and other M–M′ combinations, the study of which is still in its relative infancy, is ripe for further exploitation.

Finally, a range of examples above showed that physical and optical properties such as luminescence and vapochromism can correlate with metallophilic bonding. As an implement in the crystal engineering toolbox, aurophilicity and other metal–metal interactions are now poised to be used to target a wide variety of new multidimensional materials. Property-based studies can be anticipated to be a focus of future research in this area.

Acknowledgements

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References

1 *Making crystals by design: methods, techniques and applications*, ed. D. Braga and F. Grepioni, Wiley-VCH, Weinheim, 2007.
2 C. Janiak, *Dalton Trans.*, 2003, 2781.
3 D. Maspoch, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770.
4 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.
5 M. Bardají and A. Laguna, *J. Chem. Educ.*, 1999, **76**, 201.
6 H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3.
7 P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412.
8 A. L. Balch, *Struct. Bonding*, 2007, **123**, 1.
9 V. W.-W. Yam and E. C. C. Cheng, *Top. Curr. Chem.*, 2007, **281**, 269.
10 M. A. Rawashdeh-Omary, M. A. Omary and H. H. Patterson, *J. Am. Chem. Soc.*, 2000, **122**, 10371.
11 *Gold: Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, Wiley, New York, 1999.
12 D. R. Tyler, in *Frontiers in Transition Metal-Containing Polymers*, ed. A. S. Abd-El-Aziz and I. Manners, Wiley, New Jersey, 2007, p. 287.
13 N. L. Coker, J. A. K. Bauer and R. C. Elder, *J. Am. Chem. Soc.*, 2004, **126**, 12.
14 P. G. Jones and B. Ahrens, *Z. Naturforsch., B: Chem. Sci.*, 1998, **53**, 653.
15 H. Schmidbaur, G. Weidenhiller, O. Steigelmann and G. Müller, *Z. Naturforsch., B: Chem. Sci.*, 1990, **45**, 747.
16 S. Ahrland, B. Noren and A. Oskarsson, *Inorg. Chem.*, 1985, **24**, 1330.

