

Soft Metal Cations Trigger Sandwich-Cluster Luminescence of a New Au(I)-Vinylimidazolate Cyclic Trinuclear Complex

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Dedicated to Professor Rinaldo Poli on the occasion of his 65th birthday, with admiration and with many congratulations for all his scientific achievements

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⁺, Ag⁺, and TI⁺, **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

Introduction

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.^[1,2] 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_2 -bridging-bidentate anionic ligands between three d¹⁰ monovalent metal centres, represent a major research focus in our research groups.^[3–5] These d¹⁰-metal CTCs have been

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Special Collection	Part of the "Celebratory Collection for Rinaldo Poli".

© 2022 The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited. 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.

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.^[6-17] Beyond that, ordered materials constructed from CTCs are being pursued in very recent years for their controllable skeletons and excellent optical/catalytic performances.^[18-25]

The clusters herein are formed by sandwiching a foreign closed-shell metal cation between two gold(I) CTC molecules, resulting in an [Au₃]...M⁺...[Au₃] chemical formula for the resulting heptanuclear cluster.^[6,26-32] Since they were discovered in 1998,^[28] few reports on structure determinations and luminescence properties only cover the central metal cations of Ag $^+$ and TI $^+$.^[6,26-32] Herein, we also add Cu $^+$ 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(vinylimidazolatogold(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.



Results and Discussion

The starting CTC was synthesized by adopting Vaughan's method to Au(I) pyridinate/imidazolate complexes.[3,11,33] 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 Ph₃PAuCl (Ph₃P=triphenylphosphine) to afford the new cyclic trinuclear Au(I) complex $[Au(1-Vilm)]_3$ (1), Scheme 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⁻¹, respectively. The proton NMR spectrum shows, in addition to the signals of 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 ${}^{3}J_{AX} = 16$ Hz, ${}^{3}J_{AM} =$ 8.8 Hz, and ${}^{2}J_{MX} = 1.5$ Hz. Owing to the nature of the central metal and bridging ligands, predicted by previous literature reviews, 1 is expected to show considerable π -basic property and be capable of reacting with Lewis acidic metal cations, especially softer ones (i.e., Cu⁺, Ag⁺, and Tl⁺) to obtain supramolecular derivatives.[3,5,17]

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.[33-37] 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(η^9 -CTC) sandwiched coordination to M'+ cations.^[6,27] A similar approach was adopted to synthesize complexes 2-4 (Scheme 1) 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 {[Au(1-Vilm)]₃·M⁺·[Au(1-Vilm)]₃}X, (M⁺ = Cu⁺ (2), Ag⁺ (3), X=BF₄⁻; M⁺ $=TI^{+}$ (4), X=PF₆). 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.[6,28-32] 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 cm⁻¹ of BF₄⁻ and at 830 cm⁻¹ of PF₆⁻ 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 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 Pna21 (No. 33) space group. Detailed crystallographic data are enclosed in Table S1 and powder X-ray diffraction patterns are shown in Figure S5, 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 μ -C²,N³-1-vinylimidazolate bridging ligands. The Au(I) atoms exhibit the classical linear coordination mode with slight deviations from linearity ranging from 174.2° to 176.5°. 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.^[11,32,38-40] 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).

Unlike most d¹⁰-metal CTCs that pack in the mode of discrete monomers, dimers-of-trimer, or 1D extended chains,^[3] 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



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



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.



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°. 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.^[41]

Hirshfeld surface analyses mapped with shape index and d_{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 S6–S7 (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_{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... π interactions, hydrogen bonding, or weak metal-metal interactions (metallophilicity; in particular, aurophilicity here).

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 S8). As proposed, all the optimized metal adducts adopt sandwich-like conformations, as in previous reports of Ag⁺/TI⁺

complexes (Figure 3).^[6,23-25,29] 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 Cu⁺, Ag⁺, or Tl⁺; these distances also correspond to Au–M distances in previous sandwich-like complexes.^[6,23-25,29] 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 cm⁻¹ (Figure S10). 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 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 µs, are observed at room



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



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.



