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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<sup>−</sup> ligand; Dtbp = 3,5-di-*tert*-butylphenyl), Au–Ag (<sup>t</sup>BuC≡C<sup>−</sup> ligand), and Au–Cu, Au–Ag (C6-FluoC≡C<sup>−</sup> ligand; C6-Fluo = 9,9-dihexyl-9*H*-fluoren-2-yl) complexes as well as a trimetallic Au–Ag–Cu (C6-FluoC≡C<sup>−</sup> 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  $\lambda_{\text{max}}$  from 503 to 595 nm and  $\Phi$  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  $\pi$ – $\pi$  stacking, hydrogen bonding, metal templating, and hydrophobic interactions, have been developed to direct the assembly of interpenetrated structures.<sup>1</sup> Closed-shell metallophilic interactions could also be appealing driving forces for the formation of catenanes, as demonstrated by the [2]catenane structures of [<sup>t</sup>BuC≡CAu]<sub>2</sub>,<sup>2</sup> (RC≡CAu)<sub>10</sub>,<sup>3</sup> and Au<sub>n</sub>(SR)<sub>n</sub> ( $n = 10$ ,<sup>4</sup> 11,<sup>5</sup> and 12 (ref. 4)) which feature Au<sup>I</sup>–Au<sup>I</sup> interactions (Au–Au 2.88–3.30 Å, *e.g.* Fig. 1, upper). We previously reported a [3]catenane structure of (<sup>t</sup>BuC≡CCu)<sub>20</sub>.<sup>6</sup> This type of catenane, first reported by Mingos and co-workers,<sup>2</sup> is based on homoleptic homo-metallic alkynyl or thiolate complexes. Puddephatt and co-workers reported heteroleptic Au<sup>I</sup>-alkynyl/phosphine complexes adopting [2]catenane structures, which also feature Au<sup>I</sup>–Au<sup>I</sup> interactions.<sup>7</sup> The quest remains for hetero-metallic catenanes based on a homoleptic metal alkynyl system.

An important feature of Au<sup>I</sup>-alkynyl catenanes is the presence of two linear RC≡C–Au–C≡CR units in the locking center.<sup>2,3</sup> 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,<sup>8</sup> 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.<sup>9</sup> However, the

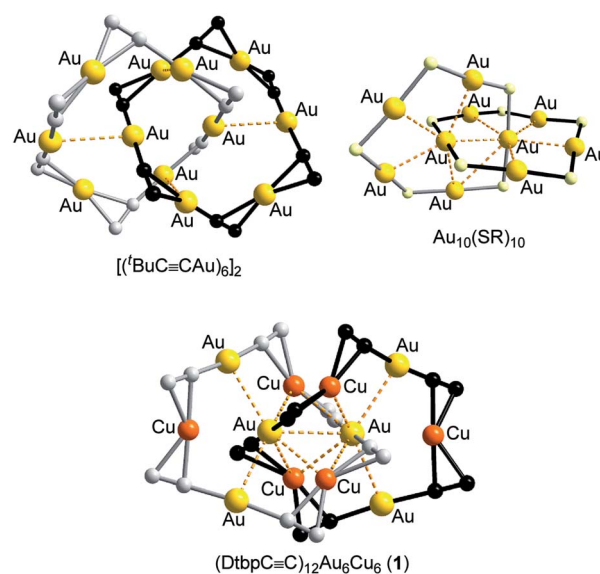


Fig. 1 Upper: Literature examples of homo-metallic [2]catenanes. Lower: Hetero-metallic [2]catenane 1, an example of five hetero-metallic [2]catenanes reported in this work. The peripheral groups (<sup>t</sup>Bu, R or Dtbp) are not shown. The metallophilic interactions are depicted as dashed lines.

