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A rigid hexa-gold trigonal prismatic metallocage that behaves as a coronene trap

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Abstract: A hexagold trigonal prismatic cage was obtained by combining a triphenylene-tris-N-heterocycic carbene ligand and a carbazolyl-bis-alkynyl linker. The metallocage has a 'slot-like' cavity of ≈300 Å^3 of volume. This cage was used for the recognition of several PAHs. Due to the perfect dimensional match, the supramolecular complex shows very high affinity for trapping coronene.

The incorporation of extended π-conjugated systems into the structures of supramolecular coordination complexes (SCCs)[1] can introduce benefits due to the band structure, electronic properties and optical absorption of extended polyaromatic systems.[2] In addition, the incorporation of polyaromatic fluorophores within SCCs may facilitate the tunability of their emission behavior, which is an important property for the fabrication of optoelectronic devices. Despite these clear benefits, the construction of SSCs based on large π-conjugated systems remains largely unexplored. This can be due to the low solubility of π-extended systems, which limits their applicability in the design of suitable Werner-type linkers for SCCs construction. The incorporation of π-extended linkers into the structures of SCCs may be facilitated by using some of the known organometallic-based polytopic ligands that now can be found in the literature.[3] Although the number of organometallic-based SCCs has increased in the recent years,[4] the number of examples that contain π-extended conjugated systems is limited to very few examples,[5] although their applicability as receptors of organic substrates via host-guest chemistry events may anticipate the fast development of this type of systems. On the other hand, polycyclic aromatic hydrocarbons (PAHs) are hazardous materials that have gathered significant environmental concern,[6] although their rigid planar structures and electronic nature make them very attractive for use as two-dimensional nanoarchitectures with optical and electronic applications.[7] This is the reason why there is a great interest in developing host molecules for selective PAH detection and separation. Given the rigid planar π-delocalized nature of PAHs, their recognition is based on designing rigid cavities endowed with convergent cofacial planar π-extended panels, ideally separated by twice the optimum distance for effective π-stacking interactions (≈7Å), for facilitating guest recognition by π−π-stacking interactions. If we combine this with a high level of shape complementarity and a good packing coefficient of the guest in the internal cavity of the host,[8] then selective receptors for specific PAH-guests may be obtained. Despite this may seem rather simple principles, there exists only few organic[9] and

metallorganic[5b, 10] cofacial cage-like structures used for the recognition of PAHs.

By using rigid bis-alkynyl connectors combined with a pyrene-imidazolylidene ligand, we recently described a series of di-gold metallo-tweezers, which we used for the recognition of 'naked' metal cations[11] and polycyclic aromatic hydrocarbons.[12] Based on these previous results, we thought that we could obtain a new interesting family of metallorganic cages by replacing the mono-NHC ligand by poly-NHC ligands connected by extended π-conjugated systems. The work that we now report is based on the assumption that the tris-NHC-Au(I) complex 1[13] (Scheme 1) should constitute an excellent building block for the preparation of trigonal metallosupramolecular structures with extended polyaromatic panels. Rigid polyaromatic tris-NHC ligands are scarce,[13b, 14] but should constitute excellent building blocks for the construction of trigonal metallocages. Hence, herein we describe our results on the preparation of a nanosized trigonal prismatic metallosupramolecular system based on the combination of three carbazolyl-bis-alkynyl units and two triphenylene-based tris-NHC ligands, connected by six gold (I) centres.
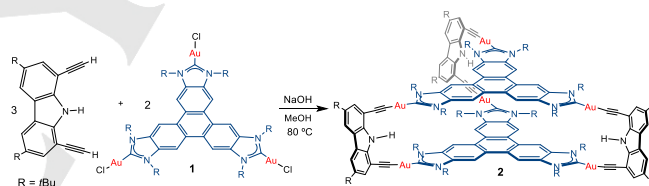

