

## Cation-Driven Self-Assembly of a Gold(I)-Based Metallo-Tweezer

Susana Ibáñez, Macarena Poyatos, and Eduardo Peris\*

**Abstract:** A combination of self-complementary  $\pi$ - $\pi$ -stacking interactions and metallophilic interactions triggered the self-assembly of a new digold(I) metallo-tweezer in the presence of several types of  $M^+$  ions. Titrations by fluorescence spectroscopy enabled the determination of the association constants of the resulting inclusion duplex complexes.

Functional structures in nature often assemble with high geometric precision from libraries of different building blocks. The rational design of programmed artificial supramolecular architectures depends on the ability to control the sequence and position of the building blocks in the product assemblies. The application of the general principles and stereoelectronic preferences of metal ions combined with rigid multidentate ligands has allowed the rational design of a wide range of highly symmetric architectures on the basis of concepts such as self-assembly,<sup>[1]</sup> self-complementarity,<sup>[1i,2]</sup> and self-sorting.<sup>[3]</sup>

Efforts have been made towards the synthesis of molecular machines that function by host-guest recognition. Such molecular devices contain specific functionalities that allow molecular motion promoted by external stimuli.<sup>[4]</sup> Among these systems, molecular clips and tweezers play a key role. A molecular tweezer is a molecular receptor containing two identical flat arms disposed in a *syn* conformation and linked by a tether.<sup>[5]</sup> The properties of a molecular tweezer may vary depending on the nature of the aromatic binding arms and the nature of the linker, which fixes the relative orientation of the aromatic groups. Tweezers with rigid linkers enabling two parallel interaction sites separated by approximately 7 Å are expected to facilitate the complexation of aromatic substrates by  $\pi$ -stacking interactions with the aromatic pincers,<sup>[5d]</sup> as aromatic groups stack at an interplanar distance of  $\leq 3.5$  Å. Molecular tweezers integrating metal centers in their structures have attracted much interest in the last two decades.<sup>[6]</sup> The presence of metal centers in supramolecular systems introduces a new dimension into supramolecular chemistry, because the predictable coordination geometries of transition-metal fragments can be used to prepare metallo-supramolecules with predefined structures,<sup>[1e,f,7]</sup> thus affording advantages over traditional organic receptors, which often require sophisticated multistep synthetic procedures.

Gold(I) complexes are known to form stable linear compounds with aryl acetylides,<sup>[8]</sup> and this behavior has

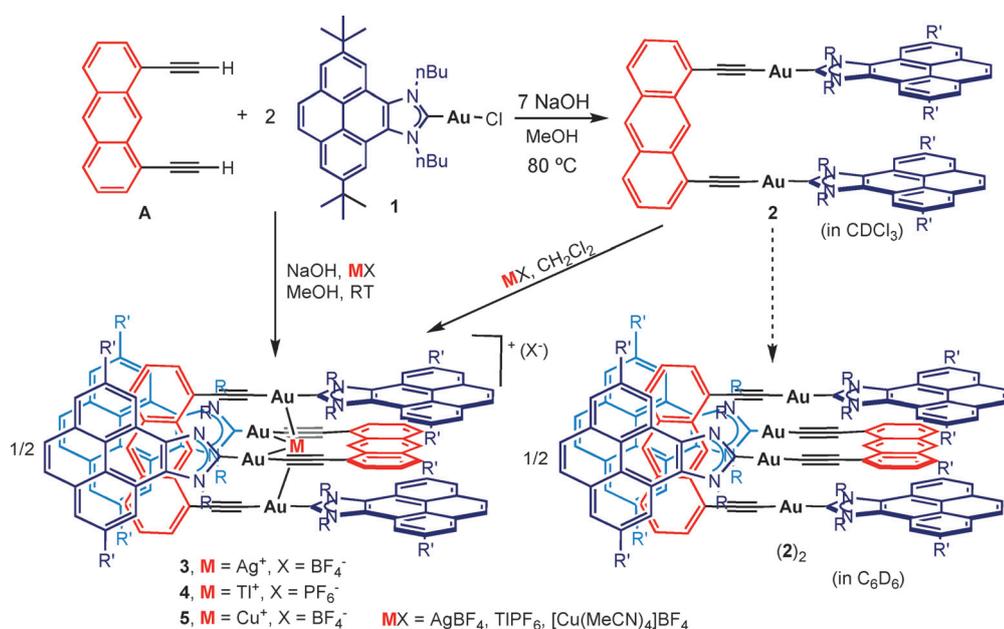
been used extensively for the synthesis of oligomeric and polymeric materials with attractive photophysical properties.<sup>[9]</sup> Furthermore, alkynyl-gold(I) fragments are able to form supramolecular architectures based on their tendency to afford linear geometries and self-assembled structures through aurophilic interactions.<sup>[10]</sup> We envisaged that the parallel *syn* orientation of the alkynyl fragments in 1,8-diethynylanthracene, in combination with an N-heterocyclic carbene ligand fused with a pyrene fragment should allow the formation of a digold(I) tweezer with interesting recognition properties. The two arms containing the pyrene moieties and the anthracene linker together provide two sites with the potential to bind aromatic guests through  $\pi$ -stacking. An additional binding motif is provided by the two gold(I) centers through aurophilic and metallophilic interactions,<sup>[11]</sup> thus introducing a new dimension in the recognition ability of the tweezer, which may also be sensitive to the presence of metal ions.