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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,<sup>8a,10,11</sup> particularly for trimetallic ones.<sup>10c,d</sup> Also, in view of their intriguing phosphorescence and potential materials application,<sup>12,13</sup> the exploration of new structures of hetero-metallic alkyne complexes with high stability could be rewarding. Based on our previous work on a Cu<sup>I</sup>-alkynyl system,<sup>9</sup> we employed bulky alkyne ligands RC≡C<sup>-</sup> (R = 3,5-di-*tert*-butylphenyl (Dtbp), 9,9-dihexyl-9H-fluoren-2-yl (C6-Fluo), or <sup>t</sup>Bu) 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)

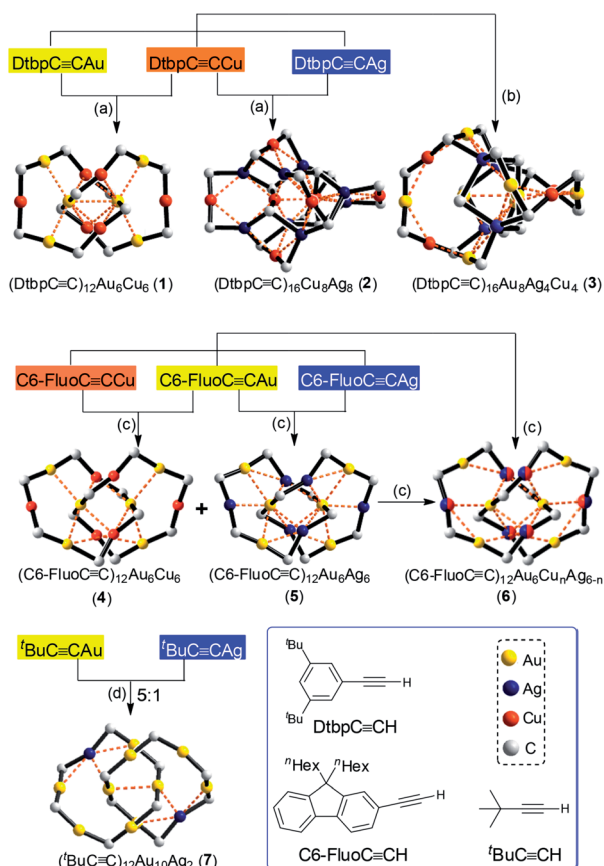


Fig. 2 The synthetic scheme and coordination cores of hetero-metallic coinage metal complexes 1–7. The metallophilic interactions are depicted as dashed lines; for each alkyne ligand, only the  $\alpha$  carbon atom is shown. Reagents and conditions: (a) CH<sub>2</sub>Cl<sub>2</sub>/MeCN; (b) chlorobenzene; (c) toluene/MeCN; (d) CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>3</sub>N.

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(SMe<sub>2</sub>)Cl, AgOTf and/or [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> (2 : 1 : 1 for 1 and 2 and 3 : 1 : 1 : 1 for 3) in the presence of Et<sub>3</sub>N (yields: 27–78%). X-ray diffraction-quality crystals of 1–7 were obtained by the slow evaporation of the CH<sub>2</sub>Cl<sub>2</sub>/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)<sub>12</sub>Au<sub>6</sub>Cu<sub>6</sub>, has a crystallographic *D*<sub>2</sub> symmetry and features two twisted (DtbpC≡C)<sub>6</sub>Au<sub>3</sub>Cu<sub>3</sub> 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<sup>I</sup>-alkynyl and -thiolate [2]catenanes (Au–Au 2.88–3.30 Å).<sup>2–5</sup> The bridging alkyne groups each coordinate to the Au and Cu ions in the  $\eta^1$ - and  $\eta^2$ -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 [(<sup>t</sup>BuC≡CAu)<sub>6</sub>]<sub>2</sub> (Au–C 1.85(4)–2.26(3) Å)<sup>2</sup> (Fig. 4). These observations make it reasonable to describe 1 as a hetero-metallic [2]catenane. In contrast, the PhC≡C<sup>-</sup> counterpart of 1, (PhC≡C)<sub>12</sub>Au<sub>6</sub>Cu<sub>6</sub>, adopts a non-catenane structure in which the six Au<sup>I</sup> ions are co-

