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Assembly of strongly phosphorescent hetero-bimetallic and -trimetallic [2]catenane structures based on a coinage metal alkynyl system†

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Homo-metallic metal alkynyl complexes exhibit interesting catenane structures, but their hetero-metallic catenane counterparts are under-developed. In this work, we report rare examples of bimetallic Au–Cu (DtbpC≡C[−] ligand; Dtbp = 3,5-di-*tert*-butylphenyl), Au–Ag (^tBuC≡C[−] ligand), and Au–Cu, Au–Ag (C6-FluoC≡C[−] ligand; C6-Fluo = 9,9-dihexyl-9*H*-fluoren-2-yl) complexes as well as a trimetallic Au–Ag–Cu (C6-FluoC≡C[−] ligand) complex, which feature [2]catenane structures. The formation of the [2]catenane structure is significantly affected by the coinage metal ion(s) and change of the structure of the alkynyl ligand. These hetero-metallic [2]catenane structures are strongly luminescent with tunable emission λ_{max} from 503 to 595 nm and Φ values up to 0.83.

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Introduction

The construction of intriguing types of interpenetrated structures, including catenanes, continues to be an active area in supramolecular science. Various strategies, including π - π stacking, hydrogen bonding, metal templating, and hydrophobic interactions, have been developed to direct the assembly of interpenetrated structures.¹ Closed-shell metallophilic interactions could also be appealing driving forces for the formation of catenanes, as demonstrated by the [2]catenane structures of [(^tBuC≡CAu)₆]₂,² (RC≡CAu)₁₀,³ and Au_{*n*}(SR)_{*n*} (*n* = 10,⁴ 11,⁵ and 12 (ref. 4)) which feature Au^I–Au^I interactions (Au–Au 2.88–3.30 Å, *e.g.* Fig. 1, upper). We previously reported a [3]catenane structure of (^tBuC≡CCu)₂₀.⁶ This type of catenane, first reported by Mingos and co-workers,² is based on homoleptic homo-metallic alkynyl or thiolate complexes. Puddephatt and co-workers reported heteroleptic Au^I-alkynyl/phosphine complexes adopting [2]catenane structures, which also feature Au^I–Au^I interactions.⁷ The quest remains for hetero-metallic catenanes based on a homoleptic metal alkynyl system.

An important feature of Au^I-alkynyl catenanes is the presence of two linear RC≡C–Au–C≡CR units in the locking center.^{2,3} These units function as a template to facilitate the

formation of the first ring and as a building block for the second ring. In view of the RC≡C–M–C≡CR species commonly seen in the literature,⁸ homoleptic hetero-metallic coinage metal alkynyl complexes might also be suitable candidates for the construction of catenanes. A key issue is the control of the complex size, which is tunable by adjusting the bulkiness and/or substitution pattern of the alkynyl ligand.⁹ However, the

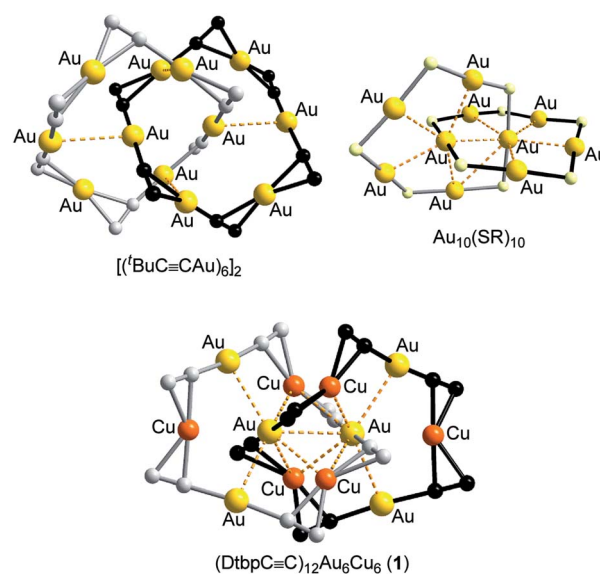


Fig. 1 Upper: Literature examples of homo-metallic [2]catenanes. Lower: Hetero-metallic [2]catenane 1, an example of five hetero-metallic [2]catenanes reported in this work. The peripheral groups (^tBu, R or Dtbp) are not shown. The metallophilic interactions are depicted as dashed lines.