The organogold tweezer **2** was prepared according to the method shown in Scheme 1. The reaction of 1,8-diethynylanthracene (**A**) with the NHC-Au<sup>I</sup> complex **1** in MeOH in the presence of NaOH afforded complex **2** as a yellow solid in 75% yield. The <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub> exhibited the expected signals due to the hydrogen atoms on the aromatic rings of the anthracene linker and the pyrene moieties. Interestingly, the <sup>1</sup>H NMR spectrum of the same product in C<sub>6</sub>D<sub>6</sub> showed the same set of signals, but shifted significantly upfield with respect to the corresponding resonances in the spectrum recorded in CDCl<sub>3</sub>. For example, in CDCl<sub>3</sub>, the resonances due to the five hydrogen atoms of the anthracene linker appeared at  $\delta = 10.42, 8.36, 8.09, 7.73,$  and 7.40 ppm, whereas in C<sub>6</sub>D<sub>6</sub>, the signals due to the same set of signals due to the hydrogen atoms appeared at  $\delta = 9.59, 7.37, 5.90, 5.30,$  and 5.07 ppm. This strong shielding is suggestive of a  $\pi$ - $\pi$ -stacking interaction.

The analysis of the complex by time-of-flight mass spectrometry (TOF MS) revealed a main peak at  $m/z$  1551.6837, which we assigned to  $[M+H]^+$ , and a small peak at 3103.1667 due to  $[2M+H]^+$ . The spectroscopic data agree with the formulation in CDCl<sub>3</sub> of the digold complex **2**, whereas in C<sub>6</sub>D<sub>6</sub> the species formed is expected to be the self-complementary duplex cleft (**2**)<sub>2</sub>, with the anthracene linker of each tweezer filling the cavity formed by the two pyrene-functionalized arms of the complementary complex. We thought that the organogold tweezer **2** could also be obtained by the treatment of bisalkyne **A** with the gold-NHC complex **1** in the presence of two equivalents of NaOH and the chloride scavenger AgBF<sub>4</sub>. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of the product of this reaction (**3**) showed that the hydrogen atoms on the anthracene linker were strongly shielded thus suggesting the self-aggregation of the complex by intermolecular  $\pi$ - $\pi$ -stacking interactions. Analysis of the complex by

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**Scheme 1.** Synthesis of organogold tweezers and self-complementary duplex complexes.