Scheme 1. Synthesis of D_{3h}-symmetric metallocage **2**

The trigonal metallocage **2** was obtained by following the synthetic procedure depicted in Scheme 1. The deprotonation of di-*tert*-butyl-diethynyl-carbazole with NaOH in refluxing methanol followed by the addition of the triphenylene-tris-imidazolylidene-gold(I) complex **1**, afforded the hexa-Au(I) compound **2** as a yellow solid in 86% yield, after purification. Compound **2** was characterized by NMR spectroscopy and gave satisfactory elemental analysis. Both, the ^1H and ^{13}C NMR spectra are consistent with the threefold symmetry of the complex. The ^{13}C NMR spectrum shows a singlet at δ 199.94 assigned to the six equivalent carbene carbons. The diffusion-ordered NMR spectroscopy (DOSY), showed that all proton resonances display the same diffusion coefficient in deuterated dichloromethane (5.41×10^{-10} m^{2}s^{-1}, see SI for details), indicating the presence of a single assembly. By using the Stokes-Einstein equation, this coefficient provides an estimated hydrodynamic radius of 9.5 Å, in a good agreement with the expected radius of **2** based on the known size of the tris-NHC and the diethynyl-carbazole ligands.

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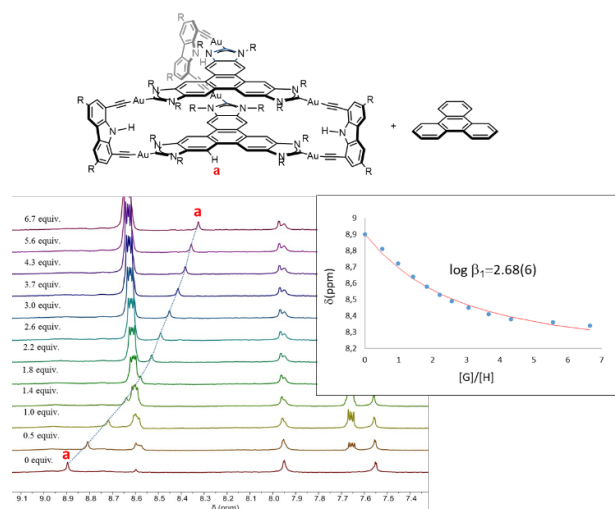
Figure 1. Representative region of the ^{1}H NMR (400 MHz) spectra of **2** with added triphenylene in CD$_2$Cl$_2$. The spectra were recorded at a constant concentration of **2** (1 mM). The inset plot is the binding isotherm for the association of **2** with triphenylene.

We tested our molecular cage **2** for the recognition of polycyclic aromatic hydrocarbons (PAHs). We thought that the dimensions of the cage should allow that one molecule of the guest could be encapsulated within the thin slot formed between the two cofacial triphenylene moieties of the cage. The binding affinities of **2** were studied by ^{1}H NMR experiments, by monitoring the variation of the chemical shifts of the signals of the ligands in **2**, upon addition of solutions containing the different polyaromatic guests. The titrations were performed at room temperature, at constant concentrations of **2** (typically 1 mM) in CD$_2$Cl$_2$. In general, the addition of increasing amounts of the guests induced a progressive upfield shift of the signal due to the protons of the triphenylene moiety of the host, indicating that the formation of the inclusion complexes showed fast kinetics on the NMR timescale. The maximum values of $\Delta\delta$ observed for the titrations with the different guests depends on the nature of the polyaromatic substrates used (see Table 1). Larger guests produce a greater upfield shift of the aromatic signal of the host, since the number of π-electrons dictates the shielding effect of the PAH guests. As an illustrative example, Figure 1 shows a series of spectra recorded from the titration of **2** with triphenylene, and the binding isotherm resulting from the plot of the variation of the chemical shift of the signal due to the protons of the triphenylene linker with the amount of guest added. The determination of the association constants was performed by nonlinear analysis of the titration data. At this point, it is important to mention that, given that we showed that N-heterocyclic carbene ligands decorated with rigid polyaromatic moieties may bind PAHs through π–π-stacking interactions,[3a, 15] we thought that our host may have two binding sites for the recognition of the polyaromatic guests. The internal cavity of **2** should be the main recognition site, but we should not discard that the outer side of the polyaromatic panel formed by the triphenylene-based tris-NHC may constitute another binding site. In order to determine if the PAH guests may show affinity for the exterior panel of the molecule, we performed a control

