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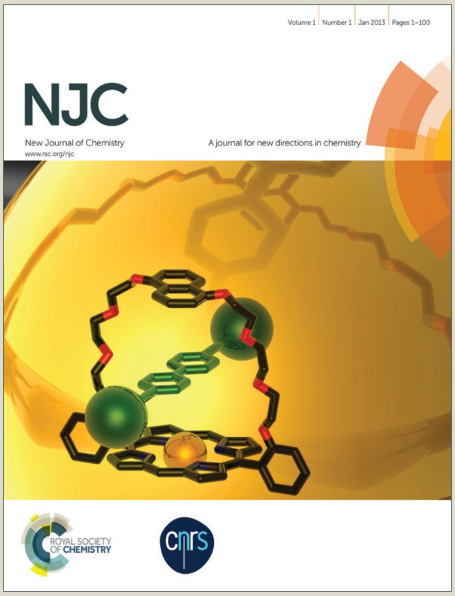

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Weaving an infinite 3-D supramolecular network *via* Au^{I}···Au^{III} aurophilicity and C-H···Cl hydrogen bonding

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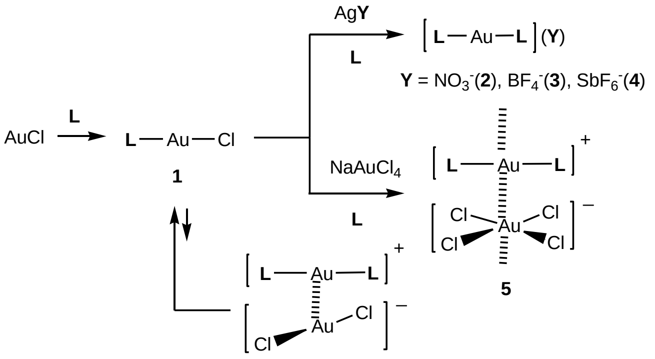
Chang-Chuan Chou,[a,]* Chia-Chi Yang,[a] Hao-Ching Chang,[b] Way-Zen Lee[b,]* and Ting-Shen Kuo[b]

An unprecedented infinite 3-D supramolecular assembly synergistically supported by mixed-valent Au^{I}···Au^{III} aurophilicity and weak C–H···Cl hydrogen bond was presented.

In supramolecular chemistry, the introduction of weak Au^{I}···Au^{I} (d^{10}–d^{10}) aurophilic interactions[1] is considered to be an effective approach to the forming of a variety of intriguing structural motifs such as dimers, oligomers, 1-D polymeric chains, 2-D extended sheets, and 3-D supramolecular networks,[1,2] because such attractive interactions are equivalent in energy to classic hydrogen bonding (6~11 kcal/mol).[3] Additionally, such an interaction could possibly result in some interesting optical properties and functional materials.[4] Based on experimental observation and theoretical calculation,[5] the existence of mixed-valent Au^{I}···Au^{III} (d^{10}–d^{8}) aurophilic interactions is unquestionable, and their bonding energies (5~6 kcal/mol) are approximate to those of corresponding Au^{I}···Au^{I} interactions; however, supramolecular structures involving Au^{I}···Au^{III} interactions, particularly unsupported modes of Au^{I}···Au^{III} interactions,[6] are rare and awaiting the development with respect to increasing structural dimensionality.[7] In this study, an unprecedented infinite 3-D supramolecular architecture synergistically supported by mixed-valent Au^{I}···Au^{III} aurophilicity and weak C−H···Cl hydrogen bonding in solid-state was revealed as a salt, $[AuL_2]^+[AuCl_4]^-$ (**5**); where L = 1,3,5-trimethylpyrazole with a sequence of ions following [+ – + – + –], containing a pair of linear bis(pyrazole)gold(I) complex cation and a square planar tetrachloroaurate(III) anion. Owing to their adequate molecular geometries, two gold ions with different oxidation states were placed in close proximity to produce a relatively short Au^{I}···Au^{III} contact (3.34 Å). The luminescence property of the bis(pyrazole)gold(I) complex cation affected by tetrachloroaurate(III) anion also exhibited a substantial red shift in the emission profile, which suggested an unsupported Au^{I}···Au^{III} interaction.



Scheme 1 Formation of complex **1**–**5**.