MS revealed an intense peak at  $m/z$  3211.4819, which corresponds to the mass of two molecules of **2** plus the mass of one  $\text{Ag}^+$  cation. These results are in agreement with the proposed structure of **3** shown in Scheme 1. To determine whether the use of another chloride scavenger would lead to the formation of the silver-free complex **2**, the same reaction was performed in the presence of  $\text{TlPF}_6$  instead of  $\text{AgBF}_4$ . Again, the  $^1\text{H}$  NMR spectrum of the reaction product in  $\text{CDCl}_3$  showed upfield shifting of the signals due to the anthracene linker, and the MS spectrum showed a main peak at 3307.2551, which corresponds to the mass of two molecules of **2** plus the mass of a  $\text{Tl}^+$  cation. These results suggested the formation of the inclusion duplex complex **4**.

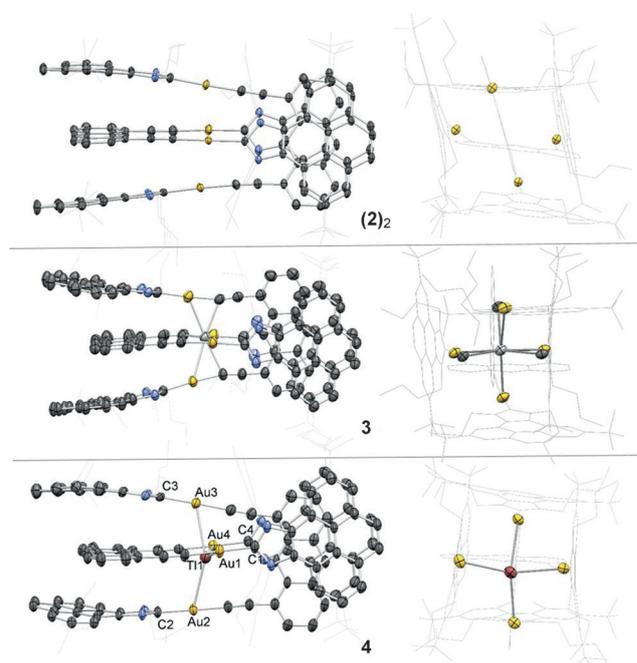
The molecular structures of (**2**)<sub>2</sub>, **3**, and **4** were confirmed by single-crystal X-ray diffraction (Figure 1). The molecular structure of (**2**)<sub>2</sub> consists of a self-assembled structure formed by two molecules of **2**, in which the two pyrene fragments of each complex sandwich the anthracene tether of the complementary molecule. The four gold atoms form a rectangle with average Au–Au distances of 3.32 and 4.90 Å, the shorter distance clearly suggestive of a strong aurophilic interaction.<sup>[10a,11a–c,h]</sup> The quasiorthogonal disposition of the polycyclic aromatic hydrocarbons in the tether (anthracene) and at the NHC ligand (pyrene), together with the presence of the  $\text{Au}^{\text{I}}$  centers, affords the self-complementarity needed for the formation of this self-assembled structure. The average distance between the planes formed by the anthracene and pyrene fragments is 3.68 Å (range: 3.35–4.18 Å).

The molecular structure of **3** contains a  $\text{Ag}^+$  ion inside the duplex molecule of (**2**)<sub>2</sub>. Formally, the silver ion is encased by four  $\text{AuC}\equiv\text{C}$  fragments, a situation that has rarely been observed.<sup>[12]</sup> A  $\text{BF}_4^-$  counteranion compensates the positive charge of the cationic complex. The distances between the silver ion and the four gold centers range between 2.86 and 2.92 Å, thus indicating the presence of strong metallophilic interactions. Three of the  $\text{Ag}-\text{C}^{\alpha}$  bond distances are between

2.59 and 2.67 Å, and thus in the range found in other reported heterometallic  $\text{Ag}^{\text{I}}-\text{Au}^{\text{I}}$ -alkynyl complexes.<sup>[12,13]</sup> The fourth  $\text{Ag}-\text{C}^{\alpha}$  distance is 3.2 Å, thus indicating negligible bonding interaction. The average distance between the planes formed by the anthracene and pyrene fragments is 3.58 Å (range: 3.40–3.73 Å).

