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## Soft metal cations trigger sandwich-cluster luminescence of a new Au(I)-vinylimidazolate cyclic trinuclear complex

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<b>Abstract:</b>	The formation of heterobimetallic complexes from parent cyclic trinuclear complexes (CTCs) of gold(I) has become straightforward in recent years with this team and others showing that the strategy leads to strengthened Au-M' bonding and optoelectronic properties. A new gold(I)-vinylimidazolate CTC, <b>1</b> , was prepared and the formation of highly-emissive sandwich adducts with the soft metal cations Cu <sup>+</sup> , Ag <sup>+</sup> , and Tl <sup>+</sup>

	<p>, 2 – 4 , respectively, was investigated. Compound 1 does not exhibit peculiar emissive properties at room or cryogenic temperatures as the adducts do. Its unit cell packing displays an unprecedented collection of repeating units for CTCs. While the intermolecular Au...Au distances are versatile (3.470, 3.673, and 4.045 Å), they connect only single Au centres from adjacent CTCs and form extended circular networks. Hirshfeld surface analyses mapped the new CTC contours underlining the possible cooperative effects of not only metallophilic interactions but also C-H...π and hydrogen bonding in the packing of 1 (as opposed to the dominance of the former in most other reported CTCs). DFT calculations validate the formation of sandwich-like structures for compounds 2 - 4 with averaged Au-M distances of 2.665 Å, 2.802 Å, and 3.036 Å, respectively, close by to experimental crystal data obtained for similar sandwich compounds.</p>
<b>Author Comments:</b>	<p>Hereby we resubmit a revised version of manuscript ejic.202100893 for the special issue dedicated to "Rinaldo Poli - by invitation only". The manuscript was first rejected upon an overall negative judgement and an overall positive judgement; however, the editor Gallardo has later informed we might have a chance to submit a revised version. As a result, we have thoroughly revised the manuscript to both carefully address all the concerns by the two reviewers as well as our own thorough review of the technical/scientific content, English writing/formatting, and aesthetic elements (quality of figures/illustrations) in both the main manuscript and related Supporting Information.</p> <p>We are also asking for adding one more author, Prof. Dr. Abdel-Monem M. Rawashdeh, due to an oversight on our part in the original submission given his genuine and significant contribution in this work.</p> <p>The point-by-point response to the referees' comments are attached below (reported in red colored character). The corresponding changes in the revised main manuscript and Supporting Information are marked in yellow in these documents attached with this submission.</p> <p>In our view, the paper provides useful and intriguing hints for future experimental developments of the gold chemistry and in its wide range of applications, spanning from sensors, photochemistry and catalytic features. In this regards, we strongly consider European Journal of Inorganic Chemistry as the most appropriate journal for the publication of the present manuscript</p>
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<b>Question</b>	<b>Response</b>
Has a previous version of this manuscript been submitted to this journal?	Yes
If yes, please provide details as follow-up to "Has a previous version of this manuscript been submitted to this journal?"	<p>Manuscript number of previous submission : ejic.202100893.</p> <p>The manuscript was first rejected upon an overall negative judgement and an overall positive judgement.</p>
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Is this manuscript, or part of it, published, posted, or in press? This includes content posted on preprint servers ( <a href="#">preprint guidelines</a> ) or published as part of a thesis.	No
Please provide us with information about the history of your manuscript, including previous submissions, transfers, or prior versions:	After rejection, and after our claim, we obtained that we might have a chance to submit a revised version . As a result, we have thoroughly revised the manuscript to both carefully address all the concerns by the two reviewers as well as our own thorough review of the technical/scientific content, English writing/formatting, and aesthetic

	elements (quality of figures/illustrations) in both the main manuscript and related Supporting Information
Does the research described in this manuscript include animal experiments or human subjects or tissue samples from human subjects?	No
Do you or any of your co-authors have a conflict of interest to declare?	No

## RESEARCH ARTICLE

# Soft metal cations trigger sandwich-cluster luminescence of a new Au(I)-vinylimidazolate cyclic trinuclear complex

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This work is dedicated to Rinaldo Poli, with admiration and with many congratulations for all his scientific achievements.