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 (λ_{em}) while emission spectra are labelled with the exciting wavelength (λ_{em}). (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.



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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 (λ_{em}) while emission spectra are labelled with the exciting wavelength (λ_{em}).

temperature, which extend to 20.19 and 46.01 μs at 70 K-as expected (Table S3).

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 cm⁻¹ to 634 nm concomitant with shortening the lifetimes to 1.70 and 3.67 µs at 298 K (as expected; cf. 28.63 and 67.71 µs at 70 K) while the intensity significantly drops to mirror the lifetime reduction (Figure S16 and Table S3). Both silver and copper adducts 2 and 3 exhibit similar photoluminescence profiles that also correspond to previously reported [Au₃]...Ag⁺ ...[Au₃] sandwich-like clusters and can be tentatively assigned to primarily metal-centred phosphorescence (³MC) and further confirmed by time-dependent DFT (TD-DFT) results (Table S4).^[6,23,29] 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 suggest significant ligand character admixed with the ³MC assignment used in the two other systems within the emissive heptanuclear cluster's exciton; TD-DFT calculations validate our hypothesis of admixed ³MC/³LMCT nature of low-lying triplet excited states (Table S4). 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^[42] or neutron^[43] diffraction.

Conclusions

In summary, we obtained a new Au(I) CTC bearing the 1vinylimidazolate 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 metallophilicity and multiple non-covalent interactions, including hydrogen bonding and C–H... π interactions. By further applying controllable synthetic doping-like methodology with definitive stoichiometric ratios, sandwich-like clusters such as $[Au_3]...M^+...[Au_3]$ with M = Cu (2), Ag (3), or 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.



Experimental Section

Materials. HPLC grade solvents, the 1-vinylimidazole, *n*-butyllithium 2.5 M in hexane, $[Cu(CH_3CN)_4]BF_4$, AgBF₄, and TIPF₆ were purchased from Merck and used without further purification. Crystals of HAuCl₄·nH₂O were obtained by storing at 4 °C a highly concentrated watery solution obtained by dissolving a chip of gold foil in aqua regia. The Ph₃PAuCl was recovered as a microcrystalline solid from a suspension obtained by adding a double amount of PPh₃ to a solution of HAuCl₄ in ethanol.^[44] Anhydrous and free-radical tetrahydrofuran (THF) was obtained by treating the solvent with sodium/acetophenone under N₂ atmosphere.

Synthesis and Characterization. Elemental analyses (C, H, N) were performed in-house with a Fisons Instrument 1108 CHNS-O elemental analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to 600 cm⁻¹ with a Perkin-Elmer SPECTRUM ONE System FT-IR instrument. Far-infrared (far-IR) spectra from 600 to 50 cm^{-1} were recorded using a Nicolet 6700 analytical FT-IR spectrometer equipped with a Smart Orbit high-performance diamond single bounce accessory for attenuated total reflectance measurements. IR annotations used: vs = very strong, s = strong, m = medium, w = weak. Steady-state luminescence spectra were recorded by a PTI Quanta Master Model QM-4 scanning spectrofluorometer equipped with a 75-watt xenon lamp and a PMT detector. Temperaturedependent studies were achieved with an Oxford optical cryostat using liquid nitrogen as a coolant. Emission lifetimes were acquired using a Xenon flash lamp or a Nitrogen laser as the pulsed light source. ¹H NMR spectra were recorded on an Oxford-400 Varian spectrometer. Chemical shifts, in ppm, for ¹H NMR spectra are relative to the internal standard Me₄Si. NMR annotations used: s = singlet, d = doublet, dd = double-of-doublets, t = triplet, m = multiplet.