The molecular structure of **4** contains a  $\text{Tl}^+$  ion inside a (**2**)<sub>2</sub> dimer. A  $\text{PF}_6^-$  anion balances the positive charge of the cationic complex. The thallium cation establishes significant metallophilic interactions with all four surrounding gold atoms, with  $\text{Tl}-\text{Au}$  bond

distances ranging from 3.10 to 3.15 Å. This molecule does not show any bonding interactions between the thallium cation and the  $\text{C}^{\alpha}$  atoms of the alkyne ligands, nor any aurophilic interactions between the four gold centers (Au–Au distances are in the range of 3.94–5.15 Å). The average



**Figure 1.** Two perspectives of the X-ray molecular structures of (**2**)<sub>2</sub>, **3**, and **4**. Hydrogen atoms, solvent molecules, and counteranions (in **3** and **4**) have been omitted for clarity. *n*-Butyl and *t*-butyl groups are represented in the wireframe form. Ellipsoids are shown at 50% probability. The figures on the right show the disposition of the metal atoms in the structure and the most representative bonding interactions.

distance between the planes formed by the anthracene and pyrene fragments is 3.78 Å (range: 3.45–4.06 Å).

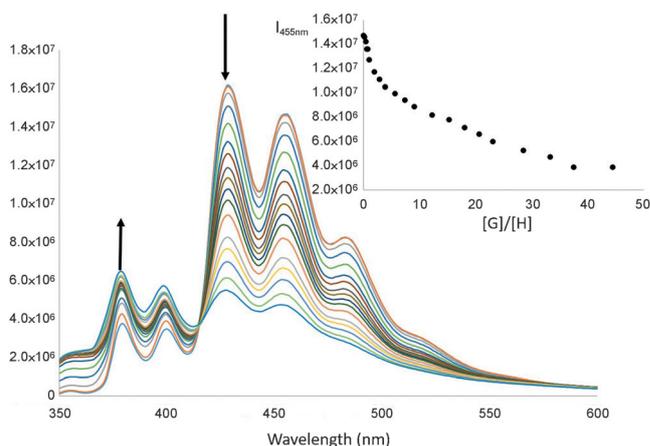
To shed some light on the formation of the inclusion self-aggregated complexes **3** and **4**, we treated complex **2** with  $\text{AgBF}_4$  and  $\text{TIPF}_6$  in  $\text{CH}_2\text{Cl}_2$ , and we quantitatively obtained **3** and **4**, respectively. This experiment indicates that these two inclusion complexes are obtained after the organogold tweezer **2** is formed, and not in the process of the formation of **2**. This result is interesting, because it suggests that the self-aggregation of **2** is triggered by the addition of  $\text{Ag}^+$  or  $\text{TI}^+$ . In fact, the titration of **2** with  $\text{AgBF}_4$  (or  $\text{TIPF}_6$ ) clearly showed the gradual formation of **3** (or **4**) upon addition of the cation. The addition of substoichiometric amounts of the cation resulted in the appearance of the two species (**2** and **3**, or **2** and **4**), which were observed in the corresponding  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$ , thus indicating that the chemical exchange between **2** and free  $\text{M}^+$ , and the self-assembly of complexes **3** or **4**, is slow on the NMR timescale. Figure 2 shows a selected region of the  $^1\text{H}$  NMR spectra of the titration of **2** with  $\text{AgBF}_4$  in  $\text{CDCl}_3$ , in which it can be clearly observed that only 0.5 equivalents of  $\text{AgBF}_4$  are needed for the quantitative formation of **3**.