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Supporting information for this article is given via a link at the end of the document.

**Abstract:** The formation of heterobimetallic complexes from parent cyclic trinuclear complexes (CTCs) of gold(I) has become straightforward in recent years with this team and others showing that the strategy leads to strengthened Au-M' bonding and optoelectronic properties. A new gold(I)-vinylimidazolate CTC, **1**, was prepared and the formation of highly-emissive sandwich adducts with the soft metal cations Cu<sup>+</sup>, Ag<sup>+</sup>, and Ti<sup>+</sup>, **2** – **4**, respectively, was investigated. Compound **1** does not exhibit peculiar emissive properties at room or cryogenic temperatures as the adducts do. Its unit cell packing displays an unprecedented collection of repeating units for CTCs. While the intermolecular Au...Au distances are versatile (3.470, 3.673, and 4.045 Å), they connect only single Au centres from adjacent CTCs and form extended circular networks. Hirshfeld surface analyses mapped the new CTC contours underlining the possible cooperative effects of not only metallophilic interactions but also C-H...π and hydrogen bonding in the packing of **1** (as opposed to the dominance of the former in most other reported CTCs). DFT calculations validate the formation of sandwich-like structures for compounds **2** – **4** with averaged Au–M distances of 2.665 Å, 2.802 Å, and 3.036 Å, respectively, close by to experimental crystal data obtained for similar sandwich compounds.

The studies of metal clusters with unique structures and fascinating materials properties have witnessed a strong momentum in recent decades, one aspect of which is noble-metal clusters of Au, Ag, Cu, Pd, or Pt metals.<sup>[1,2]</sup> Among noble-metal clusters, the chemistry (bonding and reactivity) and photophysical/materials properties of cyclic trinuclear complexes (CTCs), featuring 9-membered-ring planar metallacycles with three μ<sub>2</sub>-bridging-bidentate anionic ligands between three d<sup>10</sup> monovalent metal centres, represent a major research focus in our research groups.<sup>[3–5]</sup> These d<sup>10</sup>-metal CTCs have been

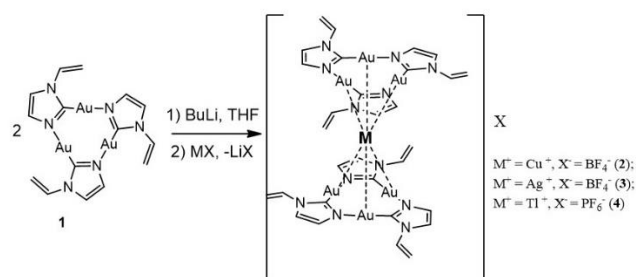
attracting attentions due to their potentials as luminophores (for sensing or optoelectronic devices), acid-base chemistry, supramolecular assemblies, and M-M or M-M' bonding -- potentially tuning all of which by easily manipulating the combinations of metals, ligands, and substituents.<sup>[6–17]</sup> Beyond that, ordered materials constructed from CTCs are being pursued in very recent years for their controllable skeletons and excellent optical/catalytic performances.<sup>[18–25]</sup>

The clusters herein are formed by sandwiching a foreign closed-shell metal cation between two gold(I) CTC molecules, resulting in an [Au<sub>3</sub>...M<sup>+</sup>...Au<sub>3</sub>] chemical formula for the resulting heptanuclear cluster.<sup>[6,26–32]</sup> Since they were discovered in 1998,<sup>[28]</sup> few reports on structure determinations and luminescence properties only cover the central metal cations of Ag<sup>+</sup> and Ti<sup>+</sup>.<sup>[6,26–32]</sup> Herein, we also add Cu<sup>+</sup> and the three ions are sandwiched in a new gold(I) CTCs, reporting the synthesis, structure, photoluminescence, and theoretical modeling of all four compounds. The new CTC that π-complexes to these cations is tris(vinylimidazolate)gold(I), **1**. It represents a unique example with unsaturated (alkenyl) substituent vs alkyl or fluoroalkyl in common CTCs. The alkenyl substituents extend the π-framework of the 9-membered ring by six additional π electrons, which likely plays a factor in the supramolecular association mode to allow both vertical and horizontal CTC packing.