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design of new structures with specific configurations is hampered by the complexity and limited understanding of the structures of such complexes,^{8a,10,11} particularly for trimetallic ones.^{10c,d} Also, in view of their intriguing phosphorescence and potential materials application,^{12,13} the exploration of new structures of hetero-metallic alkyne complexes with high stability could be rewarding. Based on our previous work on a Cu^I-alkynyl system,⁹ we employed bulky alkyne ligands RC≡C⁻ (R = 3,5-di-*tert*-butylphenyl (Dtbp), 9,9-dihexyl-9H-fluoren-2-yl (C6-Fluo), or ^tBu) to construct novel assemblies of hetero-metallic alkyne complexes. Herein, we described the formation of five hetero-metallic alkyne [2]catenanes (including bimetallic **1**, **4**, **5** and **7**, and trimetallic **6**, Fig. 1 and 2) by the self-assembly of homoleptic coinage metal alkyne systems. As revealed by the structures of these complexes and two other hetero-metallic complexes **2** and **3** (Fig. 2), the proper combination of coinage metal ions and alkyne ligands is crucial to the formation of the catenane structure.

Results and discussion

The bimetallic complexes **1**, **2**, **4**, **5** and **7** were prepared by mixing two homoleptic metal complexes in a 1 : 1 or 5 : 1 (for **7**)

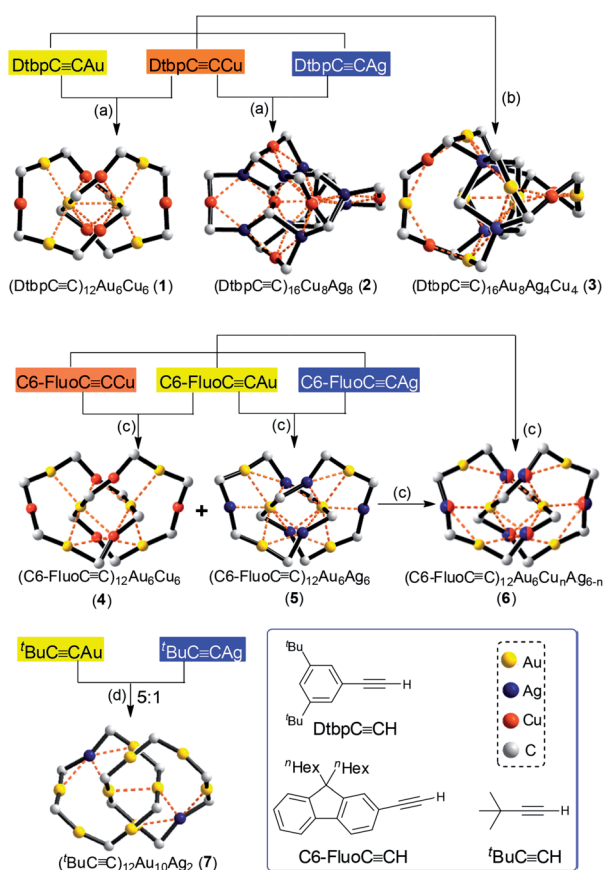


Fig. 2 The synthetic scheme and coordination cores of hetero-metallic coinage metal complexes **1**–**7**. The metallophilic interactions are depicted as dashed lines; for each alkyne ligand, only the α carbon atom is shown. Reagents and conditions: (a) CH₂Cl₂/MeCN; (b) chlorobenzene; (c) toluene/MeCN; (d) CH₂Cl₂/Et₃N.