experiment in which we used the trimetallic planar complex **1** as host for the polyaromatic guests. By performing ^{1}H NMR titrations in CD$_2$Cl$_2$, we concluded that only the larger guests (perylene and coronene) showed low, but measurable binding affinities for **1** (K$_{11}$ = 10 M^{-1} and 100 M^{-1}, for perylene and coronene, respectively). With these data in hand, we processed all the data of the ^{1}H NMR titrations of **2** with the PAH guests considering a 1:1 host:guest stoichiometric model. We also based our decision on the low solubilities of the guests in CD$_2$Cl$_2$, which did not allow adding the sufficient excess of the PAHs as for obtaining a significant concentration of the 1:2 adducts for rendering meaningful β_2 values. This gave us association constants with low uncertainties and good residuals distributions (except for coronene, as will be discussed below).[16]

The resulting association constants are given in Table 1. The results indicate that the binding affinities are in the order anthracene < pyrene < triphenylene < perylene << coronene, indicating that the stability constant of the complex increases as the guest becomes more π-electron-rich.

**Table 1.** Association constants (M^{-1}) for the complexation of **2** with PAHs.

Entry	Guest	$\Delta\delta_{max}$ (ppm)	$\log\beta_1$	$\log\beta_2$
1	anthracene	0,1	1,79±0,04[b]	--
2	pyrene	0,28	2,15±0,06[b]	--
3	triphenylene	0,57	2,68±0,06[b]	--
4	perylene	0,65	3,3±0,2[b] 3,52±0,09[c]	--
5	coronene	1,57	4,18±0,05[b] 4,70±0,07[c] 4,31±0,8[d] 4,61±0,09[e]	-- 7,9±0,8[c] 8±1[d] 6±1[e]

[a]Association constants calculated by nonlinear regression analysis. Titrations were carried out using constant concentrations of host in CD$_2$Cl$_2$ at 298 K. Errors refer to the non-linear regression fittings. [b]Values determined by NMR spectroscopy considering a 1:1 model. [c]Values obtained by fluorescence spectroscopy. [d]Values obtained by fluorescence 'inverse' titration (coronene used as host). [e]Values obtained by Uv/vis spectroscopy.

In order to obtain a more accurate insight on the bonding abilities of **2**, we decided to perform Uv/vis and fluorescence titrations. For these studies we only used coronene as guest, because its large binding affinity fits within the range for performing titrations with these spectroscopic techniques.[17] We were also aware that these two techniques allowed us to use a global fitting process that should render a more accurate analysis of the binding situation.[18] Complex **2** shows high energy absorptions at around 240-400 nm, attributed to triphenylene-centered ligand-to-ligand charge transfer transitions. Upon addition of the coronene low energy bands appear (400-450 nm), which are attributed to π–π-transitions of the polyaromatic guest. The emission spectrum of **2** shows a weak broad unresolved band centered at 500 nm, attributed to the emission of the triphenylene moieties, which show attenuated emission at longer wavelength than the emission of triphenylene (400 nm), due to their close proximity. Upon addition of the guests, the bands due to the emission of coronene appear in the region of 400-510 nm. The changes in the

