

## COMMUNICATION

## Cation-driven self-assembly of a gold(I)-based metallo-tweezer

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**Abstract:** A combination of self-complementary  $\pi$ - $\pi$ -stacking interactions and metallophilic interactions triggers the self-assembly of a new di-gold(I) metallotweezer in the presence of several  $M^+$  ions. Titrations by fluorescence spectroscopy allowed determining 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 how 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, and this has been benefited from the help of concepts such as self-assembly,<sup>[1]</sup> self-complementarity<sup>[1, 2]</sup> and self-sorting.<sup>[3]</sup>

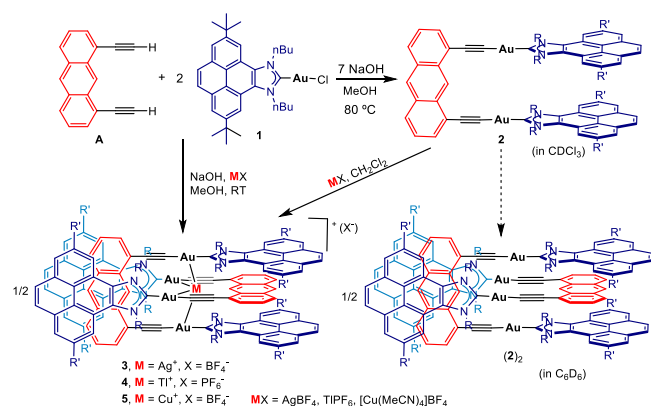
Efforts have been made to the synthesis of molecular machines that function via host-guest recognition. Such molecular devices contain specific functionalities that allow molecular motion promoted by external stimuli<sup>[4]</sup> and, among these systems, molecular clips and tweezers play a key role. 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 on 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  $\approx 7$  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 are gaining interest in the last few years.<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 for preparing metallosupramolecules with pre-defined structures,<sup>[1e, 1f, 7]</sup> thus affording advantages over traditional organic receptors, which for achieving similar goals often require sophisticated multistep synthetic procedures.

Gold (I) complexes are known to form stable linear compounds with aryl-acetylides,<sup>[8]</sup> and this has been extensively used for the synthesis of oligomeric and polymeric materials with attractive photophysical properties.<sup>[9]</sup> In addition, alkynyl-gold(I) fragments are able to form supramolecular architectures based on their tendency to afford linear geometries and self-assembly structures through aurophilic interactions.<sup>[10]</sup> Based on these precedents, we envisaged that the parallel *syn* orientation of the alkynyl fragments

in 1,8-diethynyl-anthracene, in combination with a N-heterocyclic carbene ligand fused with a pyrene fragment, should allow the formation of a di-gold(I) tweezer with interesting recognition properties. The presence of the two arms containing the pyrene moieties, together with the anthracene linker provides two sites with the potential to bind aromatic guests through  $\pi$ -stacking. In addition, the presence of the two gold(I) centers, provides an additional binding motif through aurophilic and metallophilic interactions,<sup>[11]</sup> thus introducing a new dimension in the recognizing abilities of the tweezer, which may also be sensitive to the presence of metal ions.