molar ratio, and the trimetallic complexes **3** and **6** were prepared by mixing the homoleptic gold, silver and copper alkyne complexes in a 2 : 1 : 1 molar ratio or by mixing the hetero-metallic Au–Cu and Au–Ag alkyne complexes in a 1 : 1 molar ratio. Complexes **1**–**3** were also accessible from the reactions of alkynes with Au(SMe₂)Cl, AgOTf and/or [Cu(MeCN)₄]PF₆ (2 : 1 : 1 for **1** and **2** and 3 : 1 : 1 : 1 for **3**) in the presence of Et₃N (yields: 27–78%). X-ray diffraction-quality crystals of **1**–**7** were obtained by the slow evaporation of the CH₂Cl₂/MeCN, chlorobenzene or toluene/MeCN solutions and their structures were determined by X-ray crystallography (Tables S1 and S2 in the ESI†).

The Au–Cu complex **1**, with a formula of (DtbpC≡C)₁₂Au₆Cu₆, has a crystallographic *D*₂ symmetry and features two twisted (DtbpC≡C)₆Au₃Cu₃ rings that are interlocked to form a [2]catenane structure (Fig. 3). Each ring is composed of three linear DtbpC≡C–Au–C≡CDtbp units and three Cu ions with relatively weak Au–Cu (2.9632(10) Å) and Au–Au (2.9625(3)–3.1497(8) Å) interactions (*cf.* the sums of the metallic radii: Au–Cu 2.72 Å and Au–Au 2.88 Å (ref. 14)), which are comparable to the metallophilic interactions in the well documented Au^I-alkynyl and -thiolate [2]catenanes (Au–Au 2.88–3.30 Å).^{2–5} The bridging alkyne groups each coordinate to the Au and Cu ions in the η^1 - and η^2 -modes, respectively. The M–C distances (Au–C 1.979(7)–2.009(6) Å and Cu–C 2.018(7)–2.285(14) Å) are comparable to those in the homo-metallic [2]catenane [(^tBuC≡CAu)₆]₂ (Au–C 1.85(4)–2.26(3) Å)² (Fig. 4). These observations make it reasonable to describe **1** as a hetero-metallic [2]catenane. In contrast, the PhC≡C⁻ counterpart of **1**, (PhC≡C)₁₂Au₆Cu₆, adopts a non-catenane structure in which the six Au^I ions are co-

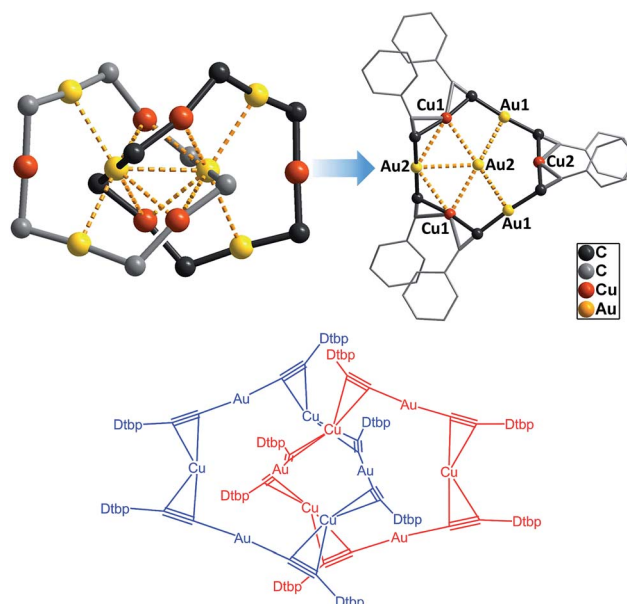


Fig. 3 The [2]catenane structure of **1**. Upper left: the coordination core. Upper right: one of the two interlocked (DtbpC≡C)₆Au₃Cu₃ rings. The ^tBu groups and hydrogen atoms are omitted for clarity, and the metallophilic interactions are depicted as dashed lines. Lower: a wire frame representation with the omission of the metallophilic interactions.