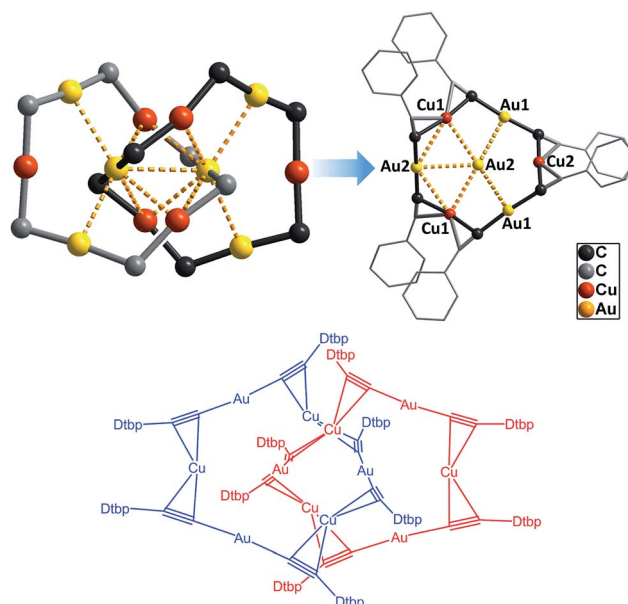


Fig. 3 The [2]catenane structure of 1. Upper left: the coordination core. Upper right: one of the two interlocked (DtbpC≡C)<sub>6</sub>Au<sub>3</sub>Cu<sub>3</sub> rings. The <sup>t</sup>Bu groups and hydrogen atoms are omitted for clarity, and the metallophilic interactions are depicted as dashed lines. Lower: a wire frame representation with the omission of the metallophilic interactions.



planar and the six Cu<sup>I</sup> ions form a trigonal prism with the PhC≡C<sup>−</sup> ligands situated on the two opposite sides, rendering the Ph groups (for each side) rather close to each other<sup>10i</sup> and reflecting the unique role of the bulky Dtbp groups of **1** in the assembly/stabilization of the [2]catenane structure of the Au<sub>6</sub>Cu<sub>6</sub> alkynyl complex. It is probable that the non-catenane structure of (PhC≡C)<sub>12</sub>Au<sub>6</sub>Cu<sub>6</sub>, upon changing its alkynyl ligands to the bulkier and more basic DtbpC≡C<sup>−</sup> ligands, is destabilized owing to the increased steric hindrance [resulting from the bulkiness of the electron-donating <sup>t</sup>Bu substituents and stronger metal-alkynyl binding (*cf.* Au–C 2.004(6)–2.045(5) Å in (PhC≡C)<sub>12</sub>Au<sub>6</sub>Cu<sub>6</sub> (ref. 10i) 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<sup>−</sup> ligand unchanged, a non-catenane complex (DtbpC≡C)<sub>16</sub>Cu<sub>8</sub>Ag<sub>8</sub> (**2**) was obtained. Complex **2** has a structure with an approximate S<sub>4</sub> 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)<sub>16</sub>Au<sub>8</sub>Ag<sub>8</sub>, also with a non-catenane structure.<sup>11b</sup> 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)<sub>16</sub>Au<sub>8</sub>Ag<sub>8</sub> molecule<sup>11b</sup> with four Cu ions. As shown in Fig. 6b, compared with (DtbpC≡C)<sub>16</sub>Au<sub>8</sub>Ag<sub>8</sub>, **3** features central Au–Au distance (Au2–Au5 2.9591(9))<sup>11b</sup> ~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)<sup>11b</sup> vs. 172.4(3)–177.0(4)°).

