**SUPPORTING INFORMATION**

# Capturing a Square Planar Gold(III) Complex Inside a Platinum Nanocage: A Combined Experimental and Theoretical Study

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## $^1$H-NMR Studies data for Host Guest Chemistry

For a typical titration experiment, a 7.7 mM solution of cage (3.87 $10^{-3}$ mmol) in $CD_3CN$/DMSO-$d_6$ (4 :1) (0.5 mL) was treated with aliquots of (2.79 mg, 3.87 $10^{-3}$ mmol) guest followed by an equilibrium time of 5 min prior to the NMR measurement.

**Figure S1**. $^1$H NMR spectra in $CD_3CN$ /DMSO (4:1) for $[Pd_2\mathbf{L}_4][OTf]_4$ (**1a**) in presence of Au(III) guest. a) the cage complex **1a** b) free [*n*-$Bu_4N$][$Au(bdt)_2$] guest c) 1 eq. of [*n*-$Bu_4N$][$Au(bdt)_2$] d) 1 eq. of [*n*-$Bu_4N$][$Au(bdt)_2$] e) excess of [*n*-$Bu_4N$][$Au(bdt)_2$] f) free ligand L.

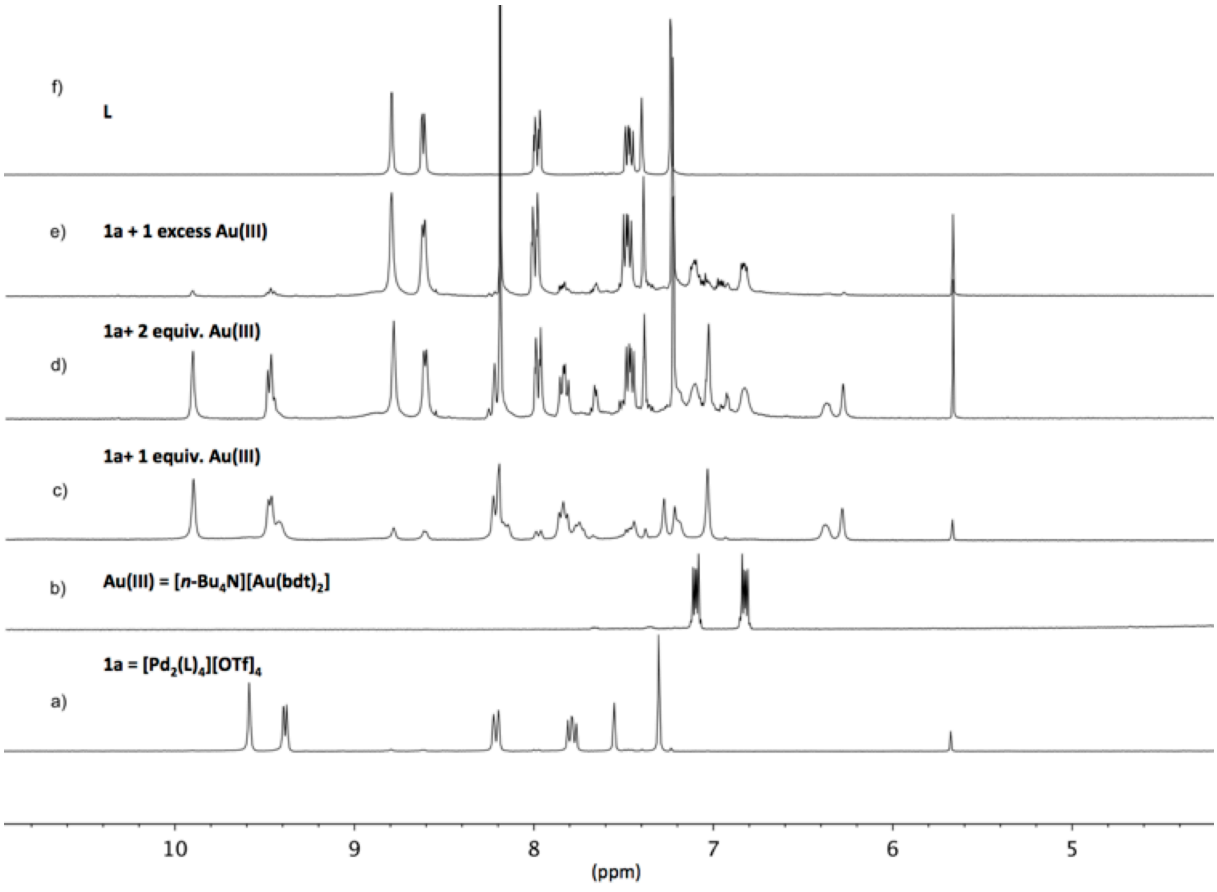


**Figure S2**. $^{1}$H NMR spectra in $CD_3CN$ for a) ligand **L** and b) the cage complex $[Pt_2\mathbf{L}_4][OTf]_4$} (**1b**).