planar and the six Cu^I ions form a trigonal prism with the PhC≡C[−] ligands situated on the two opposite sides, rendering the Ph groups (for each side) rather close to each other¹⁰ⁱ and reflecting the unique role of the bulky Dtbp groups of **1** in the assembly/stabilization of the [2]catenane structure of the Au₆Cu₆ alkynyl complex. It is probable that the non-catenane structure of (PhC≡C)₁₂Au₆Cu₆, upon changing its alkynyl ligands to the bulkier and more basic DtbpC≡C[−] ligands, is destabilized owing to the increased steric hindrance [resulting from the bulkiness of the electron-donating ^tBu substituents and stronger metal-alkynyl binding (*cf.* Au–C 2.004(6)–2.045(5) Å in (PhC≡C)₁₂Au₆Cu₆ (ref. 10*i*) vs. 1.979(7)–2.009(6) Å in **1**), and as such the steric hindrance is minimized in the [2]catenane structure of the Au–Cu complex **1**.

By changing Au–Cu to Cu–Ag, but with the same DtbpC≡C[−] ligand unchanged, a non-catenane complex (DtbpC≡C)₁₆Cu₈Ag₈ (**2**) was obtained. Complex **2** has a structure with an approximate S₄ symmetry (Fig. 5a, Cu–Ag 2.6824(3)–3.0416(4) Å) and contains a rather complicated metallacycle core (Fig. 6a, Cu–C 1.855(3)–1.889(3) Å, Ag–C 2.236(3)–2.643(2) Å); the topology of its metallophilic interactions is similar to that of the recently reported Au–Ag counterpart (DtbpC≡C)₁₆Au₈Ag₈, also with a non-catenane structure.^{11b} In the case of **3**, its structure (Fig. 5b) features a metallacycle core (Au–C 1.950(7)–2.025(9) Å, Cu–C 1.919(8)–2.038(6) Å, Ag–C 2.364(6)–2.618(7) Å) which is markedly different from that formed by simply replacing the four Ag ions of the (DtbpC≡C)₁₆Au₈Ag₈ molecule^{11b} with four Cu ions. As shown in Fig. 6b, compared with (DtbpC≡C)₁₆Au₈Ag₈, **3** features central Au–Au distance (Au2–Au5 2.9591(9))^{11b} ~0.22 Å longer vs. Au3–Au7 3.1825(4) Å) and substantially larger C–M–C (M = Cu3, Cu4) angles (139.4(5)–142.6(4)° (M = Ag1, Ag2)^{11b} vs. 172.4(3)–177.0(4)°).

Changing the R group of RC≡C[−] from Dtbp to the bulkier C6-Fluo resulted in the formation of bimetallic (C6-FluoC≡C)₁₂Au₆Cu₆ (**4**) and (C6-FluoC≡C)₁₂Au₆Ag₆ (**5**) and trimetallic (C6-FluoC≡C)₁₂Au₆Cu_nAg_{6−n} (**6**), and all of the three complexes adopt a [2]catenane structure (Fig. 7). The arrangement of the six RC≡C–Au–C≡CCR units in **4–6** is similar to that in **1**; the connection of the C6-FluoC≡C–Au–C≡CCR units by π-C≡C–Cu/Ag coordination forms the [2]catenane structures. The Cu and Ag atoms in **6** are in substitutional

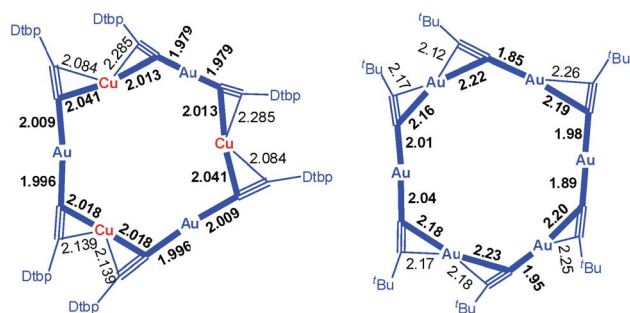


Fig. 4 The comparison of the M–C distances in the [2]catenanes **1** (left) and [(^tBuC≡CAu)₆]₂ (right). Only one ring is depicted in each case; the metallophilic interactions are not shown.