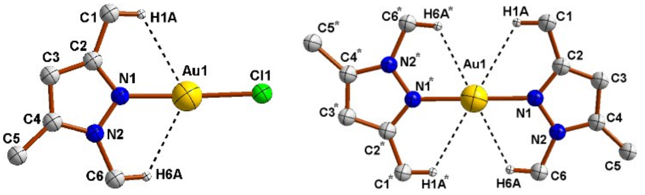


Fig. 1 Structures of complex **1** (left) and cation **4**$^+$ (right). Selected bond distances (Å) and bond angles (°) for **1**: Au1–N1 2.011(7), Au1–Cl1 2.253(2), H1A···Au1 2.7878(6), H6A···Au1 2.6829(4), C1···Au1 3.381(8), C6···Au1 3.300(9); N1–Au1–Cl1 177.3(2), C6–N2–N1 120.7(7), N2–N1–Au1 124.9(6), Au1–N1–C2 128.8(6), Au1–H6A–C6 121.3(5), Au1–H1A–C1 119.5(5); and for cation **4**$^+$: Au1–N1 2.010(9), H1A···Au1 2.8343(9), H6A···Au1 2.6472(6), C1···Au1 3.42(1), C6···Au1 3.27(1), N1–Au1–N1* 180.0, Au1–H6A–C6 121.6(7), Au1–H1A–C1 119.0(7), Au1–N1–C2 129.6(8), Au1–N1–N2 123.3(7).

As shown in scheme 1, a new (pyrazole)gold(I) chloride precursor, LAuCl (**1**), and a series of bis(pyrazole)gold(I) complexes with anions having different geometry were synthesized: $[AuL_2]Y$, Y = NO_3^- (**2**), BF_4^- (**3**), SbF_6^- (**4**) and $AuCl_4^-$ (**5**). The elemental analyses of **1**–**5** are in agreement with the proposed empirical formula. The IR (KBr) spectrum confirmed the typical pyrazole absorption bands for **1**–**5**, and the

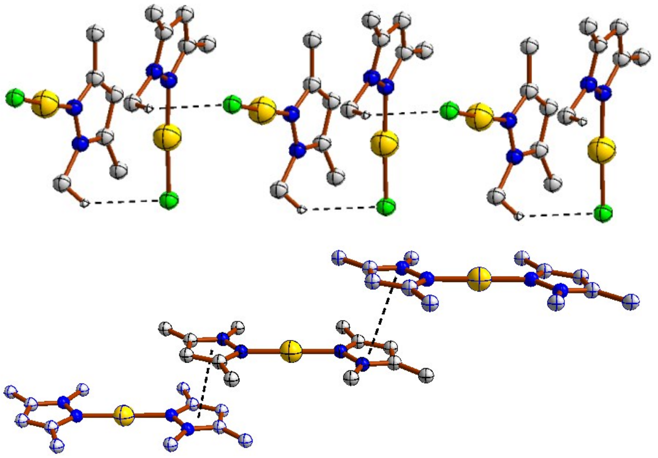


Fig. 2 The extended supramolecular structures of **1** (up) supported by weak C–H···Cl interactions (2.817(2) Å; 137.2(5)°) and cation $\mathbf{4}^+$ (down) supported by weak π–π interactions (3.8478(8) Å) to form 1-D polymeric chain