Changing the R group of RC≡C<sup>−</sup> from Dtbp to the bulkier C6-Fluo resulted in the formation of bimetallic (C6-FluoC≡C)<sub>12</sub>Au<sub>6</sub>Cu<sub>6</sub> (**4**) and (C6-FluoC≡C)<sub>12</sub>Au<sub>6</sub>Ag<sub>6</sub> (**5**) and trimetallic (C6-FluoC≡C)<sub>12</sub>Au<sub>6</sub>Cu<sub>n</sub>Ag<sub>6−n</sub> (**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

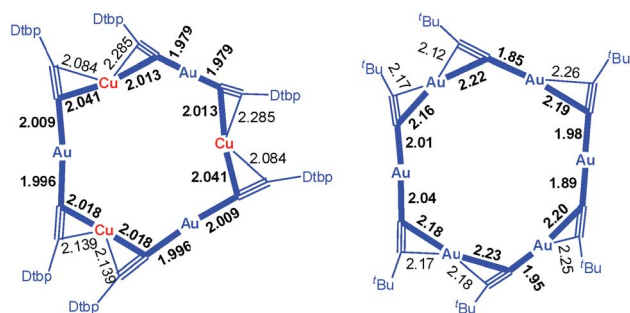


Fig. 4 The comparison of the M–C distances in the [2]catenanes **1** (left) and [(<sup>t</sup>BuC≡CAu)<sub>6</sub>]<sub>2</sub> (right). Only one ring is depicted in each case; the metallophilic interactions are not shown.

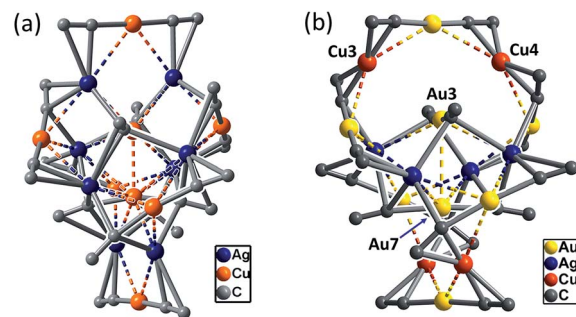


Fig. 5 A perspective view of **2** (a) and **3** (b). The Dtbp groups of the alkynyl ligands are omitted for clarity. The metallophilic interactions are depicted as dashed lines.

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 [(<sup>t</sup>BuC≡CAu)<sub>6</sub>]<sub>2</sub> (ref. 2) with [(<sup>t</sup>BuC≡CAG)<sub>n</sub>] (molar ratio 5 : 1), and obtained **7**, adopting a [2]catenane structure similar to that of [(<sup>t</sup>BuC≡CAu)<sub>6</sub>]<sub>2</sub> except for the replacement of one bis(η<sup>2</sup>-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<sup>−4</sup> M, using ESI-MS and <sup>1</sup>H NMR measurements (see the ESI<sup>†</sup>); the results for **1** are discussed here as examples. The ESI mass spectrum of **1** (~10<sup>−4</sup> M) in CH<sub>2</sub>Cl<sub>2</sub> features a prominent cluster peak at *m/z* 4146.4 attributed to [**1** + Na]<sup>+</sup> (Fig. S1, ESI<sup>†</sup>), like the observation of cluster peaks at *m/z* 5876.4, 6142.2, and 6009.3, which are attributed to [**4** + Na]<sup>+</sup>, [**5** + Na]<sup>+</sup>, and [**6** + Na]<sup>+</sup> for **4**, **5**, and **6**, respectively. In the <sup>1</sup>H NMR spectrum of **1** in CD<sub>2</sub>Cl<sub>2</sub> and 1,2-dichlorobenzene-*d*<sub>4</sub> (~10<sup>−2</sup> M, Fig. 9), three sets of coordinated DtbpC≡C<sup>−</sup> signals were observed at room

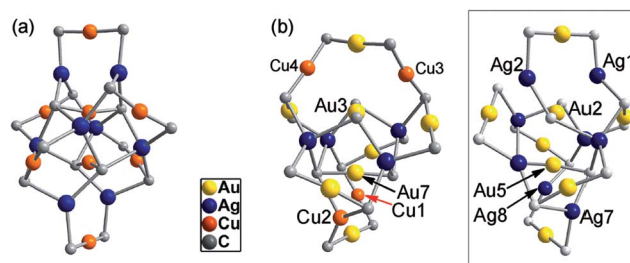


Fig. 6 The metallacycle cores in **2** (a) and **3** (b) as compared with that in (DtbpC≡C)<sub>16</sub>Au<sub>8</sub>Ag<sub>8</sub> (ref. 11b) (inset) with the omission of all the metallophilic interactions (for each alkynyl ligand, only the α carbon atom is shown).