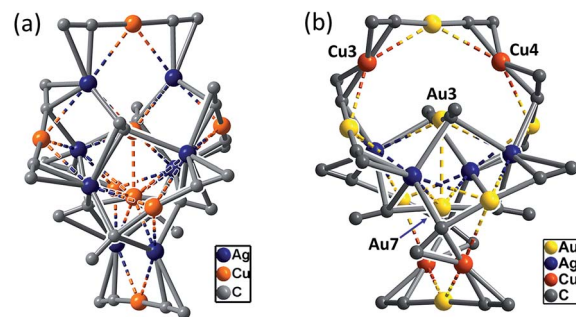


Fig. 5 A perspective view of **2** (a) and **3** (b). The Dtbp groups of the alkynyl ligands are omitted for clarity. The metallophilic interactions are depicted as dashed lines.

disorder (Fig. 7c): each π-C≡C–M is partially occupied by Cu and Ag atoms, the occupancy of the Ag atom of the outlier positions 1 and 2 (0.77 and 0.62, respectively) is slightly higher (Fig. 7c), and the overall Cu/Ag ratio (3.1 : 2.9) is close to the molar ratio (1 : 1) of **4** and **5** used in the preparation of **6**. The average Cu/Ag–C(α) distance in **6** is 0.14 Å longer than the average Cu–C(α) distance in **4** and 0.12 Å shorter than the average Ag–C(α) distance in **5**, while the difference of the average Au–C(α) distances between **4–6** is <0.03 Å.

As [2]catenane **6** can be formed by mixing the [2]catenanes **4** and **5** in solution, we also mixed the previously reported [2]catenane [(^tBuC≡CAu)₆]₂ (ref. 2) with [(^tBuC≡CAG)_n] (molar ratio 5 : 1), and obtained **7**, adopting a [2]catenane structure similar to that of [(^tBuC≡CAu)₆]₂ except for the replacement of one bis(η²-C≡C) coordinated Au ion in each ring by one Ag ion (Fig. 8).

We examined the solution behavior of the hetero-metallic [2]catenanes **1** and **4–7**, which are stable in solution at a concentration >10^{−4} M, using ESI-MS and ¹H NMR measurements (see the ESI[†]); the results for **1** are discussed here as examples. The ESI mass spectrum of **1** (~10^{−4} M) in CH₂Cl₂ features a prominent cluster peak at *m/z* 4146.4 attributed to [**1** + Na]⁺ (Fig. S1, ESI[†]), like the observation of cluster peaks at *m/z* 5876.4, 6142.2, and 6009.3, which are attributed to [**4** + Na]⁺, [**5** + Na]⁺, and [**6** + Na]⁺ for **4**, **5**, and **6**, respectively. In the ¹H NMR spectrum of **1** in CD₂Cl₂ and 1,2-dichlorobenzene-*d*₄ (~10^{−2} M, Fig. 9), three sets of coordinated DtbpC≡C[−] signals were observed at room

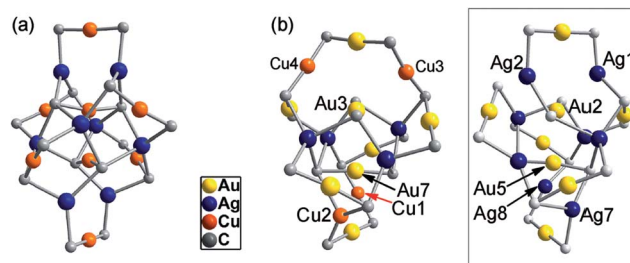


Fig. 6 The metallacycle cores in **2** (a) and **3** (b) as compared with that in (DtbpC≡C)₁₆Au₈Ag₈ (ref. 11b) (inset) with the omission of all the metallophilic interactions (for each alkynyl ligand, only the α carbon atom is shown).