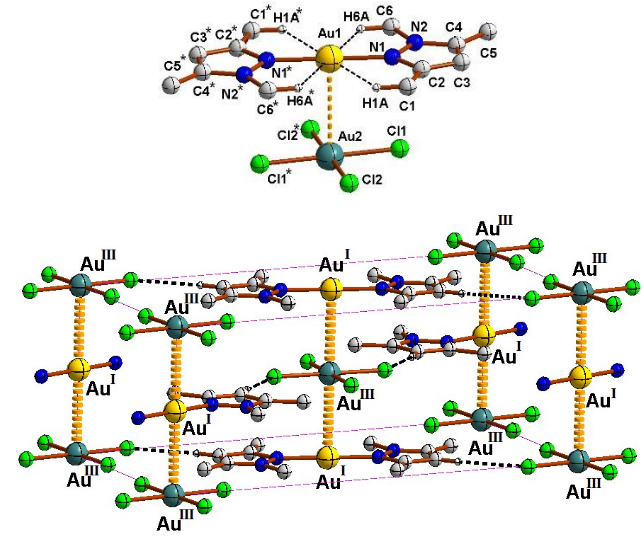


Fig. 3 Structure of **5** (up). Selected bond distances (Å) and bond angles (°): Au1···Au2 3.3412(2), Au1–N1 1.995 (6), H1A···Au1 2.7611(2), H6A···Au1 2.5737(1), C1···Au1 3.369(9), C6···Au1 3.222(9), Au2–Cl1 2.298(2), Au2–Cl2 2.281(3), Au1–H6A–C6 123.7(5), Au1–H1A–C1 120.7(6), Au1–N1–C2 129.5(6), Au1–N1–N2 124.8(5), Cl1–Au2–Cl2 90.19(10); and the lattice of **5** (down) supported by a combination of C–H···Cl interactions (2.799(2) Å; 169.7(6)°) and $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ interactions ($\mathrm{Au^I}$–$\mathrm{Au^{III}}$–$\mathrm{Au^I}$ 180°) to form 3-D network (part of blue nitrogens connected with $\mathrm{Au^I}$ represent 1,3,5-trimethylpyrazoles for clarity).

anion absorption bands of $\mathrm{NO_3^-}$ (1349 $\mathrm{cm^{-1}}$) for **2**, $\mathrm{BF_4^-}$ (1061 $\mathrm{cm^{-1}}$) for **3**, and $\mathrm{SbF_6^-}$ (654 $\mathrm{cm^{-1}}$) for **4**, respectively. A positive ESI-MS for complexes **2**–**4** gave an identical peak value of m/z as 417 (100%), which was attributable to the bis(pyrazole)gold(I) cation $[\mathrm{L_2Au}]^+$. ^{1}H and ^{13}C NMR spectra of **1**–**5** were similar to each other. All of these complexes were structurally characterized *via* X-ray diffraction analysis and their luminescence properties were investigated in the solid-state revealing the influence of the $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ interaction. Fortunately, there is no intermolecular $\mathrm{Au^I}$···$\mathrm{Au^I}$ interaction to interfere with verification of the $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ interaction in complex **5**. The emission spectra in the solid-state would reflect directly the $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ interaction. However, the $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ interactions in **5** seem to be disrupted by the solvent molecules because the conductivities of **2**–**5** were virtually the same. As with **1**–**4**, the emission for **5** was too weak to be observed in the glass state at 77 K.

Generally, a facile ligand-scrambling reaction of [L′AuCl] (L′ = neutral ligand) complexes would occur to form an ion pair, $[\mathrm{L'_2Au}]^+[\mathrm{AuCl_2}]^-$,[8] wherein the $\mathrm{Au^I}$···$\mathrm{Au^I}$ interaction could be observed. Based on the variable-temperature (VT) ^{1}H NMR spectra (Fig. S1), the ligand-scrambling reaction of **1** barely occurred in $\mathrm{CH_2Cl_2}$ (less than 1%, estimated from VT ^{1}H NMR spectra), suggesting that complex **1** is an appropriate candidate for the synthesis of complexes **2**–**5**, as shown in scheme 1.

The crystal structure of **1** (Fig. 1) consisted of a monomeric unit with a gold(I) center in an almost linear arrangement with a N(pyrazole)–Au–Cl angle of 177.3(2)°. The contacts of hydrogen atoms, H1A and H6A, with the central gold(I) ion appeared at 2.79 and 2.68 Å, respectively, which was shorter than the van der Waal's radii (2.86 Å),[9] suggesting the probability of weak $\mathrm{Au^I}$···H–C interactions.[10] In the crystal packing of **1**, each mononuclear gold(I) chloride complex was connected by an intermolecular C(Me)–H···Cl hydrogen bonding[11] to form a 1-D polymeric chain (Fig. 2). The intermolecular C···Cl distance was 3.60 Å, the H···Cl distance was 2.82 Å, which was less than the sum of the van der Waals radii (2.95 Å),[9] and the C–H···Cl bond angle was 137.2°. The closest intermolecular $\mathrm{Au^I}$···$\mathrm{Au^I}$ distance was 4.04 Å, indicating the absence of any significant aurophilic interactions. It is noteworthy that complex **1** represents the first structurally characterized gold(I) chloride complex supported with a pyrazolyl-derived ligand; gold(I) chloride complex with a similar ligand has been proposed with a spectroscopic analysis about 30 years ago.[12]