absorbances and in the emissions were found to give saturation upon addition of 40 equivalents of the guest. Based on the changes observed, the binding constants were determined by using a global fitting analysis. The data were processed using a 1:2 stoichiometric model, which allowed us to obtain the association constants for the formation of both, the 1:1 and the 1:2 H:G adducts. The association constants obtained from UV/vis and emission spectroscopy were in excellent agreement, and also reasonably coincident with the one obtained from the ^{1}H NMR titration. However, while the values obtained for the first binding constant (β_1) looked very accurate, the values found for the second binding constant (β_2) showed large expanded uncertainties, as a consequence of the large differences found between K_1 (β_1) and K_2 (β_2/β_1), but it seems rather clear that K_2 ranges between 100-1000 M^{-1}. At this point, it may be convenient to mention that a third molecule of coronene may also bind to the second outer face of the metallacage, but the binding constant for this third association must be negligible, and therefore impossible to estimate by using spectroscopic means. Further evidence to confirm the large binding affinity of coronene was obtained by performing an 'inverse' fluorescence titration, in which coronene was used as host. The results obtained were fully consistent with the ones obtained by all other techniques, although, again, the value obtained for second binding step showed a large expanded uncertainty.
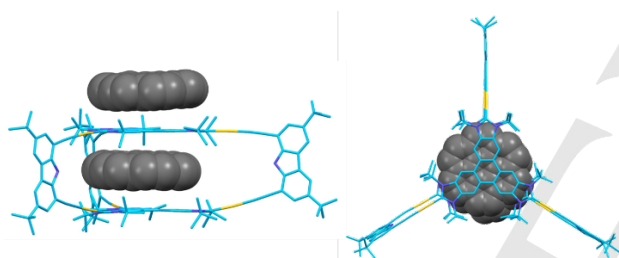
Figure 2. Two perspectives of the X-ray diffraction molecular structure of (coronene)$_2$@**2**. Hydrogen atoms and solvent (methylene chloride) were removed for clarity. The molecule of **2** is represented in the stick-diagram mode, while the two molecules of coronene are depicted with the space filling diagram.

Mixtures of **2** and coronene in methylene chloride afforded single crystals that contained **2** with two molecules of coronene [(coronene)$_2$@**2**]. The molecular structure of this adduct was unambiguously confirmed by single crystal X-ray diffraction (Figure 2). The structure consists of a trigonal prismatic hexa-gold cage with one molecule of coronene trapped inside the cavity of **2**, and a second molecule of coronene outside of the metallacage. The structure of **2** shows an almost perfect D_{3h} symmetry. The metallacage is formed by six gold atoms bound by two cofacial parallel triphenylene-tris-NHC ligands, and three carbazolyl-bis-alkynyls. The average distance between the gold atoms bound to the same carbazolyl-bis-alkynyl ligand is 6.75 Å. The average distance between the gold atoms bridged by the triphenylene-tris-NHC ligand is 13.5 Å. The distance between the two planes formed by the two triphenylene moieties is 7.05 Å, thus optimum for establishing effective π–π-stacking interactions with a polyaromatic guest hosted inside the cavity. The plane formed by the molecule of coronene located inside of the cage shows an

average distance of 3.5 Å with the two convergent triphenyelene-tris-NHC panels of the metallocage, and the same distance is observed for the separation between the outside molecule of coronene with the plane of the closest tris-NHC ligand. The two molecules of coronene are cofacial, and are disposed in a relative eclipsed conformation. It is important to mention that the *tert*-butyl moieties of the tris-NHC ligand clearly contribute to the 'fixation' of the molecule of coronene inside the cavity of **2**, as can be observed from the perspective views shown in Figures 2 and 3c. The cage has an internal cavity depth of 3.65 Å between opposing triphenylene platforms (Figure 3a), and measures 13 Å between the coplanar gold atoms (Figure 3b), as measured by taking the van der Waals radii into account. The sides of the triangular surface are flanked by the *tert*-butyl groups of the tris-NHC ligand (Figure 3b), therefore the guest-accessible volume is restricted to an almost regular trigonal prismatic cavity of 270 Å^3. This volume is not far from the cavity volume that can be computationally estimated (301 Å^3).[19] When these volumes were used to calculate the percent occupancy of coronene within **2**, we obtained values of 92% and 83%, depending on whether we used the former or the computationally calculated one, respectively, therefore very far from Rebek's 55% rule.[8] It has to be pointed out that Rebek's rule predicts a favourable 55% occupancy assuming only the weakest of interactions between the host and the guest. In our case, the maximization of the face-to-face π–π-stacking interactions make that the K_a value for coronene is greatly increased compared to the smaller PAH guests. This makes that in our case the contribution of enthalpy to binding should become larger (while the entropy contribution decreases), as the percent volume occupancy increases, in agreement with previously published results.[9b]
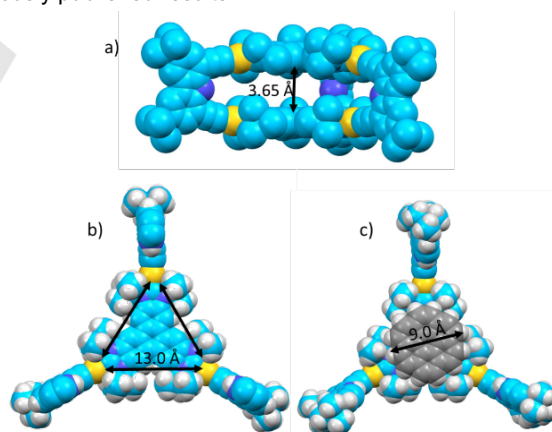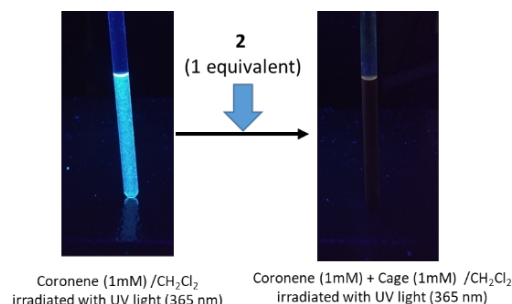