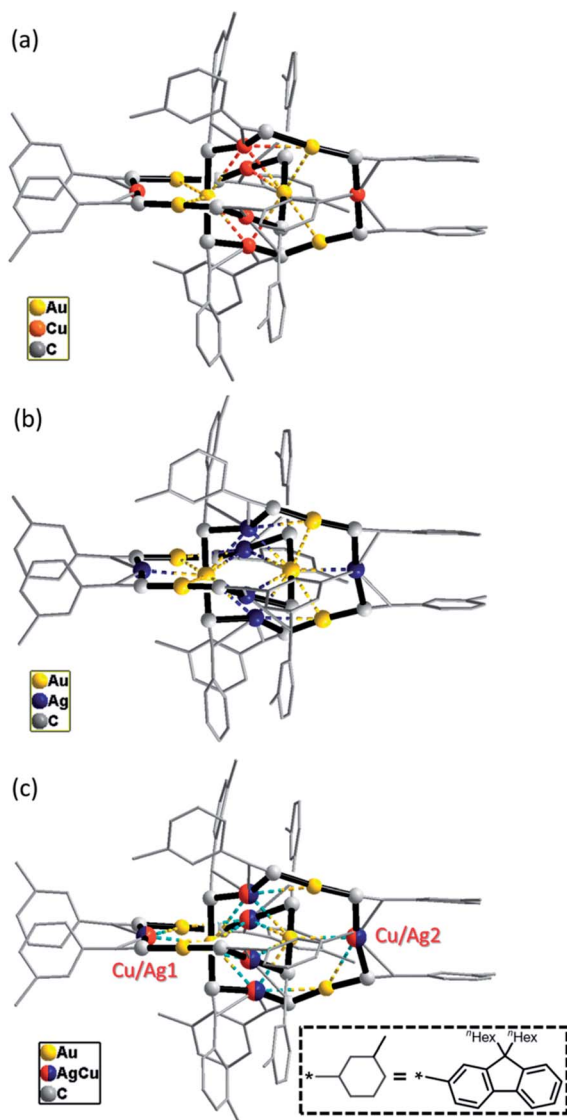


Fig. 7 A perspective view of the C6-FluoC≡C[−] ligand based complexes 4 (a), 5 (b) and 6 (c). All of the hydrogen atoms and parts of the C6-FluoC≡C[−] ligands are omitted for clarity. The metallophilic interactions are depicted as dashed lines.

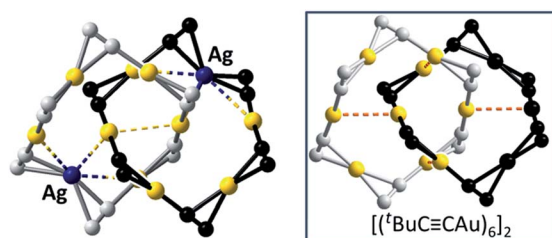


Fig. 8 A perspective view of the [2]catenane 7. Inset: a perspective view of [(^tBuC≡CAu)₆]₂ (ref. 2) for comparison. The ^tBu groups are omitted for clarity. The metallophilic interactions are depicted as dashed lines.

temperature (consistent with the D_2 symmetry in the crystal structure of **1**), which were broadened into one set upon increasing the temperature to 353 K and were then recovered by cooling back to room temperature (Fig. 9, upper right). These spectral changes could be associated with the dependence of the metallophilic interactions in **1** on temperature. We further examined the solution of **1** in CD₂Cl₂ at room temperature by ¹H DOSY NMR measurements; the spectrum obtained (Fig. S4, ESI[†]) reveals that the observed signals of DtbpC≡C[−] belong to a single complex (diffusion constant $D = 8.32 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), thus providing additional evidence for the purity of **1** in solution.

DFT calculations were performed to examine the electronic details of the hetero-metallic [2]catenanes using **1** as an example. The DFT-optimized geometry of **1** is comparable to that determined by X-ray crystal analysis. For example, the computed structure of **1** features average values of Au–C 1.997 Å, C–Au–C 176.2°, and Cu–C 2.053 Å; these values compare well with the corresponding ones in the crystal structure of **1** (average values: Au–C 1.995(7) Å, C–Au–C 176.9(8)° and Cu–C 2.097(7) Å). To gain insight into why the [2]catenane of (DtbpC≡C)₁₂Au₆M₆ was obtained for M = Cu (**1**) but not for M = Ag, we attempted to perform DFT optimization of (DtbpC≡C)₁₂Au₆Ag₆ with a hypothetical similar [2]catenane structure, which did not converge. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **1** are depicted in Fig. 10. The HOMO is mainly localized on the 5d_{z²} orbitals of the two Au atoms in the locking center of the [2]catenane structure, while the LUMO is distributed on the empty 6p orbitals of the same two Au atoms.