The organogold tweezer **2** can be obtained according to the method shown in Scheme 1. The reaction of 1,8-diethynyl-anthracene (**A**) with the NHC-Au(I) complex **1** in MeOH in the presence of NaOH, affords complex **2** as a yellow solid in 75% yield. The <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub> confirms the presence of the signals due to the protons at 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> shows the same set of signals, but significantly upfield shifted with respect to the related resonances in the spectrum taken in CDCl<sub>3</sub>. For example, in CDCl<sub>3</sub> the resonances due to the five protons of the anthracene linker appear at  $\delta$  10.42, 8.36, 8.09, 7.73 and 7.40 ppm, while in C<sub>6</sub>D<sub>6</sub> the signals due to the same set of protons appear 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 event. The analysis of the complex by time-of-flight-mass-spectrometry (TOFMS) reveals a main peak at  $m/z$  1551.6837, that we assigned to  $[M+H]^+$ , and a small peak at 3103.1667 due to  $[2M+H]^+$ . Anticipating the crystal structure results below, the spectroscopic data agree with the formulation in CDCl<sub>3</sub> of the di-gold complex **2**, while 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 reaction of the bisalkyne **A** with the gold-NHC complex **1** in the presence of two equivalents of NaOH and AgBF<sub>4</sub> as chloride scavenger. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of the product of this reaction (**3**) showed that the signals due to the anthracene linker were strongly shielded, suggesting the self-aggregation of the complex by intermolecular  $\pi$ - $\pi$ -stacking interactions. The analysis of the complex by 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 Ag<sup>+</sup> cation. These results are in agreement with the proposed structure of **3** shown in Scheme 1. In order to determine if the use of other chloride scavenger should lead to the formation of the silver-free complex **2**, the same reaction was performed in the presence of TlPF<sub>6</sub> instead of AgBF<sub>4</sub>. Again, the <sup>1</sup>H NMR spectrum of the reaction product in CDCl<sub>3</sub> showed the upfield shifting of the signals due to the anthracene linker, and the MS spectrum showed a mean peak at 3307.2551, which corresponds to the mass of two molecules of **2** plus the mass of a Tl<sup>+</sup> cation. These results suggested the formation of the inclusion duplex complex **4**.

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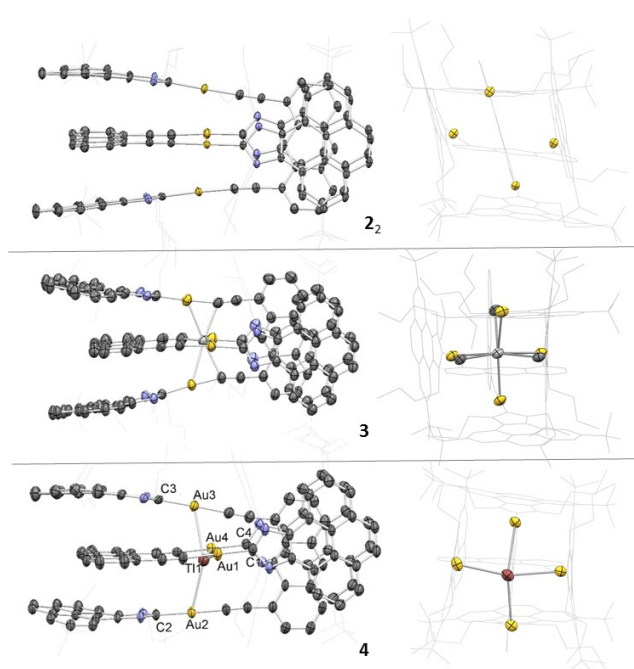


**Scheme 1.** Synthesis of organogold tweezers and self-complementary duplex complexes.

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 are sandwiching the anthracene tether of the complementary molecule. The four gold atoms are forming 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, 11h]</sup> The quasi-orthogonal disposition of the polycyclic aromatic hydrocarbons at the tether (anthracene), and at the NHC ligand (pyrene), together with the presence of the Au(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)

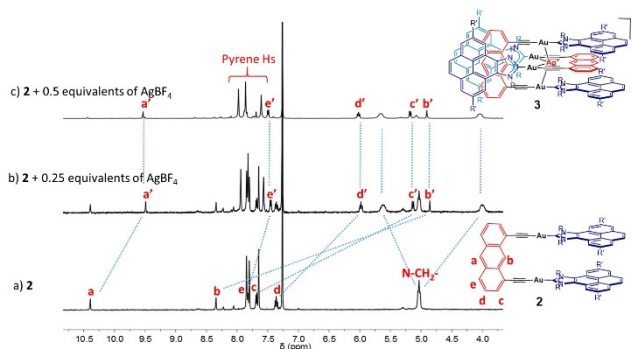
The molecular structure of **3** contains a Ag<sup>+</sup> ion inside the duplex molecule of (**2**)<sub>2</sub>. Formally, the silver ion is encased by four AuC≡C fragments, a situation that has been rarely observed.<sup>[12]</sup> A BF<sub>4</sub><sup>-</sup> counter-anion compensates the positive charge of the cationic complex. The distances between the silver ion and the four gold centers range between 2.86–2.92 Å, thus indicating the presence of strong metallophilic interactions. Three of the Ag-C $\alpha$  bond distances range between 2.59 and 2.67 Å, in the range found in other heterometallic Ag(I)-Au(I)-alkynyl complexes reported in the literature,<sup>[12–13]</sup> The third Ag-C $\alpha$  distance is 3.2 Å, therefore 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 Tl<sup>+</sup> ion inside a **2**<sub>2</sub> dimer. A PF<sub>6</sub><sup>-</sup> anion balances the positive charge of the cationic complex. The thallium cation establishes significant metallophilic interactions with all four surrounding centers, with Tl-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 C $\alpha$  of the alkynyl 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 distance between the planes formed by the anthracene and pyrene fragments is 3.78 Å (range 3.45–4.06 Å).