The starting CTC was synthesized by adopting Vaughan's method to Au(I) pyridinate/imidazolate complexes.<sup>[3,11,33]</sup> The deprotonation of 2-C in the 1-vinylimidazole by *n*-butyllithium in dry tetrahydrofuran (THF) yields a C,N-bridging ligand, which further reacts with Ph<sub>3</sub>PAuCl (Ph<sub>3</sub>P = triphenylphosphine) to afford the new cyclic trinuclear Au(I) complex [Au(1-Vilm)]<sub>3</sub> (**1**). The resulting complex **1** is an air-stable white solid that is slightly soluble in common organic solvents except THF. The FT-IR spectrum of **1** confirms the deprotonation of the imidazole to form an imidazolate ligand and the formation of Au-N and Au-C coordinate-covalent bonds; the C-H and C=C stretching of the vinyl groups' signals appear at 3100 and 1642 cm<sup>-1</sup>, respectively. The proton NMR spectrum shows, in addition to the signals of

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protons in the 4,5-C imidazolate ring position, the typical AMX spin system of the vinyl group with the spin-spin coupling constants being  $^3J_{AX} = 16$  Hz,  $^3J_{AM} = 8.8$  Hz, and  $^2J_{MX} = 1.5$  Hz. Owing to the nature of the central metal and bridging ligands, predicted by previous literature reviews, **1** is expected to show considerable  $\pi$ -basic property and be capable of reacting with Lewis acidic metal cations, especially softer ones (i.e.,  $\text{Cu}^+$ ,  $\text{Ag}^+$ , and  $\text{Ti}^+$ ) to obtain supramolecular derivatives.<sup>[3,5,17]</sup>

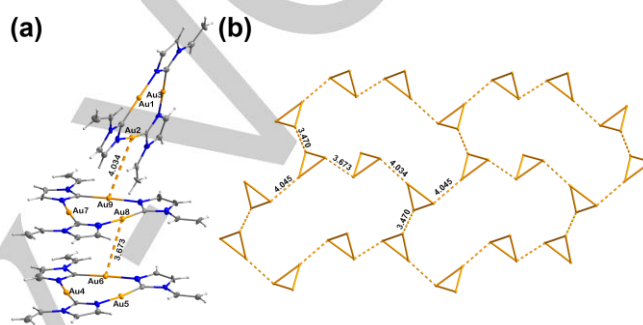


**Scheme 1.** Chemical structure of  $[\text{Au}(1\text{-Vilm})]_3$  (**1**) and the synthetic routes to obtain complexes **2** – **4**.

Previously-reported approaches to heterometallic clusters, including intercluster reactions, co-reduction of multiple metal sources, and/or metal tailoring to metal clusters, lacked definitive Au-M' stoichiometric ratio or positions/geometries of reactions.<sup>[33–37]</sup> The herein-reported synthesis involves controllable insertion of metal cations into gold complexes in a solution-based reaction with a definitive Au:M' stoichiometric ratio (6:1) and bis( $\eta^9$ -CTC) sandwiched coordination to  $\text{M}^+$  cations.<sup>[6,27]</sup> A similar approach was adopted to synthesize complexes **2** – **4** based on different closed-shell metal cations in good or quantitative yields. The general chemical formulae of these heterometallic complexes are assigned on the basis of the analytical and spectroscopic data, as well as by analogy with similar sandwich-like complexes, to give  $\{[\text{Au}(1\text{-Vilm})]_3 \cdot \text{M}^+ \cdot [\text{Au}(1\text{-Vilm})]_3\} \text{X}^-$  ( $\text{M}^+ = \text{Cu}^+$  (**2**),  $\text{Ag}^+$  (**3**),  $\text{X}^- = \text{BF}_4^-$ ;  $\text{M}^+ = \text{Ti}^+$  (**4**),  $\text{X}^- = \text{PF}_6^-$ ). For these heterometallic clusters, according to reported crystal structures, the inserted metal cations are intercalated between two planar CTCs by six gold(I) atoms in distorted trigonal prismatic coordination geometries.<sup>[6,28–32]</sup> The heterometallic clusters **2** and **3** are sparingly-soluble in common organic solvents while **4** is quite soluble in acetone. FT-IR spectra of complexes **2** – **4** do not show significant differences from the FT-IR spectrum of **1** in the mid-IR range, excluding the peaks at  $1050\text{ cm}^{-1}$  of  $\text{BF}_4^-$  and at  $830\text{ cm}^{-1}$  of  $\text{PF}_6^-$  counterions. The above evidence suggests that the insertions of metal cations have not influenced the frameworks of CTCs, which is substantiated by density functional theory (DFT) data below. This is also confirmed by the proton NMR spectrum of **4**, for example, whereby  $\text{Ti}^+$  coordination leads to small changes in chemical shifts and coupling constants of the vinyl groups.