The crystal structures of **2**, **3** and cation $\mathbf{4}^+$ are shown in Fig. S6, S7 and 1, respectively. The two linear bis(pyrazole)gold(I) complex cations seen in complexes **2**–**4** had similar planar structures but different orientations for the coordinated pyrazoles (*cis*- for **2** and **3**; and *trans*- for **4**). Basically, the parameters of bond lengths and angles of these complexes were almost identical. Complex **4**, however, had a short $\mathrm{Au^I}$···H–C contact and weak intermolecular π–π interactions between neighboring pyrazoles to form an extended 1-D polymeric chain in the crystal packing (Fig. 2). The closest intermolecular $\mathrm{Au^I}$···$\mathrm{Au^I}$ distances for **2**–**4** were 5.53, 5.52 and 7.94 Å, respectively, and, therefore, the $\mathrm{Au^I}$···$\mathrm{Au^I}$ interactions were absent in these three complexes.

The X-ray structure of **5** (Fig. 3) consisted of a linear bis(pyrazole)gold(I) complex cation and a square planar $[\mathrm{Au^{III}Cl_4}]^-$ anion with normal Au–N and Au–Cl bond lengths. The two pyrazoles were coplanar and adopted a trans orientation. Similar to complex **1**, The contacts of hydrogen atoms, H1A and H6A, with the central gold(I) ion were also shorter than the van der Waal's radii at distances of 2.76 and 2.57 Å, respectively, suggesting weak $\mathrm{Au^I}$···H–C interactions.[9] The complex cation and anion were associated perpendicularly along the C_2-axis direction with a short contact of $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ (3.3412 Å), suggesting weak $\mathrm{Au^I}$···$\mathrm{Au^{III}}$ interactions. Meanwhile, the crystal lattice of **5** (Fig. 3) showed that the neighboring ion-pairs were further connected through an identical contact to produce a linear chain of equidistant gold atoms running along the crystal axis with alternating $\mathrm{Au^I}$ and $\mathrm{Au^{III}}$ ions. It is also noteworthy that the orientation with the chloride of the $[\mathrm{AuCl_4}]^-$ ion interacting with the cationic gold(I) center would be favored if electrostatic forces alone were present. The existence of the weak hydrogen bonds,

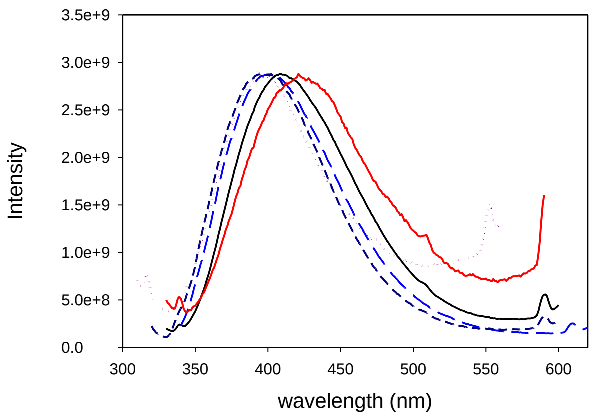


Fig. 4 Normalized emission spectra of **1** (black line, λ_{max} 409 nm), **2** (dark pink doted line, λ_{max} 394 nm), **3** (blue long-dash line, λ_{max} 401 nm), **4** (dark blue short-dash line, λ_{max} 395 nm) and **5** (red line, λ_{max} 421 nm) in the crystalline state at 100 K.

C(pyrazole)−H···Cl,[11] was intriguing as they appeared along different perpendicular directions of the C_2-axis, and may integrate to form an infinite 3-D supramolecular network (Fig. 3). The intermolecular C···Cl distance was 3.74 Å, the H···Cl distance was 2.80 Å, and the C–H···Cl bond angle was 169.7°.