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

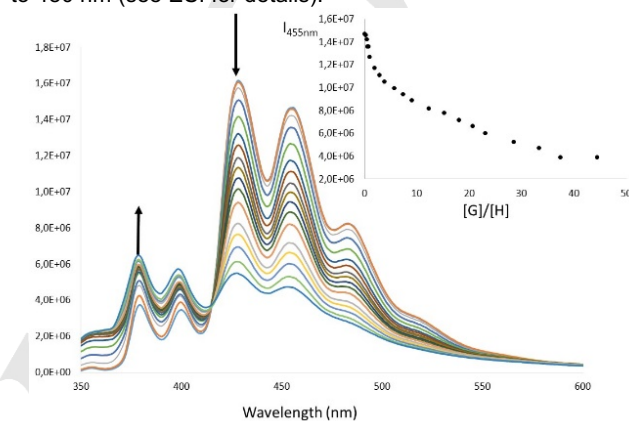
In order to shed some light on the formation of the inclusion self-aggregated complexes **3** and **4**, we reacted complex **2** with AgBF<sub>4</sub> and TlPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, and we quantitatively obtained **3** and **4**, respectively. This experiment indicates that these 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 Ag<sup>+</sup> or Tl<sup>+</sup>. In fact, the titration of **2** with AgBF<sub>4</sub> (or TlPF<sub>6</sub>) clearly shows the gradual formation of **3** (or **4**) upon addition of the cation. The addition of sub-stoichiometric amounts of the cation, results in the appearance of the two species (**2** and **3**, or **2** and **4**), which are observed in the related <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>, indicating that the chemical exchange between **2** and free M<sup>+</sup> and the self-assembly complexes **3** or **4**, is slow on the NMR timescale. Figure 2 shows a selected region of the <sup>1</sup>H NMR spectra of the titration of **2** with AgBF<sub>4</sub> in CDCl<sub>3</sub>, where it can be clearly observed that only 0.5 equivalents of AgBF<sub>4</sub> are needed for the quantitative formation of **3**. We also wanted to know if metals other than Ag<sup>+</sup> or Tl<sup>+</sup> should also facilitate the formation of the cation-driven self-assembly of **2**. The addition of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> to a dichloromethane solution of **2** afforded complex **5**, a self-aggregated inclusion complex that encapsulates a Cu<sup>+</sup> cation. Complex **5** was characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The <sup>1</sup>H NMR spectrum of **5** resembles the spectra shown by **3** and **4**, thus indicating that the nature of the species formed is very similar to these two species.