X-ray-suitable single crystals of **1** were obtained by slow evaporation of a THF solution of the complex; however, multiple attempts of suitable single crystals of heterometallic clusters failed. Complex **1** crystallizes in the orthorhombic  $Pna2_1$  (No. 33) space group. Detailed crystallographic data are enclosed in Table S1, whereas selected bonds and angles are listed in Table S2 (Supporting Information). Figure 1a shows a thermal ellipsoid plot

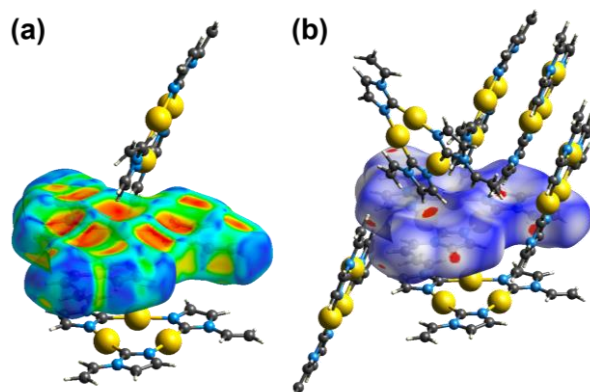
of the asymmetric unit of **1** while Figure 1b depicts the stacking mode in the repeating units. The molecular structure of **1** consists of a planar nine-membered ring formed by three gold(I) atoms and three  $\mu\text{-C}^2\text{,N}^3\text{-1-vinylimidazolate}$  bridging ligands. The Au(I) atoms exhibit the classical linear coordination mode with slight deviations from linearity ranging from  $174.2^\circ$  to  $176.5^\circ$ . The Au–C and Au–N bond lengths range from  $1.964(8)$  to  $1.988(9)$  Å and from  $2.036(6)$  to  $2.042(6)$  Å, respectively, which are similar to those found in other Au(I)-imidazolate CTCs.<sup>[11,32,38–40]</sup> The C=C bond lengths of the vinyl groups are varied either within the same CTC or in the others of the asymmetric unit, from  $1.263(10)$  to  $1.373(11)$  Å. Additional data about the crystal structure of **1** may be obtained from the Cambridge Structural Database, at <https://www.ccdc.cam.ac.uk> (CCDC No. 2115095).



**Figure 1.** (a) ORTEP plot of the asymmetric unit of **1** of 50% probability under 100 K. (b) Stacking mode of **1** in the repeating unit. Colour representation: Au, yellow; N, blue; C, grey; H, white. All the ligands are omitted in the (b) for clarify and only gold atoms with intratrimer contacts (solid lines) and intertrimer contacts (dash lines) are shown.