X-ray Crystal Structure Determination. Crystal structure determination for compound 1 was carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer equipped with a low-temperature device and Mo-target X-ray tube (wavelength = 0.71073 Å). Measurements were taken at 100(2) K. Data collection, indexing, and initial cell refinements were carried out using APEX2,^[45] whereas frame integration and final cell refinements were done using the SAINT software.^[46] An absorption correction was applied using the program SADABS.^[47] All non-H atoms were refined anisotropically. The H atoms in the compounds were placed in idealized positions and refined as riding atoms. Structure solution, refinement, graphics, and generation of publication materials were performed using the SHELXTL software.^[48,49] Refinement details and structural parameters for the investigated compound 1 are summarized in Table S1. Powder XRD patterns are enclosed in Figure S5 under the Cu X-ray source (wavelength = 1.54018 Å).

Synthesis of [Au(1-Vilm)]₃, 1. To a solution of 1-vinylimidazole (0.2078 g; 2.2 mmol) in 15 mL of anhydrous freshly distilled THF, cooled at -40°C, n-butyllithium (2.5 M in n-hexane; 0.88 mL; 2.2 mmol) was added. The solution was stirred for 1 h to obtain a deep orange solution, then the temperature was raised to 0°C and stirred for a further 0.5 h, resulting in a wine-red solution. Ph₃PAuCl (1.0883 g; 2.2 mmol) was added to the above solution and the reaction mixture was stirred for another 2 h at room temperature until a brown solution was observed. The reaction mixture was exposed to air and evaporated to dryness; the residue was extracted with dichloromethane and the brown extract was washed with water (5×10 mL), dried over sodium sulphate. After filtration, the deep yellow solution was evaporated to dryness. The crude oil obtained was treated with n-hexane and left under vigorous stirring overnight. The ivory-coloured powder was dissolved in hot THF (30 mL) and the solution was filtered and left to evaporate. After two days white crystals of the analytical sample 1 were obtained. Yield: 60% (based on PPh₃AuCl). Elemental analysis, anal. calcd. (%) for $C_{15}H_{15}N_6Au_3$: C 20.69, H 1.74, N 9.66; found: C 20.86, H 1.68, N 9.53. M.p. 260–263 °C with decomposition. FT-IR (cm⁻¹): 3149 (w), 3126 (w), 3100 (w), 3039 (w), 1642 (vs), 1567 (w), 1530 (w), 1474 (w), 1450 (w), 1419 (vs), 1347 (s), 1286 (w), 1258 (vs), 1146 (vs), 1116 (m), 1029 (m), 963 (s), 953 (s), 868 (vs), 735 (s), 722 (vs), 707 (s), 676 (vs), 659 (vs). ¹H-NMR (acetone-d⁶, r. t.): δ): 7.91 (d, ³J = 1.8 Hz, 3H), 7.59 (dd, ³J = 16 Hz, ³J = 8.8 Hz, 3H), 7.12 (d, ³J = 1.8 Hz, 3H), 5.51 (dd, ³J = 16 Hz, ²J = 1.5 Hz, 3H).

Synthesis of $\{[Au(1-Vilm)]_3 \cdot Cu^+ [Au(1-Vilm)]_3](BF_4^-)$, **2**. At room temperature, to a solution of **1** (0.030 g; 0.034 mmol) in 10 mL of anhydrous/freshly distilled THF, solid $[Cu(CH_3CN)_4]BF_4$ (0.0054 g; 0.017 mmol) was added. Immediately, the formation of an orange precipitate was observed. The reaction mixture was stirred for 1 h then centrifuged. The orange precipitate isolated was washed with cooled THF (2×3 mL) and dried under vacuum, giving the analytical sample **2**. Yield: 65%. Elemental analysis, anal. calcd. (%) for C₃₄H₃₈N₁₂OAu₆CuBF₄: C 20.79, H 1.95, N 8.56; found: C 19.92, H 1.71, N 8.30. M.p. 258–260 °C with decomposition. FT-IR (cm⁻¹): 3155 (w), 3130 (w), 2966 (w), 2848 (w), 1645 (vs), 1533 (w), 1423 (vs), 1353 (m), 1274 (vs), 1151 (s), 1126 (m), 1052 (vs), 1032 (vs), 959 (s), 868 (s), 733 (s), 700 (m), 678 (vs), 665 (vs).