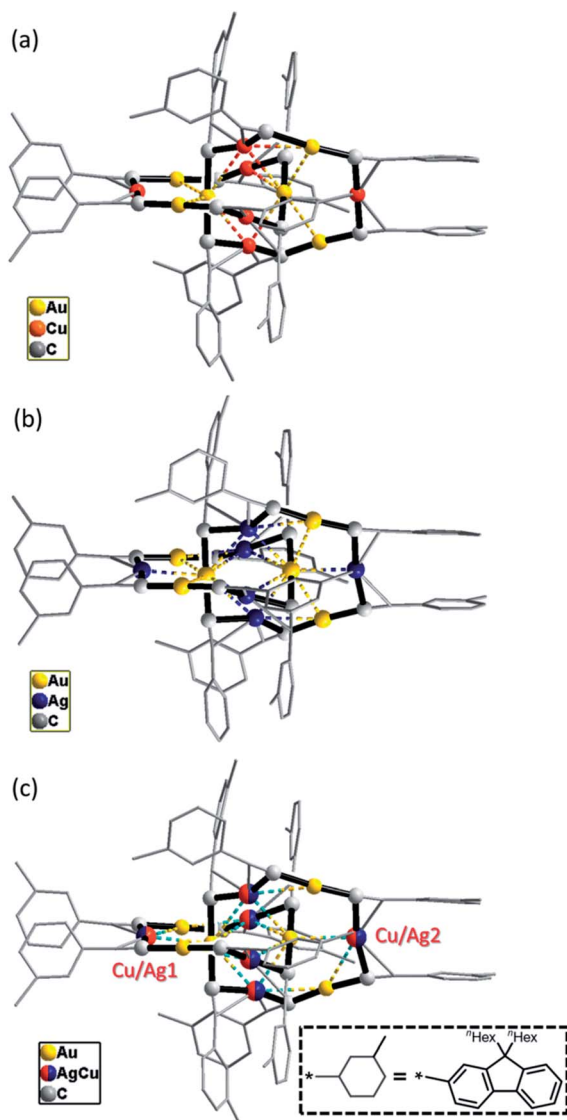


Fig. 7 A perspective view of the C6-FluoC≡C<sup>−</sup> ligand based complexes 4 (a), 5 (b) and 6 (c). All of the hydrogen atoms and parts of the C6-FluoC≡C<sup>−</sup> ligands are omitted for clarity. The metallophilic interactions are depicted as dashed lines.

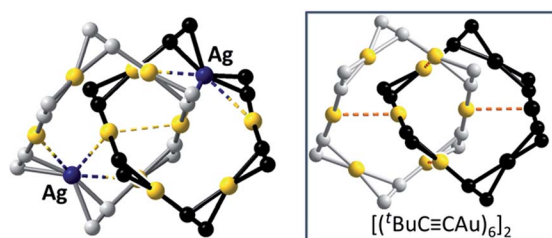


Fig. 8 A perspective view of the [2]catenane 7. Inset: a perspective view of [(<sup>t</sup>BuC≡CAu)<sub>6</sub>]<sub>2</sub> (ref. 2) for comparison. The <sup>t</sup>Bu groups are omitted for clarity. The metallophilic interactions are depicted as dashed lines.