17 R. E. Bachman, M. S. Fioritto, S. K. Fetics and T. M. Cocker, *J. Am. Chem. Soc.*, 2001, **123**, 5376.
18 H. Ecken, M. M. Olmstead, B. C. Noll, S. Attar, B. Schlyer and A. L. Balch, *J. Chem. Soc., Dalton Trans.*, 1998, 3715.
19 W. E. van Zyl, J. M. Lopez-de-Luzuriaga, A. A. Mohamed, R. J. Staples and J. P. Fackler, Jr, *Inorg. Chem.*, 2002, **41**, 4579.
20 J. A. Schuerman, F. R. Fronczek and J. Selbin, *J. Am. Chem. Soc.*, 1986, **108**, 336.
21 P. M. van Calcar, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5231.
22 R. J. Puddephatt, *Coord. Chem. Rev.*, 2001, **216–217**, 313.
23 A. Sladek and H. Schmidbaur, *Inorg. Chem.*, 1996, **35**, 3268.
24 D. B. Leznoff, B.-Y. Xue, R. J. Batchelor, F. W. B. Einstein and B. O. Patrick, *Inorg. Chem.*, 2001, **40**, 6026.
25 A. Stützer, P. Bissinger and H. Schmidbaur, *Z. Naturforsch., B: Chem. Sci.*, 1992, **47**, 1261.
26 D. B. Leznoff, B.-Y. Xue, B. O. Patrick, V. Sanchez and R. C. Thompson, *Chem. Commun.*, 2001, 259.
27 J. Lefebvre, R. J. Batchelor and D. B. Leznoff, *J. Am. Chem. Soc.*, 2004, **126**, 16117.
28 M. J. Katz, P. M. Aguiar, R. J. Batchelor, A. A. Bokov, Z.-G. Ye, S. Kroeker and D. B. Leznoff, *J. Am. Chem. Soc.*, 2006, **128**, 3669.
29 M. J. Katz, H. Kaluarachchi, R. J. Batchelor, A. A. Bokov, Z.-G. Ye and D. B. Leznoff, *Angew. Chem., Int. Ed.*, 2007, **46**, 8804.
30 M. J. Katz, T. Ramnial, H.-Z. Yu and D. B. Leznoff, *J. Am. Chem. Soc.*, 2008, DOI: 10.1021/ja801773p.
31 B. F. Hoskins, R. Robson and N. V. Y. Scarlett, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1203.
32 M. Bardají and A. Laguna, *Eur. J. Inorg. Chem.*, 2003, 3069.
33 E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, J. Pérez, A. Laguna, A. A. Mohamed and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 2003, **125**, 2022.
34 O. Schüster, U. Monkowius, H. Schmidbaur, R. S. Ray, S. Krüger and N. Rösch, *Organometallics*, 2006, **25**, 1004.
35 J. P. Fackler, Jr., *Inorg. Chem.*, 2002, **41**, 6959.
36 J. C. F. Colis, C. Larochelle, R. Staples, R. Herbst-Irmer and H. H. Patterson, *Dalton Trans.*, 2005, 675.
37 R. Hayoun, D. K. Zhong, A. L. Rheingold and L. H. Doerrer, *Inorg. Chem.*, 2006, **45**, 6120.
38 M. Stender, R. L. White-Morris, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 2003, **42**, 4504.
39 A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schröder, *Coord. Chem. Rev.*, 2001, **222**, 155.
40 P. J. Steel and C. M. Fitchett, *Coord. Chem. Rev.*, 2008, **252** 990.
41 P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy and S. P. Nolan, *Organometallics*, 2005, **24**, 6301.
42 M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237.
43 C. J. Shorrock, B.-Y. Xue, P. B. Kim, R. J. Batchelor, B. O. Patrick and D. B. Leznoff, *Inorg. Chem.*, 2002, **41**, 6743.
44 L. Dobrzanska, H. G. Raubenheimer and L. J. Barbour, *Chem. Commun.*, 2005, 5050.
45 N. D. Draper, R. J. Batchelor and D. B. Leznoff, *Cryst. Growth Des.*, 2004, **4**, 621.
46 T. Yamaguchi, F. Yamazaki and T. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 743.
47 H. L. Hermann, G. Boche and P. Schwerdfeger, *Chem.–Eur. J.*, 2001, **7**, 5333.
48 M. Al-Anber, B. Walfort, S. Vatsadze and H. Lang, *Inorg. Chem. Commun.*, 2004, **7**, 799.
49 Y. Jin, Y. Che and J. Zheng, *J. Coord. Chem.*, 2006, **59** 691.
50 G. Gliemann and H. Yersin, *Struct. Bonding*, 1985, **62**, 87.
51 W. B. Connick, R. E. Marsh, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1997, **36**, 913.
52 C. E. Buss, C. E. Anderson, M. K. Pomije, C. M. Lutz, D. Britton and K. R. Mann, *J. Am. Chem. Soc.*, 1998, **120**, 7783.
53 N. Masciocchi, M. Moret, P. Cairati, F. Ragaini and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1993, 471.
54 V. W.-W. Yam, K. M.-C. Wong and N. Zhu, *J. Am. Chem. Soc.*, 2002, **124**, 6506.
55 K. Matsumoto and K. Sakai, *Adv. Inorg. Chem.*, 2000, **49** 375.
56 K. Sakai, E. Ishigami, Y. Konno, T. Kajiwara and T. Ito, *J. Am. Chem. Soc.*, 2002, **124**, 12088.
57 P. Batail, K. Boubekeur, M. Fourmigué and J.-C. P. Gabriel, *Chem. Mater.*, 1998, **10**, 3005.
58 M. E. Prater, L. E. Pence, R. Clérac, G. M. Finniss, C. Campana, P. Auban-Senzier, D. Jérome, E. Canadell and K. R. Dunbar, *J. Am. Chem. Soc.*, 1999, **121**, 8005.
59 M. Mitsumi, H. Goto, S. Umebayashi, Y. Ozawa, M. Kobayashi, T. Yokoyama, H. Tanaka, S. Kuroda and K. Toriumi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4164.
60 C. J. Shorrock, H. Jong, R. J. Batchelor and D. B. Leznoff, *Inorg. Chem.*, 2003, **42**, 3917.