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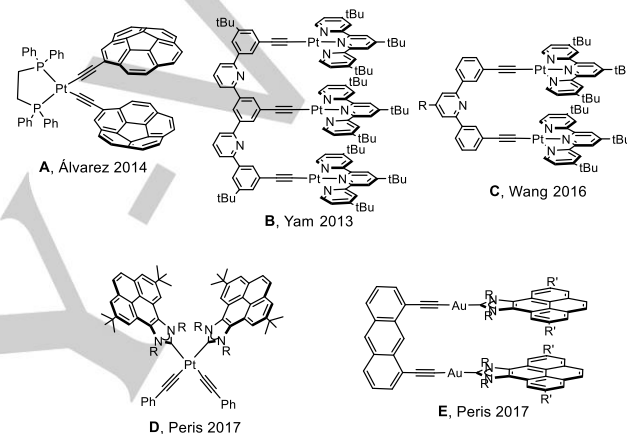
Chiara Biz,^a Susana Ibáñez,^a Macarena Poyatos,^a Dmitry Gusev,^b and Eduardo Peris^{*a}

Abstract: Two gold(I)-based metallo-tweezers with bis(Au-NHC) pincers and a carbazole connector have been obtained and used for the recognition of polycyclic aromatic hydrocarbons (PAHs). In the case of the tweezer with pyrene-NHC ligands, the presence of the pyrene fragment and the N-H bond in the carbazole linker enable the receptor to show significant enhanced binding abilities toward PAHs functionalized with H-bonding groups, through combined π - π stacking and H-bonding.

The preparation of supramolecular coordination complexes (SCCs) has benefited from the directional nature of coordination compounds that facilitates the rational and predictable design of supramolecular architectures.^[1] During the past three decades, research in this field has led to a variety of molecular architectures whose shapes and sizes are easily controlled by the careful selection of the metal centers and ancillary ligands.^[2] The presence of cavities with well-defined shapes and internal functionalities have positioned SCCs in a privileged position for the design of materials with applications in catalysis,^[3] molecular recognition^[4] and biochemistry.^[5]

A molecular tweezer may be defined as a molecular receptor containing two polyaromatic "hands" extended from a more or less rigid joint (spacer). The tweezers must possess an inner void of ca. 7 Å in order to facilitate the complexation of aromatic substrates via π -stacking interactions,^[6] as aromatic groups stack at an average interplanar distance of ca. 3.5 Å. While most original molecular tweezers were based on organic entities,^[6-7] during the last decade some research groups integrated metal centers in the structures of clips and tweezers, thus introducing a new dimension in their properties and applications.^[8] Some recent noteworthy and elegant examples of metallo-tweezers that have been used for the recognition of guest molecules include the bis-corannulene-based platinum(II) complex used by Alvarez and co-workers for the recognition of fullerenes (**A**),^[8a] the double-decker tweezer described by Yam and co-workers that established strong host-guest interactions with square platinum(II) guest complexes (**B**),^[8b] or the bis-alkynylplatinum(II) terpyridine molecular tweezer described by Wang and co-workers that exhibited enhanced complexation abilities toward naphthol-derived guests due to the intermolecular hydrogen bonding to the nitrogen

of the central pyridine ring of the spacer ligand (**C**).^[8c] We recently utilized the π -stacking abilities of N-heterocyclic carbene ligands decorated with rigid polyaromatic fragments^[9] for the preparation of a metallo-folder for the recognition of electron-deficient aromatic molecules (**D**),^[10] and a Au(I)-based tweezer that dimerized in the presence of M^+ ions, as a consequence of the combination of π -stacking and metallophilic interactions (**E**).^[11]



Scheme 1. Some selected recent metallo-tweezers

Considering these precedents, we now describe the preparation of two new Au(I) metallo-tweezers for the recognition of polycyclic aromatic hydrocarbons (PAHs). The presence of the pyrene fragments at the NHC backbones and the N-H group of the carbazole linker allow these tweezers to bind polyaromatic guests through combined π -stacking and H-bonding interactions.