Synthesis of {[Au(1-Vilm)]₃·Ag⁺·[Au(1-Vilm)]₃/(BF₄⁻), **3**. A procedure identical to that applied for **2** was followed, using AgBF4 (0.0033 g; 0.017 mmol) as the metal source. Immediately, the formation of a yellow precipitate was observed. The reaction mixture was stirred for 1 h then centrifuged. The yellow precipitate was isolated, washed with cooled THF (2×3 ml) and dried under vacuum, giving the analytical sample **3**. Yield: 93 %. Elemental analysis, anal. calcd. (%) for $C_{30}H_{30}N_{12}Au_6AgBF_4$: C 18.61, H 1.56, N 8.68; found: C 19.00, H 1.24, N 8.31. M.p. 239–242 °C with decomposition. FT-IR (cm⁻¹): 3154 (w), 3130 (w), 2953 (w), 2854 (w), 1645 (vs), 1533 (w), 1420 (vs), 1350 (m), 1272 (vs), 1149 (s), 1125 (m), 1053 (vs), 1030 (vs), 958 (s), 871 (s), 727 (s), 703 (m), 676 (vs), 663 (vs).

Synthesis of $\{[Au(1-Vilm)]_3:Tl^+ \cdot [Au(1-Vilm)]_3](PF_6^-), 4$. A procedure identical to that applied for **2** was followed, using solid TlPF₆ (0.0064 g; 0.017 mmol) as the metal source. Immediately, the formation of a pale-green precipitate was observed. The reaction mixture was stirred for 1 h then centrifuged. The pale-green precipitate was isolated, washed with cooled THF (2×3 ml) and dried under vacuum, giving the analytical sample **4**. Yield: 68%. Elemental analysis, anal. calcd. (%) for C₃₄H₃₈N₁₂OAu₆TlPF₆: C 18.88, H 1.77, N 7.77; found: C 17.32, H 1.34, N 7.04. M.p. 257–260 °C with decomposition. FT-IR (cm⁻¹): 3162 (w), 3136 (w), 2961 (w), 2839 (w), 1646 (vs), 1532 (w), 1419 (vs), 1349 (m), 1272 (vs), 1150 (s), 1122 (m), 1065 (vs), 1031 (vs), 962 (s), 876 (s), 829(s), 739 (s), 727 (m), 676 (vs), 663 (vs). ¹H-NMR (acetone-d⁶, r. t., δ): 7.80 (s, 6H), 7.48 (dd, ³J = 16.5 Hz, ³J = 9.0 Hz, 6H), 6.99 (s, 6H), δ 5.46 (d, ³J = 16.5 Hz, 6H), 4.89 (d, ³J = 9 Hz, 6H), 3.62 (t, 4H), 1.79 (m, 4H).

Computational Details. Density functional theory (DFT), unrestricted density functional theory (U-DFT) and time-dependent density functional theory (TD-DFT) calculations were conducted by the Gaussian 16 A.03 program,^[50] employing the hybrid PBE0 functional and Grimme's D3 dispersion correction with Becke-Johnson (BJ) damping.^[51-54] The Karlsruhe def2-TZVP basis set was adopted for all elements.^[55] Full ground-state geometry optimizations were performed and no imaginary frequencies were found for complexes **1**, **2**, or **3** to ensure the energies were true minima. Two small negative frequencies (-6.71 and -8.64 cm⁻¹) were found for complex **4**, showing skeleton breathing that does not influence the sandwich-like structure. Figure 3 was visualized by the CYLview software.^[56] U-DFT was employed to optimize the lowest-triplet excited state (T_1) structure and no imaginary frequencies were



found. TD-DFT calculations were conducted to simulate the absorption spectra based on the S_0 ground-state structures and phosphorescence energies based on the T_1 structures. The first 20 singlet and triplet excited states were taken into consideration. Electron density difference (EDD) maps were analysed by the Multiwfn 3.8 software.^[57]

Deposition Number 2115095 (for 1) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www. ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Cyclic trinuclear complexes · Cluster compounds · Heterometallic clusters · Metallophilicty · Photoluminescence

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