Complexes **1–7** are emissive in the solid state (Fig. 11). In view of their structural fluxional behavior in solution, their photo-physical properties in solution were not included in this study. The [2]catenanes **1** and **4–6** exhibit moderate yellow to strong orange emissions in the solid state ($\Phi = 0.37–0.83$). Changing the ligand from DtbpC≡C[−] to C6-FluoC≡C[−] resulted in a bathochromic shift in emission energy and a significant

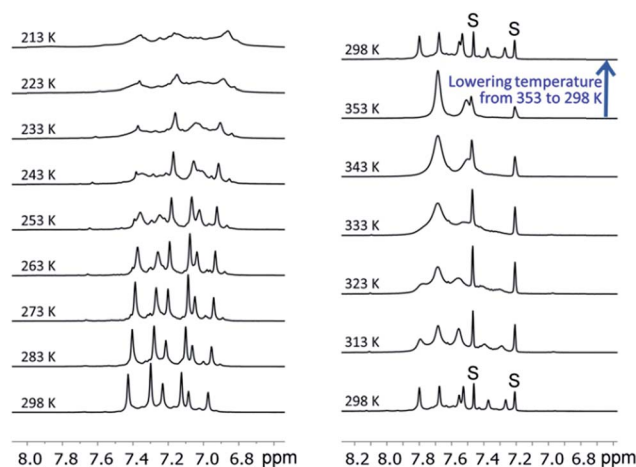


Fig. 9 The variable-temperature ¹H NMR spectra (in the aromatic region) of **1** in CD₂Cl₂ (left, 298 K → 213 K) and in 1,2-dichlorobenzene-*d*₄ (right, 298 K → 353 K → 298 K).



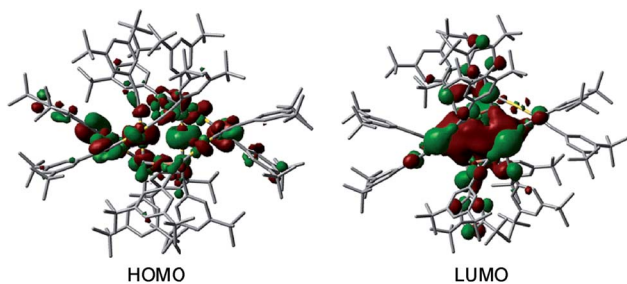


Fig. 10 The HOMO and LUMO of **1**. The hydrogen atoms are omitted for clarity. Color code: carbon (grey), gold (gold), and copper (orange).

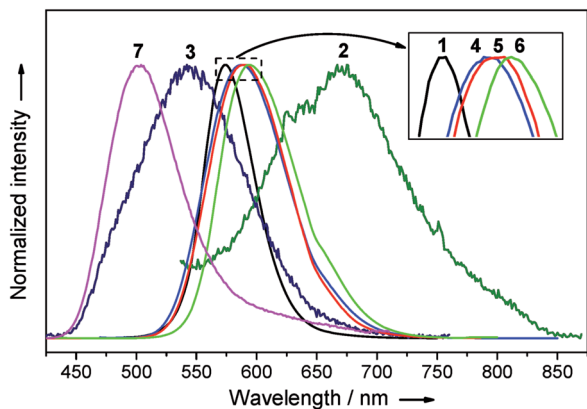


Fig. 11 The emission spectra of **1**–**7** in the solid state.