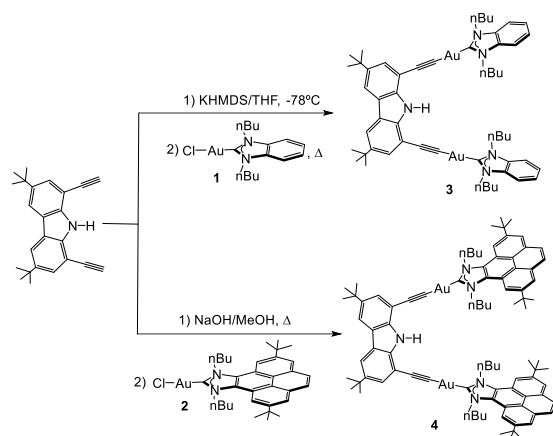
The metallo-tweezers **3** and **4** were obtained following the synthetic procedure depicted in Scheme 2. The preparation of the benzimidazolylidene-based Au(I) tweezer **3** was performed by deprotonating 3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole with potassium bis(trimethylsilyl)amide (KHMDs) in THF at -78°C, followed by addition of the benzimidazolylidene-Au(I) complex **1**. Complex **3** was obtained in 32% yield after purification. Complex **4** was obtained by deprotonating di-*tert*-butyl-diethynyl-carbazole with NaOH in refluxing methanol, followed by the addition of the pyrene-imidazolylidene-gold(I) complex **2**. This procedure afforded complex **4** in 69% yield after purification. Complexes **3** and **4** were characterized by NMR spectroscopy and electrospray mass spectrometry, and gave satisfactory elemental analyses. The ESI mass spectrum of **3** showed two main peaks at m/z values of 1180.4 and 1191.9, which can be assigned to $[M+H]^+$ and $[M+Na]^+$, respectively. The ESI mass spectrum of **4**, shows one peak at $m/z = 1652.8$, which can be attributed to $[M+H]^+$.

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Scheme 2. Preparation of metallo-tweezers **3** and **4**

The ^1H NMR spectra of **3** and **4** in toluene- d_6 confirm the effective C_{2v} symmetry of the molecules in solution. The distinctive singlet due to the N-H proton of the carbazole linker is observed at 9.26 and 9.63 ppm for **3** and **4**, respectively. The ^{13}C NMR spectra displayed the characteristic signals due to the carbene carbons at 195.5 and 195.0 for **3** and **4**, respectively.

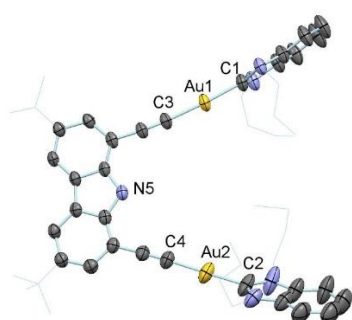


Figure 1. Molecular structure of **3**. Hydrogen atoms were removed for clarity. *n*Bu and *t*Bu groups are represented in the wireframe style for clarity. Ellipsoids at 50% probability. Selected distances (Å) and angles($^\circ$): Au(1)-C(1) 2.013(6), A(1)-C(3) 1.993(6), Au(2)-C(2) 2.005(8), Au(2)-C(4) 1.970(7), C(3)-Au(1)-C(1) 174.8(3), C(4)-Au(2)-C(2) 177.9(4).

The molecular structures of **3** and **4** were determined by X-ray crystallography. The molecular structure of **3** consists of two Au(I)-benzimidazolylidene fragments connected by the carbazole-di-alkynyl ligand. The dihedral angles between the planes of the benzimidazolylidene ligands of the tweezer, and the plane of the carbazole spacer are 55.4 and 85.4 $^\circ$. The planes of the benzimidazolylidene ligands are at 52.3 $^\circ$. The Au-C_{carbene} bond distances are 2.013(6) and 2.005(8) Å, and the Au-C_{alkynyl} bonds are 1.993(6) and 1.970(7) Å long. The molecule possesses two gold atoms at 8.22 Å from each other.