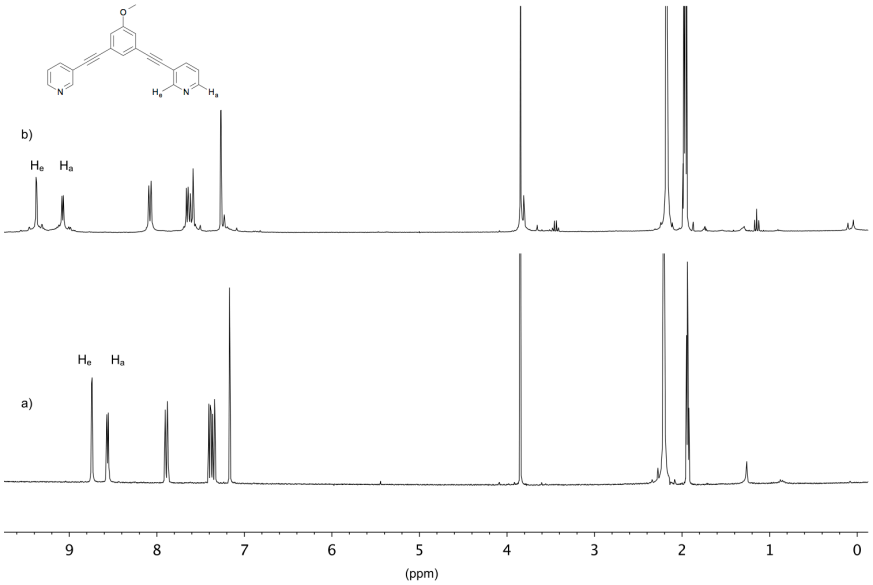



**Figure S3**. Full $^{1}$H NMR spectra in $CD_3CN$ /DMSO (4:1) for $[Pt_2\mathbf{L}_4][OTf]_4$ (**1b**) in presence of Au(III) guest. a) free $[n\text{-}Bu_4N][Au(bdt)_2]$ guest b) the cage complex **1b** c) 1 eq. of $[n\text{-}Bu_4N][Au(bdt)_2]$ d) excess of $[n\text{-}Bu_4N][Au(bdt)_2]$. (Hint = H interior, Hext = H exterior).