improvement in the quantum yield. Notably, the emission energy and efficiency show only minor variation with the metal compositions of **4**–**6** ($\lambda_{\text{max}} = 588$ – 595 nm, $\Phi = 0.71$ – 0.83 , and $\tau = 0.7$ – 1.0 μs). The comparison of the emission spectra of $(\text{DtbpC}\equiv\text{C})_{12}\text{Au}_8\text{Ag}_8$ ($\lambda_{\text{max}} = 489$ nm (ref. 11*b*)) and **3** reveals that the replacement of the four Ag ions by four Cu ions resulted in a broader and red-shifted emission band ($\lambda_{\text{max}} = 542$ nm). The excitation of **7** in the solid state gave a strong green emission at $\lambda_{\text{max}} 503$ nm with a tail up to 710 nm ($\Phi = 0.82$). The wide span in emission energy (λ_{max} from 503 to 595 nm) and high solid state emission quantum yields highlight the prospect of hetero-metallic [2]catenanes based on a coinage metal alkynyl system as useful photo-functional molecular materials.

The use of the $\text{C6-FluoC}\equiv\text{C}^-$ ligand to result in the assembly of hetero-bimetallic and hetero-trimetallic [2]catenanes $(\text{RC}\equiv\text{C})_{12}\text{Au}_6\text{M}_6$ ($\text{M} = \text{Cu}$ **4** and Ag **5**) and $(\text{RC}\equiv\text{C})_{12}\text{Au}_6\text{Cu}_n\text{Ag}_{6-n}$ (**6**) is remarkable. As **4**–**6** are nearly isostructural, it appears that their $\text{C6-FluoC}\equiv\text{C}^-$ ligands dominate the intermolecular interactions, with the effect of the Ag and Cu ions being minor in these cases. As revealed by the crystal structures of **4** and **5**, replacing the Cu ions with Ag ions slightly expands the metallacycle core owing to the longer Ag–C than Cu–C distances (Fig. S5, ESI[†]). The expansion of the metallacycle core would reduce the repulsion between the peripheral alkynyl ligands and increase the tendency of the complex to re-assemble to higher nuclearity species. The bulky $\text{C6-FluoC}\equiv\text{C}^-$ ligand with flexible C_6 -alkyl chains is likely to

restrict such tendency. For the complexes of the $\text{DtbpC}\equiv\text{C}^-$ ligand, which is sterically less demanding and relatively rigid, the replacement of the Cu ions by Ag ions leads to a core enlargement from M_{12} (**1**) to M_{16} (**3**). On the other hand, an Ag ion, compared with a Cu ion, is a stronger Lewis acid and is inclined to form weak interactions with more alkynyl ligands (cf. **2** and **3** in Fig. 5); the extra $\pi\text{-C}\equiv\text{C-Ag}$ interactions may distort the ring unit and then break the [2]catenane structure. Moreover, the preference of Au^{I} for a linear two-coordinate configuration should also play an important role in the assembly of the hetero-metallic [2]catenanes in view of the core enlargement from M_{12} (**1**) to M_{16} (**2**), upon replacing the Au ions with Ag ions, and the presence of linear $\text{RC}\equiv\text{C-Au}^{\text{I}}\text{-C}\equiv\text{CR}$ units in all of the [2]catenanes **1**, **4**–**6**, and **7**.

Conclusions

We have prepared and structurally characterized five hetero-metallic [2]catenanes based on coinage metal alkynyl complexes, including bimetallic Au–Cu and Au–Ag complexes and a trimetallic Au–Cu–Ag complex, by employing bulky $\text{DtbpC}\equiv\text{C}^-$, $\text{C6-FluoC}\equiv\text{C}^-$, and $^t\text{BuC}\equiv\text{C}^-$ ligands. The structure of the trimetallic [2]catenane **6** is analogous to its corresponding Au–Ag bimetallic [2]catenanes with some of the Ag atoms replaced by Cu atoms; mixing the Au–Cu and Au–Ag complexes is a feasible and efficient method to prepare the trimetallic complex. The formation of [2]catenanes relies upon a delicate balance between various intermolecular interactions. The structural characterization of **1**–**7** provides useful insight into a better understanding of hetero-metallic coinage metal alkynyl complexes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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