Figure 2 shows the molecular structure of complex **4**. The structure consists of two pyrene-imidazolylidene-Au(I) fragments bound by the carbazole-di-alkynyl ligand. The angles between the

planes of the pyrene fragments and the plane of the carbazole spacer are 53.1 and 58.5 $^\circ$, and the angle between the two pyrene fragments is 28.5 $^\circ$. The distance of the two Au-C_{carbene} bonds is 2.022(4) Å and the distance of the two Au-C_{alkynyl} bonds is 1.992(4) Å. The distance between the two Au centers is 7.38 Å, which is significantly shorter than the corresponding distance in **3** (8.22 Å), therefore indicating that the carbazole-bis-alkynyl linker possesses some flexibility that can be useful for trapping aromatic guests between the flat ends of the molecular “tongs”. The crystal packing shows one-directional anti-parallel π -stacking of the pyrene-imidazolylidene ligands along the *c*-axis of the crystal.

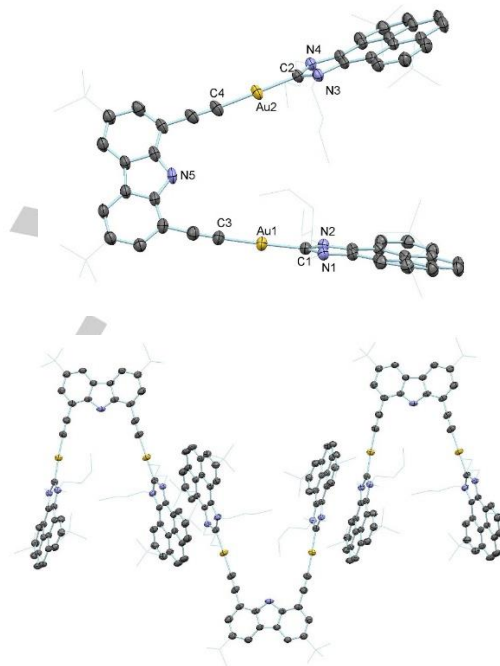


Figure 2. Molecular structure of **4**. Hydrogen atoms and solvent (fluorobenzene) were removed for clarity. *n*Bu and *t*Bu groups are represented in the wireframe style for clarity. Ellipsoids at 50% probability. Selected distances (Å) and angles($^\circ$): Au(1)-C(1) 2.022(4), A(1)-C(3) 1.992(4), Au(2)-C(2) 2.022(4), Au(2)-C(4) 1.992(4), C(3)-Au(1)-C(1) 176.74(16), C(4)Au(2)-C(2) 179.45(17). The figure below shows the π -stacking interactions of the molecule along the *c*-axis of the crystal.

The molecular structure of **4** resembles our previously described complex **E** (Scheme 1), in which the two pyrene-imidazolylidene-Au(I) fragments were bound by an anthracene-bis-alkynyl ligand.^[11] In the case of **E**, the relative disposition of the two pyrene-imidazolylidene ligands and the anthracene linker facilitated the self-association of the complex yielding stable dimers, in which the anthracene connector was sandwiched between the two pyrene fragments of an adjacent molecule by π -stacking interactions. This self-complementarity does not occur in the case of **4**, for which the separation of the planes formed by the pyrene-imidazolylidenes exceeds the optimal distance of 7 Å as a consequence of the 28.5 $^\circ$ angle between the alkynyls.

We thought that complexes **3** and **4** could be used as hosts for the recognition of polycyclic aromatic hydrocarbon (PAHs) guests due to the presence of the polyaromatic fragments located at the edges of the tweezer, which should be useful for establishing π -

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stacking interactions with the PAHs. The N-H bond at the carbazole linker is another potential binding site through hydrogen bonding, if H-bonding accepting groups are present in the aromatic guests, so our molecular hosts provide an excellent opportunity to compare binding of aromatic guests with and without H-bonding accepting groups.

Table 1. Association constants (M^{-1}) for the complexation of **4** with PAHs.