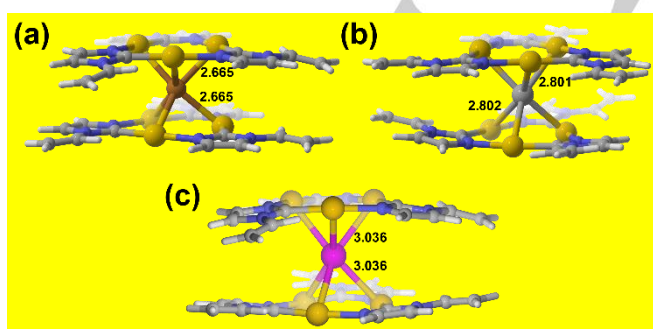
Unlike most  $d^{10}$ -metal CTCs that pack in the mode of discrete monomers, dimers-of-trimer, or 1D extended chains,<sup>[3]</sup> the spatial arrangement of **1** is quite complicated as combination of parallel and vertical packing. By considering three CTC molecules in the asymmetric unit, two of them are mutually-parallel but close-to-staggered and only two out of six gold atoms (one pair) interact with the intertrimer Au(6)–Au(8) distance of  $3.673$  Å. The third trimer is in a vertical position with respect to the plane defined by the other two parallel trimers with an angle of approximately  $77^\circ$ . Another pair of intertrimer Au(2)–Au(9) distance in the asymmetric unit is observed at a rather long,  $4.034$  Å, separation. Besides, two more intertrimer Au–Au contacts are found to be  $3.470$  and  $4.045$  Å. To analyse the stacking modes in **1** and find the underlying interacting sites and potential steric hindering effects, Hirshfeld surface analyses were performed.<sup>[41]</sup>





**Figure 2.** Hirshfeld surfaces for complex **1** mapped with (a) shape index (-1.00 to +1.00) and (b)  $d_{\text{norm}}$  (-0.02 to +1.00) plotted on the promolecular density.

Hirshfeld surface analyses mapped with shape index and  $d_{\text{norm}}$  for the monomer of complex **1** are plotted in Figure 2, and those for the asymmetric unit (containing three monomers) are enclosed in Figures S5-S6 (Supporting Information). Figure 2a illustrates the shape index (from -1.00 to +1.00) to identify the characteristic stacking mode. It is found that even for such a planar molecule, concave sides (red regions) cover the majority of the *xy*-plane and both convex (blue regions) and concave (yellow-orange regions) edges dominate the side of the molecule, which shapes the molecule an uneven surface. The differences in shape on the upper and side surface make other molecules approach from different directions to form close contacts, as depicted in Figure 2b. Note in Figure 2b that  $d_{\text{norm}}$  is plotted on the promolecular density and reflects the distances between the atoms of analysed and neighbouring molecules. The red region represents the distances shorter than the sum of van der Waals radii while the blue region depicts the separating distances. It can be observed that neighbouring molecules follow the unpredictable stacking mode that approaches in all directions by C-H... $\pi$  interactions, hydrogen bonding, or weak metal-metal interactions (metallophilicity; in particular, *aurophilicity* here).



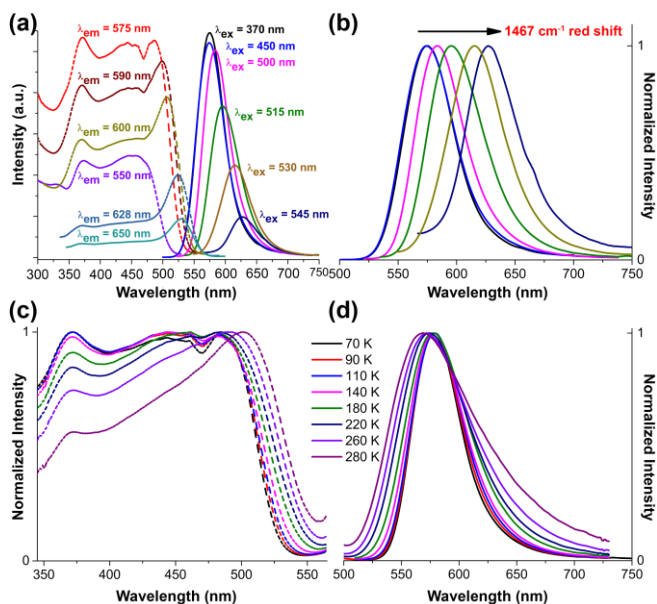
**Figure 3.** Optimized structures of metal adducts (a) Cu — **2**, (b) Ag — **3**, and (c) Tl — **4**. Au-M distances are labelled in the figure in Å.