To further examine the $Au^I\cdots Au^{III}$ interactions, the solid-state luminescence properties were investigated to determine the extent of the perturbation of the emissive state of the ligand by its coordination with the gold (I) ion. As shown in Fig. 4, complex **1** exhibited an emission profile at λ_{max} 409 nm, whereas complexes **2**, **3** and **4** showed a blue shift of the emission maxima to lower wavelengths at λ_{max} values of 394, 401 and 395 nm, respectively, when the anionic Cl ligand was substituted by a neutral pyrazole ligand. Such a phenomenon is similar to that of a previous report.[13] However, compared with complex **1**, a significant red shift to a λ_{max} of 421 nm was displayed when the anions NO_3^-, BF_4^- or SbF_6^- were replaced by the $AuCl_4^-$ anion, reflecting the mixed-valent $Au^I\cdots Au^{III}$ interaction. With reference to the previous reports, the red shift may also occur for homo-valent $Au^I\cdots Au^I$ or $Au^{III}\cdots Au^{III}$ interactions.[14,15]

In summary, by taking advantage of weak $Au^I\cdots Au^{III}$ interactions, weak C–H···Cl hydrogen bonds and additional electrostatic forces between a bis(pyrazole) gold(I) cation and a tetrachloroaurate(III) anion, a new MOF type of compound **5** was synthesized and its luminescence properties were investigated. Although gold(I) chloride complexes with hard neutral N-donor ligands are rare and normally very unstable (such as [AuCl(py)],[16] $[AuCl(NH_3)]$[17] and [AuCl(piperdine)],[18] etc.), gold(I) chloride **1** is stable enough to be a useful precursor for preparing bis(pyrazole)gold(I) complexes with anions having different geometry. Meanwhile, these complexes could allow a special opportunity to identify the influence of weak $Au^I\cdots Au^{III}$ aurophilic interactions *via* an examination of their emission profiles in the solid-state. Similar to conventional $Au^I\cdots Au^I$ interactions, the use of unsupported $Au^I\cdots Au^{III}$ interactions as a tool to increase the structural dimensions to that of a 3-D array proved feasible for the first time. As homo-valent $Au^I\cdots Au^I$ or $Au^{III}\cdots Au^{III}$ interaction,[15] such an $Au^I\cdots Au^{III}$ interaction could possibly result in some interesting optical properties that could be applied to functional materials in the field of solid-state inorganic chemistry.

Experimental

Syntheses of LAuCl (1)

A mixture of AuCl (0.628 mmol) and 1,3,5-trimethyl-1H-pyrazole (0.628 mmol) in 4 ml of CH_2Cl_2 was stirred under N_2 at room temperature for 1 h. Then 10 ml of hexane was added and a white precipitate was formed. After filtering, the product was washed by hexane and dried *in vacuo* to give a 93% yield. Single crystals were grown from CH_2Cl_2/hexane.

Syntheses of $[AuL_2]Y$ (Y = NO_3^- (2), BF_4^- (3), SbF_6^- (4))

A mixture of **1** (0.318 mmol) and $AgNO_3$ (0.318 mmol) in 10ml of CH_2Cl_2 was stirred under N_2 at room temperature for 1h. The precipitates formed was filtered off and the resulting solution was dried *in vacuo* to give a 77 % yield. Complexes **3** and **4** follow the similar procedure as **1** to give 88% and 98% yields, respectively. Single crystals were grown from CH_2Cl_2/hexane.

Syntheses of $[AuL_2][AuCl_4]$ (5)

A mixture of **1** (0.580 mmol) and $Na[AuCl_4]\cdot 2H_2O$ (0.580 mmol) in 5 ml CH_2Cl_2 was stirred for 2 h under N_2. The precipitates formed was filtered off and the filtrate was added 10 ml hexane to give yellow precipitates. After filtering, the yellow solid was washed by hexane and dried *in vacuo* to give an 87 % yield. Single crystals were grown from CH_2Cl_2/hexane.

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Notes and references

[a] *Center for General Education, Chang Gung University of Science and Technology, Tao-Yuan 33303, Taiwan, R.O.C. E-mail: ccchou@mail.cgust.edu.tw*

[b] *Department of Chemistry, National Taiwan Normal University, Taipei 11650, Taiwan, R.O.C. E-mail: wzlee@ntnu.edu.tw*

Electronic Supplementary Information (ESI) available: Experimental details, ^1H & ^{13}C NMR spectra and crystal structures. CCDC1008362, 1427451-1427454. See DOI: 10.1039/c000000x/

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Table of Content

The use of ligand-unsupported Au^{I}···Au^{III} interactions to increase the structural dimensionality to 3-D array was demonstrated.