Entry	Guest	K (M^{-1})
1	phenanthrene	---
2	pyrene	10 ± 3
3	triphenylene	35 ± 2
4	perylene	145 ± 20
5	coronene	250 ± 40
6	1-pyrene-carboxaldehyde	40 ± 3
7	1-pyrene-butanol	79 ± 20
8	1-pyrene-methylamine	108 ± 9
9	1-pyrene-methanol	340 ± 7
10	1-perylene-methanol	1350 ± 30

^aAssociation constants calculated by global nonlinear regression analysis,^[12] using the HypNMR2008 program. Titrations were carried out using constant concentrations of host of 0.3-0.4 mM in toluene- d_6 at 298 K. Errors refer to the non-linear regression fittings.

The recognition abilities of **3** and **4** were studied by 1H NMR titration experiments, by monitoring the shifts of the signals of the complexes upon incremental addition of the aromatic guests. For our studies, we chose toluene- d_6 , because it provided the best combination of solubilities and quality of the 1H NMR spectra. Other solvents such as $CDCl_3$ and CD_3CN , also provided good solubilities, but the hosts decomposed in a few hours. We performed the titrations in toluene- d_6 , at a constant concentration of the hosts (0.3-0.4 mM). Addition of the unfunctionalized polycyclic aromatic guests (pyrene, triphenylene, perylene and coronene) resulted in upfield shifts of the signals due to the protons of the pyrene fragment and the N-CH₂ groups of the *n*Bu wingtip of complex **4**, suggesting the formation of host-guest complexes showing fast kinetics on the NMR timescale. For example, when titrating **4** with coronene, one of the pyrene signals shifted by 0.4 ppm, while the signal due to N-CH₂ shifted by 0.45 ppm. Presumably, the bimetallic complex **4** interacts with the PAH guests through π - π -interactions. On the contrary, titrations performed using the benzimidazolyliene complex **3** as the host, did not reveal any appreciable perturbation of the signals of the metal complex, thus suggesting that **3** does not possess a binding affinity for the aromatic guests under study. The assessment of the association constants was performed by nonlinear analysis of the titration data, by simultaneously fitting the shifts experienced by all resonances that showed perturbations.^[12-13] The stoichiometry of the host:guest aggregates was 1:1 in all cases, according to the analyses of the curve fittings and the comparison of the residuals distribution of the 1:1 and 1:2 models.^[13-14] The 1:1 stoichiometry of the host:guest complexes formed was also supported by the Job plot analysis of some selected examples (see ESI for details).

From the results shown in Table 1, it can be concluded that the binding affinities of the unfunctionalized polyaromatic guests increase in the order phenanthrene < pyrene < triphenylene < perylene < coronene (entries 1-5). This trend has been observed in some previous reports when receptors with large portals are used,^[8h, 15] and indicates that the host:guest interaction is dominated by the π -surface area of the guests, rather than by their degree of aromaticity.

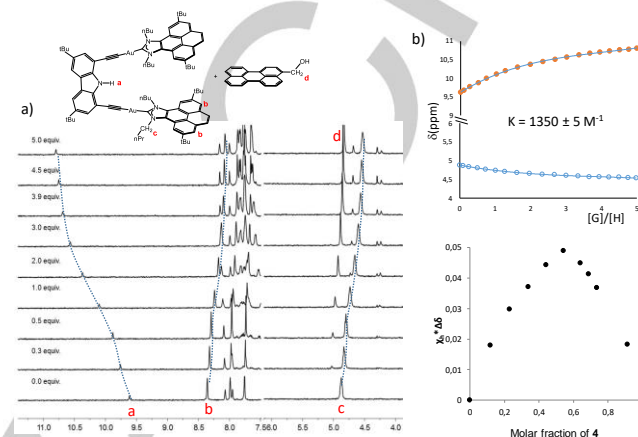


Figure 3. a) Representative region of the 1H NMR (500 MHz) spectra of **4** with added 1-perylene-methanol in toluene- d_6 . The spectra were recorded at a constant concentration of **4** (0.4 mM). b) Binding isotherm for the association of **4** with 1-perylene-methanol, in toluene- d_6 (the global analysis of the changes produced on the signals due to Ha and Hc were used for the determination of the association constant). c) Job plot for the inclusion complex formed between **4** and 1-perylene-methanol.