To validate the possible conformations of metal adducts, in absence of crystal structures, DFT calculations were performed to optimize and determine the possible structures. The CTC alone was also optimized to compare with the crystal structure data,

hence validate the feasibility of the level of theory (Figure S7). As proposed, all the optimized metal adducts adopt sandwich-like conformations, as in previous reports of  $\text{Ag}^+/\text{Tl}^+$  complexes (Figure 3).<sup>[6,23–25,29]</sup> The average Au-M distances are 2.665 Å for **2**, 2.802 Å for **3**, and 3.036 Å for **4**, all significantly shorter than the summed van der Waals radii of Au(I) and  $\text{Cu}^+$ ,  $\text{Ag}^+$ , or  $\text{Tl}^+$ ; these distances also correspond to Au-M distances in previous sandwich-like complexes.<sup>[6,23–25,29]</sup> Moreover, the average intratrimer Au-Au distances in the metal adducts (3.51 Å in **2**, 3.55 Å in **3**, and 3.56 Å in **4**) are slightly longer than that in Au CTC alone (3.47 Å in single crystal and 3.48 Å in the DFT-optimized structure), suggesting stronger Au-M than Au-Au interactions.

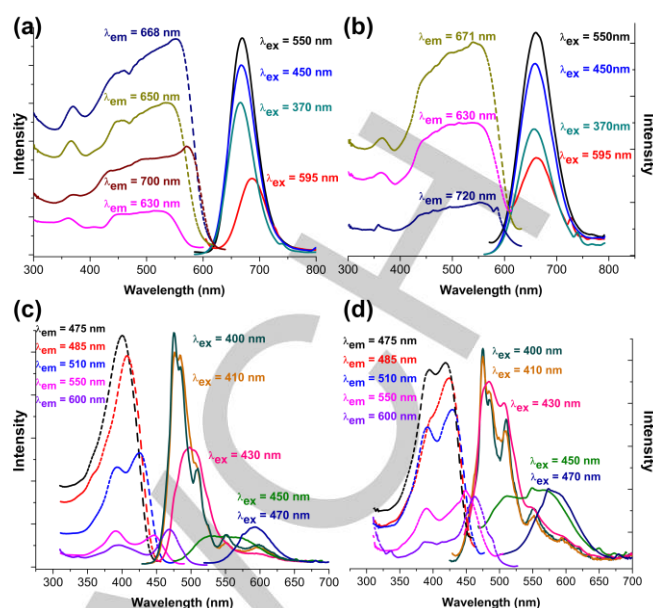
Owing to the considerable metal-metal interactions, CTCs are famous for their remarkably-rich photophysical properties. The crystalline solid of the vinylimidazolate trimer **1** encompasses multiple intertrimer Au-Au distances that are shorter than 3.7 Å; however, at room temperature, it does not display any detectable photoluminescence and only show very weak emissions at cryogenic temperatures. At 90 K, an exceptionally feeble yellow emission centres at 565 nm under the low-energy excitation wavelength of 425 nm with a large Stokes shift of 5830  $\text{cm}^{-1}$  (Figure S9). Unfortunately, the emission lifetime could not be acquired because of the faint emission even when solid **1** was immersed in liquid nitrogen.

After adducting with a foreign metal cation, complexes **2–4** display emissions in different colours, especially at lower temperatures. The silver adduct **3** has a yellow physical colour and shows bright yellow emission, with an emission maximum of 570 nm (Figure 4a). Multiple excitation peaks are also confirmed by using different emission wavelengths, two of which are higher-energy at around 370 and 445 nm for the emissions from 550 to 600 nm. The lowest-energy excitation peaks, ranging from 486 to 530 nm, can only be triggered by lower-energy emission band. The resulting emission shift under multiple excitation wavelengths is up to 1467  $\text{cm}^{-1}$  at 70 K, reflecting the nature of excitation-dependent emission profiles (Figure 4b). Varied-temperature photoluminescence measurements were also conducted and their results summarized in Figures 4c-d. Upon heating the solid crystalline powders from 70 K to 280 K, the low-energy excitation band around 500 nm dominates while the emission band stays still at around 570 nm with broadening its full-width-at-half-maximum (FWHM). Two corresponding lifetimes, 2.25 and 9.85  $\mu\text{s}$ , are observed at room temperature, which extend to 20.19 and 46.01  $\mu\text{s}$  at 70 K -- as expected (Table S3).