We also wanted to know if metals other than  $\text{Ag}^+$  or  $\text{TI}^+$  could facilitate the cation-driven self-assembly of **2**. The addition of  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  to a solution of **2** in dichloromethane afforded complex **5**, a self-aggregated inclusion complex that encapsulates a  $\text{Cu}^+$  cation. Complex **5** was characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The  $^1\text{H}$  NMR spectrum of **5** resembles those of **3** and **4**, thus indicating that the three species are very similar in nature.

Aiming to determine the association constants related to the formation of **3–5**, we performed UV/Vis and fluorescence titrations. The UV spectroscopic titration of **2** with  $\text{AgBF}_4$ ,  $\text{TIPF}_6$ , or  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  led to small changes in the absorption spectra; therefore, we did not use these titrations for the quantitative determination of the related association

constants. However, in the case of the titration of **2** with  $\text{TIPF}_6$ , the series of spectra showed the appearance of five clear isosbestic points (see the Supporting Information for details), thus providing evidence for the conversion of free **2** into **4** without the involvement of detectable intermediate species. On the other hand, the emission spectrum of **2** changed significantly upon the gradual addition of any one of these three salts.

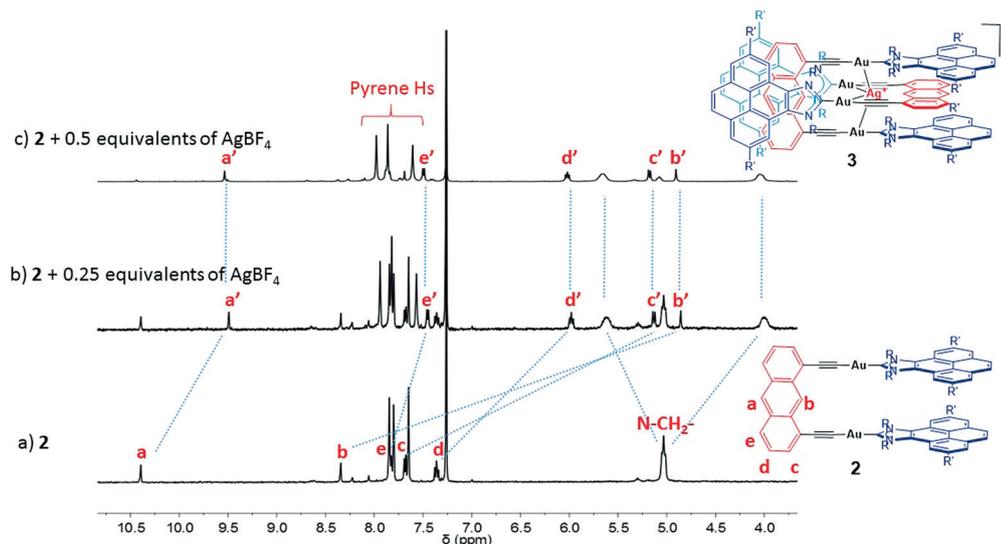
Figure 3 shows the changes observed in the emission spectrum of **2** ( $1 \times 10^{-5} \text{ M}$ ) in  $\text{CH}_2\text{Cl}_2$  upon the incremental



**Figure 3.** Fluorescence spectra acquired during the titration of **2** ( $1 \times 10^{-5} \text{ M}$ ) with  $\text{TIPF}_6$  in  $\text{CH}_2\text{Cl}_2$  at 298 K ( $\lambda_{\text{ex}} = 320 \text{ nm}$ ). In the inset,  $I_{455}$  (emission intensity at 455 nm) is plotted against the  $[\text{T}^+]/[\text{2}]$  ( $[\text{G}]/[\text{H}]$ ) ratio.