Figure 3. a) Space-filling diagram of 'empty' **2**, highlighting the van der Waals top-to-bottom surface separation. b) Cut-away space-filling plan view of the cavity inside **2**, showing the triangular surface available for the binding of the PAH guests. c) Cut-away space-filling view of **2** illustrating the location of coronene, highlighting the van der Wals radius of this guest.

In view of the large binding affinity of **2** with coronene, we tested the metallocage as coronene scavenger in CH_2Cl_2. For this we prepared 0,4 mL of a 1 mM solution of coronene in methylene chloride. The irradiation of this solution with UV light (365 nm) produces a strong blue emission due to the presence of the fluorescent PAH. Then one equivalent of **2** was added. The UV

irradiation of the resulting solution showed that the emission disappeared, thus indicating that coronene was trapped within the cavity of **2** (Figure 4).

2
(1 equivalent)

Coronene (1mM) /CH$_2$Cl$_2$
irradiated with UV light (365 nm)

Coronene (1mM) + Cage (1mM) /CH$_2$Cl$_2$
irradiated with UV light (365 nm)

Figure 4. A sample of coronene (1 mM) in CH$_2$Cl$_2$ irradiated with UV light before (left) and after (right) adding one equivalent of **2**.

In summary, we prepared a rigid hexa-gold-based trigonal prismatic cage combining a triphenylene-tris-NHC ligand and a carbazole-bis-alkynyl. The resulting metallocage has a well-defined cavity of about 300 Å^3 of volume. The cage was used as receptor for the recognition of PAHs, showing increasing affinity as the size of the rigid polyaromatic substrate increases. A very high binding affinity was observed for the case of coronene, as a consequence of the optimum dimensional matching, and to the presence of a 'slot-like' cavity. We think that our work not only describes a new type of metallocage that may be used as a 'coronene trap', but also introduces a planar trigonal tris-NHC ligand that will surely have important implications in the design of future trigonal-symmetry self-assemblies.

Acknowledgements

Keywords: N-heterocyclic carbenes • Gold • Supramolecular coordination complexes • host-guest • PAHs

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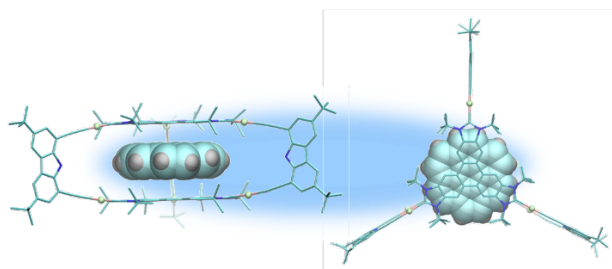[19] N. Guex, M. C. Peitsch, *Electrophoresis* **1997**, *18*, 2714-2723.

Entry for the Table of Contents

COMMUNICATION

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A rigid hexa-gold trigonal prismatic metallocage that behaves as a coronene trap

A hexa-gold trigonal prismatic cage with a 'slot-like' cavity with perfect dimensional match for the trapping of coronene.