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

Aiming to determine the association constants related to the formation of **3-5**, we performed UV-Vis and fluorescence titrations. The UV spectroscopic titrations of **2** with either  $\text{AgBF}_4$ ,  $\text{TIPF}_6$  or  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  showed small changes in the absorption spectra, thus we did not use these titrations for the quantitative determination of the related association constants. However, it is worth mentioning that 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 ESI for details), thus evidencing the conversion of free **2** into **4**, without the involvement of detectable intermediate species. On the other hand, the emission spectra of **2** changed significantly upon the gradual addition of either of these three salts. Figure 3 shows the changes observed in the emission spectra of **2** ( $1 \times 10^{-5}$  M) in  $\text{CH}_2\text{Cl}_2$  upon incremental addition of  $\text{TIPF}_6$ . Upon excitation at  $\lambda = 320$  nm, a degassed dichloromethane solution of **2** exhibits 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, as shown in related anthracene-diacetylide di-gold(I) complexes<sup>[14]</sup> and pyrene-based NHC ligands.<sup>[15]</sup> The addition of incremental amounts of  $\text{TIPF}_6$  gradually quenches the fluorescence intensity at 430 nm, and increases the intensity of the band at 378 nm. In agreement with the UV-vis titrations, the presence of an isoemissive point at 414 nm indicates the presence of two emitting species in solution, thus indicating that the formation of **4** is directly produced from **2** without the formation of any other reaction intermediates (i.e., if we consider that **4** is an inclusion complex of the type  $\text{Ti}^+@2_2$ , there is no experimental evidence of the formation of the  $\text{Ti}^+@2_2$  intermediate). The fluorescence titrations of **2** with  $\text{AgBF}_4$  and  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  to form **3** and **5** displayed similar features as those shown for the titration with  $\text{TIPF}_6$  (see Supplementary Information for details). The nonlinear least-square analysis of the three titrations to form complexes **3-5** allowed calculating the related association constants with low residual errors. These constants were  $2.7 \times 10^9$ ,  $4.2 \times 10^8$  and  $7.9 \times 10^5 \text{ M}^{-2}$ , for **3**, **4** and **5**, respectively (see ESI for details regarding the determination of the constants), therefore indicating a high binding affinity, which is significantly larger for the case of the formation of the silver containing inclusion complex (**3**). These

high binding constants may be attributed to a combination of three bonding interactions, namely: 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 ( $\text{Ag}^+$ ,  $\text{Ti}^+$  or  $\text{Cu}^+$ ) and the four gold atoms of the complexes, and 3) the  $\pi$ -alkyne coordination established between the encapsulated silver cation and the alkynyl groups of the structure. We also performed the solid-state emission spectra of **2-5**, which showed the broad and featureless band typical for the pyrene excimer emission in the range of 470 to 480 nm (see ESI for details).



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

We also used competitive ESI-TOF-MS experiments for confirming the binding affinity trend obtained by 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 performed from a dichloromethane solution of **2** and 0.5 equivalents of  $\text{AgBF}_4$ ,  $\text{TIPF}_6$  and  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ . The spectrum showed a main peak at  $m/z$  3210.9090 due to  $[\text{3-BF}_4]^+$ , and a very small peak at 3307.2551 due to  $[\text{4-PF}_6]^+$ . We did not observe any traces of the formation of the peak due to the inclusion complex formed with  $\text{Cu}^+$ . This results are in accordance with the calculated association constants obtained by fluorescence titrations, which establish that the tendency of **2** to form inclusion complexes goes in the order  $\text{Ag}^+ > \text{Ti}^+ > \text{Cu}^+$ .

In summary, we prepared a new metallosupramolecular tweezer that forms dimers in the solid state and in the presence of several  $\text{M}^+$  cations. The quasi-orthogonal disposition of the polycyclic aromatic hydrocarbons at the tether (anthracene), and at 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 here, this new tweezer represents a novel architectural motif for hosting metal cations in solution, and has the potential to host aromatic guests.

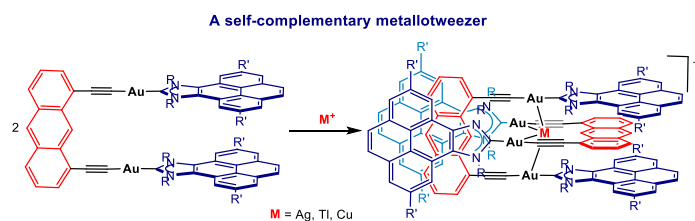
## Acknowledgements

We gratefully acknowledge financial support from MINECO of Spain (CTQ2014-51999-P) and the Universitat Jaume I (P11B2014-02 and P11B2015-24). We are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC-UJI) for providing with spectroscopic facilities. We also thank Dr. Louise N. Dawe (Wilfrid Laurier University) for her valuable advices for the resolution of the X-ray crystal structures.

**Keywords:** Metallo-tweezer • N-Heterocyclic carbene • gold • supramolecular • self-assembly

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## COMMUNICATION



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Cation-driven self-assembly of a gold(I)-based metallo-tweezer

A di-gold(I) metallo-tweezer self-aggregates in the presence of several  $M^+$  cations by a combination of self-complementary  $\pi$ - $\pi$ -stacking and metallophilic interactions.