addition of  $\text{TIPF}_6$ . Upon excitation at  $\lambda = 320 \text{ nm}$ , a solution of **2** in degassed dichloromethane exhibited strong luminescence featuring two vibronically resolved bands with peak maxima at 430 and 378 nm, which are coincident with the typical monomer emission bands of anthracene and pyrene, respectively, in related anthracene–diacetylide

digold(I) complexes<sup>[14]</sup> and pyrene-based NHC ligands.<sup>[15]</sup> The addition of incremental amounts of  $\text{TIPF}_6$  gradually quenched the fluorescence intensity at 430 nm and increased the intensity of the band at 378 nm. In agreement with the UV/Vis titrations, the presence of an isoemissive point at 414 nm indicated the presence of two emitting species in solution, thus indicating that **4** is produced directly from **2** without the formation of any other reaction intermediates (i.e., if we consider that **4** is an inclusion



**Figure 2.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectra of a) complex **2**, b) complex **2** +  $\text{AgBF}_4$  (0.25 equiv), c) complex **2** +  $\text{AgBF}_4$  (0.5 equiv). The series of spectra shows the upfield shift of the signals due to the anthracene linker upon formation of the duplex complex **3**.

complex of the type  $Tl^+@(\mathbf{2})_2$ , there is no experimental evidence of the formation of the  $Tl^+@2$  intermediate). The fluorescence titrations of **2** with  $AgBF_4$  and  $[Cu(MeCN)_4]BF_4$  to form **3** and **5** displayed similar features to those shown for the titration with  $TlPF_6$  (see the Supporting Information for details). Nonlinear least-squares analysis of the three titrations to form complexes **3–5** enabled calculation of the related association constants with low residual errors. These constants were  $2.7 \times 10^9$ ,  $4.2 \times 10^8$ , and  $7.9 \times 10^5 M^{-2}$  for **3**, **4**, and **5**, respectively (see the Supporting Information for details), thus indicating a high binding affinity, which is larger by a significant margin for the formation of the silver-containing inclusion complex **3**. These high binding constants may be attributed to a combination of three bonding interactions: 1) the  $\pi$ - $\pi$ -stacking interactions between the pyrene fragments of the imidazolylidene ligand and the anthracene linker, 2) the metallophilic interactions between the encapsulated metal cation ( $Ag^+$ ,  $Tl^+$ , or  $Cu^+$ ) and the four gold atoms of the complexes, and 3) the  $\pi$ -coordination of the alkynyl groups in the structure with the encapsulated silver cation. We also recorded solid-state emission spectra of **2–5**, which showed a broad and featureless band typical for pyrene excimer emission in the range of 470–480 nm (see the Supporting Information for details).

We carried out competitive ESI-TOF MS experiments to confirm the binding-affinity trend observed in the fluorescence titration experiments. MS-based methods are known to be very useful for quantitatively evaluating host:guest binding events.<sup>[16]</sup> The competitive ESI-TOF mass spectrum was recorded for a solution in dichloromethane of **2** and 0.5 equivalents each of  $AgBF_4$ ,  $TlPF_6$ , and  $[Cu(MeCN)_4]BF_4$ . The spectrum showed a main peak at  $m/z$  3210.9090 due to  $[3-BF_4]^+$ , and a very small peak at  $m/z$  3307.2551 due to  $[4-PF_6]^+$ . We did not observe any trace of the peak due to the inclusion complex formed with  $Cu^+$ . These results are in accordance with the calculated association constants obtained by fluorescence titrations, according to which the tendency of **2** to form inclusion complexes decreases in the order  $Ag^+ > Tl^+ > Cu^+$ .

In summary, we have prepared a new metallo-supramolecular tweezer that forms dimers in the solid state and in the presence of several  $M^+$  cations. The quasiorthogonal disposition of the polycyclic aromatic hydrocarbons in the tether (anthracene) and the NHC ligand (pyrene), together with the presence of the  $Au^I$  centers, affords the self-complementarity needed for the formation of self-assembled structures with a cavity capable of recognizing small molecules or ions. The self-aggregated structures are stabilized by a combination of  $\pi$ -stacking and metallophilic interactions. As demonstrated herein, this tweezer represents a novel architectural motif for hosting metal cations in solution, and has the potential to host aromatic guests.

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## Conflict of interest

The authors declare no conflict of interest.

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