We thought that the presence of a H-bonding group in a polyaromatic guest should enhance the host-guest affinity as a consequence of the hydrogen bonding interaction with the N-H group of the carbazole linker. For this reason, we carried out NMR titrations using a series of 1-substituted pyrenes (1-pyrene-methanol, 1-pyrene-butanol, 1-pyrene methylamine, and 1-pyrene carboxaldehyde) and 1-perylene-methanol. Compared with the titrations performed with pyrene and perylene, the experiments with the corresponding functionalized guests showed an important downfield shift of the NH resonance of the carbazole unit. This shift is highly suggestive of a hydrogen bonding interaction between the N-H group of the carbazole and the oxygen atom (or nitrogen, in the case of 1-pyrene-methylamine) of the guest, most likely with the heteroatom of the guest acting as the hydrogen-bond acceptor. Together with this, the signals due to the hydrogen atoms of the pyrene and N-CH₂ groups in **4**, experienced important upfield shifts suggestive of a π - π -stacking interaction between the host and the guest. Figure 3 shows the titration of complex **4** with 1-perylene-methanol, evidencing that the shifts of the resonances of the host are quite pronounced. In accordance with this finding, the presence of a heteroatom group in the guests produced important enhancements in their binding affinities (compare entries 2 and 4 with entries 7-10, in Table 1), but the largest differences were observed when a -CH₂OH group was introduced in the guest

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(compare entries 2 with 9, and 4 with 10), which produced an increase in the binding affinities of about one order of magnitude. We also performed UV-vis and fluorescence titrations of **4** with 1-pyrene-methanol and with 1-perylene-methanol. These spectroscopic techniques allowed the use of **4** at lower concentrations than those used for the ^1H NMR titrations. The UV-vis spectrum of **4** shows absorptions between 290 and 320 nm, attributed to pyrene-centered ligand-to-ligand (LLCT) charge transfer transitions. The titrations with 1-pyrene-methanol or with 1-perylene-methanol produced a decrease in the intensity of these bands, although we did not consider these titrations valid for an accurate determination of the binding affinities, because the changes were small, and the residual absorption of the guests in this region of the spectra prevents obtaining an accurate estimation of the constants. Upon excitation at $\lambda = 305$ nm, a degassed toluene solution of **4** shows weak luminescence featuring a vibronically resolved band with peak maximum at 380 nm, which is coincident with the typical emission band of pyrene, as shown in other complexes containing pyrene-based NHC ligands.^[16] The addition of 1-perylene-methanol produced a gradual quenching of the emission of the complex, together with the appearance of the $\pi-\pi^*$ emission bands ascribed to the guests, and one band with a maximum at 368 nm which is attributed to the host-guest complex formed (Figure 4). As for the case of the UV-vis titration, we did not use these titrations to estimate the binding constants, because the changes in the emission bands of the host were too small as to get an accurate determination. However, these experiments serve to support that the interaction of **4** with 1-perylene-methanol and 1-pyrene-methanol occurs even at micromolar concentrations.

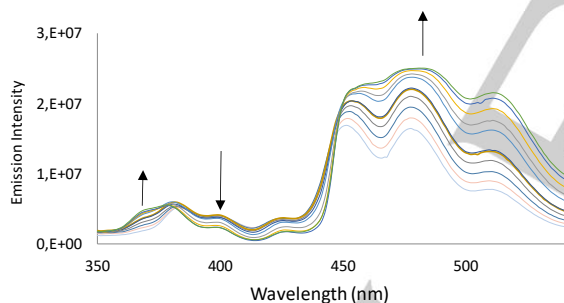


Figure 4. Fluorescence spectra acquired during the titration of **4** (1×10^{-5} M) with 1-perylene-methanol in toluene at 298 K ($\lambda_{\text{exc}} = 305$ nm).