**Figure 4.** (a) Photoluminescence (dashed lines/left: excitation; solid lines/right: emission) spectra of **3** in the solid state at 70 K; excitation spectra are labelled with the emission wavelength monitored ( $\lambda_{em}$ ) while emission spectra are labelled with the exciting wavelength ( $\lambda_{ex}$ ). (b) Normalized emission spectra of **3** in the solid state at 70 K. Normalized (c) excitation and (d) emission spectra of **3** in the solid state at varied temperatures. The monitoring excitation and emission wavelengths are 480 and 575 nm, respectively.

The copper adduct **2** displays an orange physical colour and a deep-red emission at ambient temperature. The emission peak appears at 668 nm at 70 K with multiple excitation peaks at 370, 450, and 552 nm, as shown in Figure 5a. Upon heating to 220 K, the emission peak undergoes a slight blue shift to 659 nm while the excitation peaks only undergo changes in intensity, not energy (Figure 5b). Further heating back towards room temperature results in the emission peak blue-shifting by 803  $\text{cm}^{-1}$  to 634 nm concomitant with shortening the lifetimes to 1.70 and 3.67  $\mu\text{s}$  at 298 K (as expected; cf. 28.63 and 67.71  $\mu\text{s}$  at 70 K) while the intensity significantly drops to mirror the lifetime reduction (Figure S15, Table S3). Both silver and copper adducts **2** and **3** exhibit similar photoluminescence profiles that also correspond to previously-reported  $[\text{Au}_3]\dots\text{Ag}^+\dots[\text{Au}_3]$  sandwich-like clusters and can be tentatively assigned to primarily metal centred phosphorescence ( $^3\text{MC}$ ).<sup>[6,23,29]</sup> As illustrated in Figures 5c-d, the thallium adduct **4** can only emit under cryogenic environment. Unlike the two other heterometallic clusters, the emission profiles of **4** exhibit multiple peaks and mostly 100 nanosecond range lifetimes (151 and 637 ns at 180 K; 508 and 1734 ns at 70 K; Table S3). Low-energy broad emission could only be achieved by adopting longer excitation wavelengths > 450 nm. The structured emission peaks observed in **4** suggests significant ligand character admixed with the  $^3\text{MC}$  assignment used in the two other systems within the emissive heptanuclear cluster's exciton. More definitive assignments in all emissive systems in this work must await rigorous excited-state DFT calculations and/or experimental "photocrystallography" studies such as time-resolved single crystal X-ray or neutron diffraction.<sup>[42]</sup>



**Figure 5.** Photoluminescence (dashed lines/left: excitation; solid lines/right: emission) spectra of copper (**2**) and thallium (**4**) adducts in the solid state at different temperatures under varied excitation and emission wavelengths. (a) **2**, 70 K; (b) **2**, 220 K; (c) **4**, 70 K; (d) **4**, 180 K; excitation spectra are labelled with the emission wavelength monitored ( $\lambda_{em}$ ) while emission spectra are labelled with the exciting wavelength ( $\lambda_{ex}$ ).

In summary, we obtained a new Au(I) CTC bearing the 1-vinylimidazolate ligand and furthered the controllable synthetic pathway to afford heterometallic sandwich-like clusters. The stacking mode of CTC **1** is rationalized as the synergistic effect of metalphilicity and multiple non-covalent interactions, including hydrogen bonding and C-H... $\pi$  interactions. By further applying controllable synthetic doping-like methodology with definitive stoichiometric ratios, sandwich-like clusters such as  $[\text{Au}_3]\dots\text{M}^+\dots[\text{Au}_3]$  with  $\text{M} = \text{Cu}$  (**2**),  $\text{Ag}$  (**3**), or  $\text{Tl}$  (**4**), are first reported herein to show bright emissions with remarkably-rich properties (e.g., color changes dependent on the sandwich cation, excitation wavelength, and/or temperature). Based on DFT simulations and other chemical analyses, the sandwich-like conformations of these heterometallic clusters were confirmed. These results shed light on the syntheses and photoluminescence studies of heterometallic clusters while further research on different foreign metal ion intercalation and excited state properties are ongoing.

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**Keywords:** cyclic trinuclear complex • cluster • metallophilicity • photoluminescence • heterometallic cluster

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