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 CD<sub>2</sub>Cl<sub>2</sub> at room temperature by <sup>1</sup>H DOSY NMR measurements; the spectrum obtained (Fig. S4, ESI<sup>†</sup>) reveals that the observed signals of DtbpC≡C<sup>−</sup> 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)<sub>12</sub>Au<sub>6</sub>M<sub>6</sub> was obtained for M = Cu (**1**) but not for M = Ag, we attempted to perform DFT optimization of (DtbpC≡C)<sub>12</sub>Au<sub>6</sub>Ag<sub>6</sub> 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<sub>z<sup>2</sup></sub> 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 ( $\Phi = 0.37\text{--}0.83$ ). Changing the ligand from DtbpC≡C<sup>−</sup> to C6-FluoC≡C<sup>−</sup> resulted in a bathochromic shift in emission energy and a significant

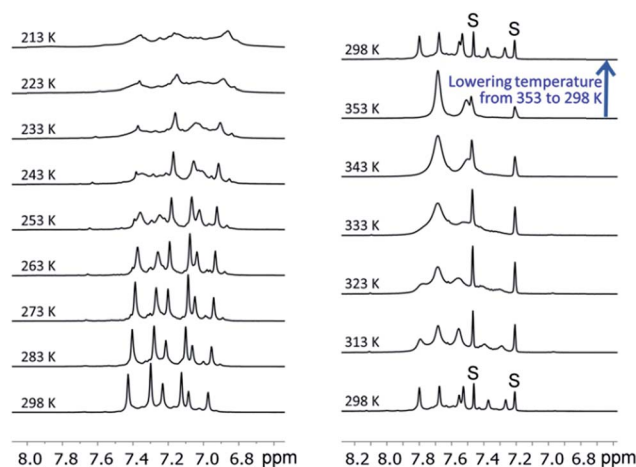


Fig. 9 The variable-temperature <sup>1</sup>H NMR spectra (in the aromatic region) of **1** in CD<sub>2</sub>Cl<sub>2</sub> (left, 298 K → 213 K) and in 1,2-dichlorobenzene-*d*<sub>4</sub> (right, 298 K → 353 K → 298 K).



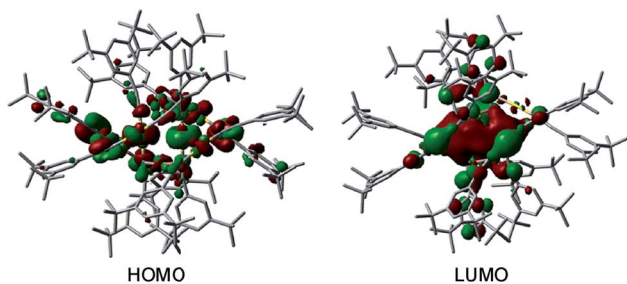


Fig. 10 The HOMO and LUMO of **1**. The hydrogen atoms are omitted for clarity. Color code: carbon (grey), gold (gold), and copper (orange).

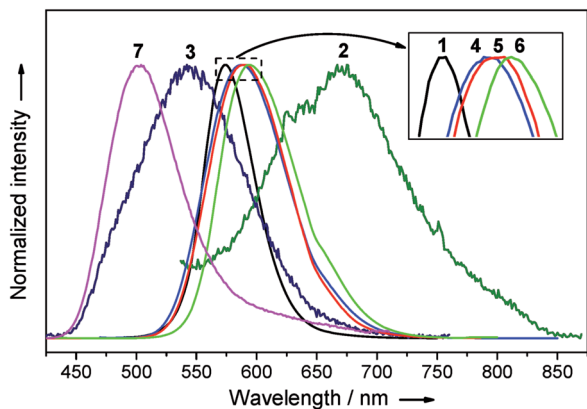


Fig. 11 The emission spectra of **1**–**7** in the solid state.

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  $\tau = 0.7$ – $1.0$   $\mu\text{s}$ ). 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 ( $\lambda_{\text{max}}$  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  $\text{Ag}$  **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<sup>†</sup>). 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  $\text{C}_6$ -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  $\text{M}_{12}$  (**1**) to  $\text{M}_{16}$  (**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  $\text{Au}^{\text{I}}$  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  $\text{M}_{12}$  (**1**) to  $\text{M}_{16}$  (**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.

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