To obtain additional insights into the structure and bonding of the supramolecular systems we performed DFT calculations (M06L-D3/Def2SVP(H,C,O,N); Def2QZVP(Au)//M06LD3/Def2QZVP in toluene) on the host-guest complexes of **4** with 1-pyrene methanol and 1-methylpyrene. We were interested in establishing the structural features of these systems together with estimating the energy differences of the hydrogen-bonded complexes vs. the corresponding systems devoid of hydrogen bonding. The optimized geometries of two models of **4** with 1-pyrene methanol are presented in Figure 5. The top structure exhibits the anticipated $\text{NH}\cdots\text{O}$ hydrogen bond (1.93 Å) and what appears to be another possible weak interaction between the OH and a carbon (C1) of one alkynyl fragment at 2.24 Å. Although the -

CH_2OH group appears to be “sandwiched” between the gold atoms, the non-bonding Au-H distances are relatively long (2.78, 2.82 Å). The optimized geometry of a model of **4** with 1-pyrene methanol pointing *outside* the host-guest complex is the bottom structure of Figure 5. The latter has most structural features closely resembling the first model, except that it, naturally, does not possess an intermolecular hydrogen bonding interaction. Two further calculations were performed on the analogs of the systems of Figure 4, with the $-\text{CH}_2\text{OH}$ group replaced by $-\text{CH}_3$, i.e. host-guest complexes of **4** with 1-methylpyrene. These additional calculations established a zero-enthalpy difference between the complex of 1-methylpyrene with the $-\text{CH}_3$ group pointing toward the NH of the carbazole or in the opposite direction, i.e. outside the complex. This observation allows us to conclude that the enthalpy difference of the structures of Figure 4, $\Delta H = 4.2$ kcal/mol can be regarded as the enthalpy of the hydrogen bond in **4** with 1-pyrene methanol.

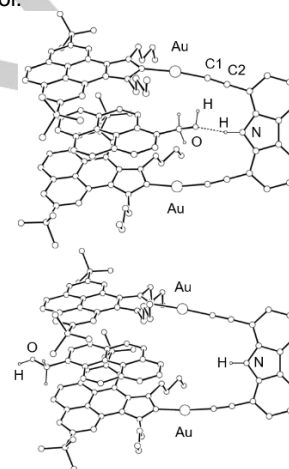


Figure 5. Calculated structures of the host-guest systems modelling **4** with 1-pyrene methanol with (top) and without (bottom) hydrogen bonding. Most hydrogen atoms are not shown for clarity. Two *t*-Bu groups of the carbazole in **4** have been replaced by hydrogen atoms in the DFT calculations.

In summary, we developed a simple method to prepare two gold-based metallo-tweezers with two planar pincers bound by a carbazole unit. The metallo-tweezer with two pyrene-based NHC ligands is able to bind a series of polycyclic aromatic hydrocarbons due the π -stacking interactions between the polyaromatic guests and the pyrene fragments of the NHC ligands. The presence of the NH group at the carbazole linker enhances the binding affinity of PAHs bearing functionalities capable of hydrogen bonding, and the association constants of these guests are up to one order of magnitude higher compared to those shown by unfunctionalized PAHs. The work constitutes an example in which both π -stacking and H-bonding interactions are combined for the design of more effective metallo-receptors. The selectivity shown by receptor **4** for functionalized PAHs is of interest, because it is well accepted that the functionalities and the periphery of PAHs crucially determine their electronic properties, reactivity, shape and solubility,^[17] therefore designing sensors to selectively recognize PAHs with specific functionalities will very likely be a demand in the near future. Finally, the studies shown

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in this work give insights on the intimate interaction between substrates and metal complexes, and this may have interesting consequences on the design of future homogeneous catalysts.

Acknowledgements

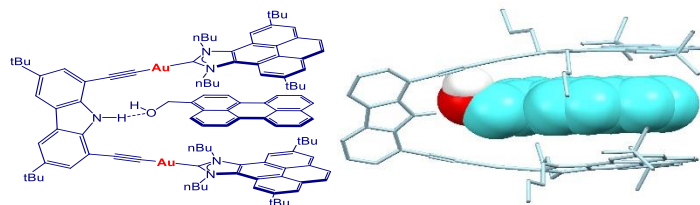
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Keywords: Metallo-tweezer • N-heterocyclic carbene • gold • Host-guest • Polycyclic aromatic hydrocarbons (PAHs)

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Page No. – Page No.

Title

The presence of pyrene tags at the NHC ligands and the N-H group of a carbazole linker enables Au(I)-tweezers to bind polyaromatic guests through combined π -stacking and H-bonding.

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