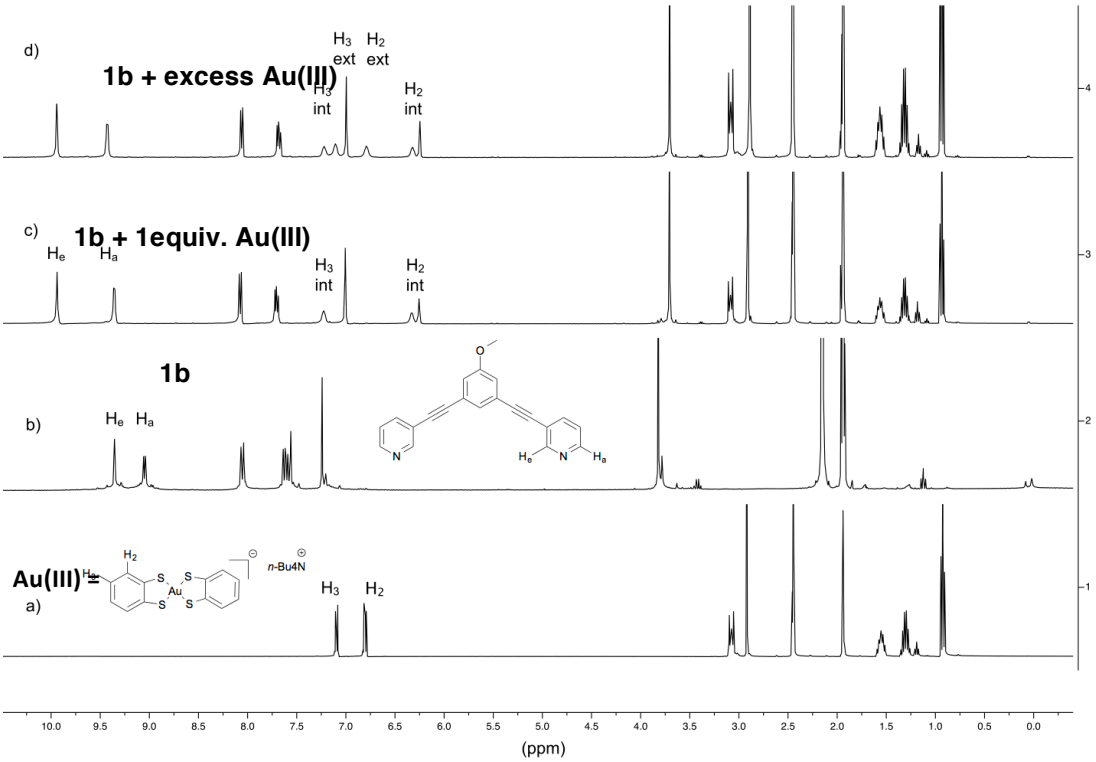


**Figure S4**. $^{1}$H NMR spectra in $CD_3CN$ /DMSO (4:1) of the aromatic region for $[Pt_2\mathbf{L}_4][OTf]_4$ (**1b**) in presence of sequential additions of Au(III) guest. Signals due to free cage and complexed-cage are visible suggesting a slow exchange is occurring between the Pt-cage and guest Au(III) complex . Ha (star) , Hb (circle) and He (diamond) are denoted in the spectra : Free cage (white symbols ); Complexed cage (black symbols).

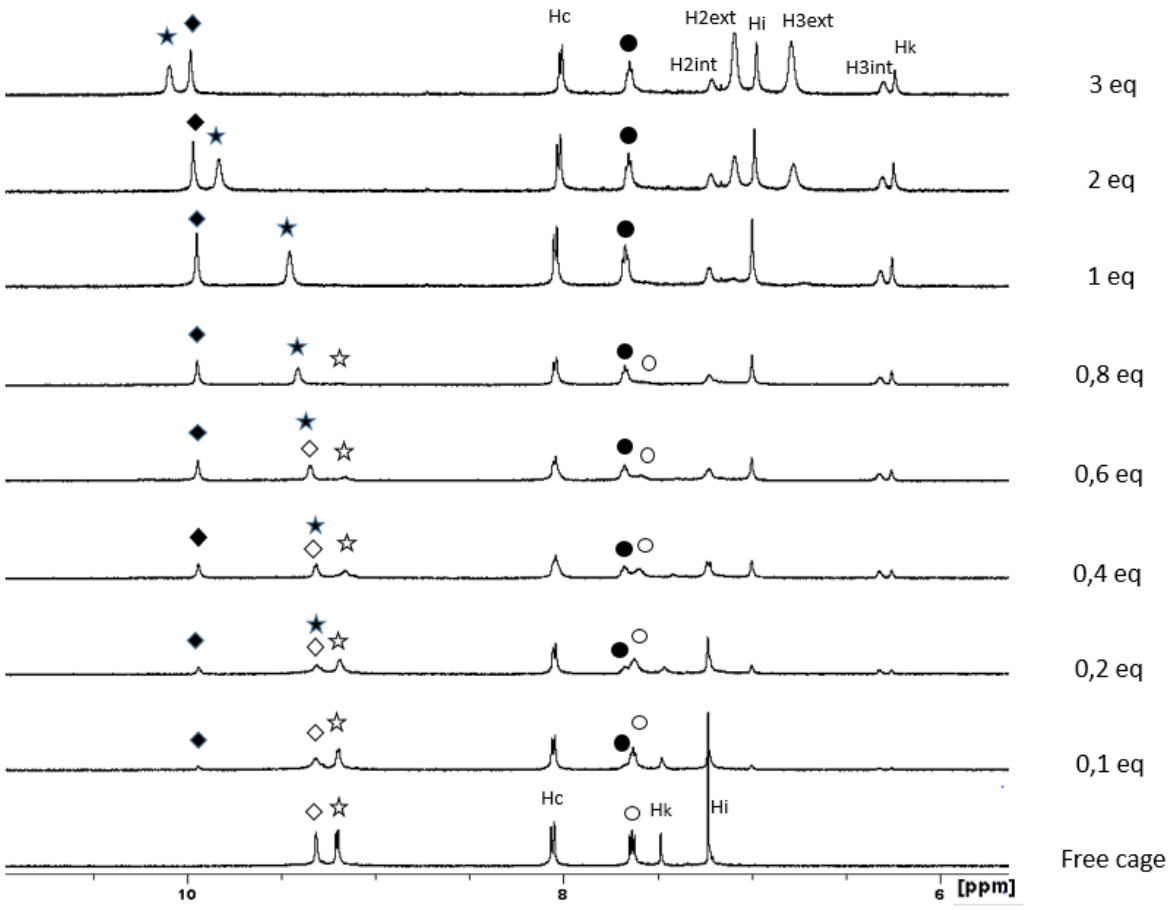
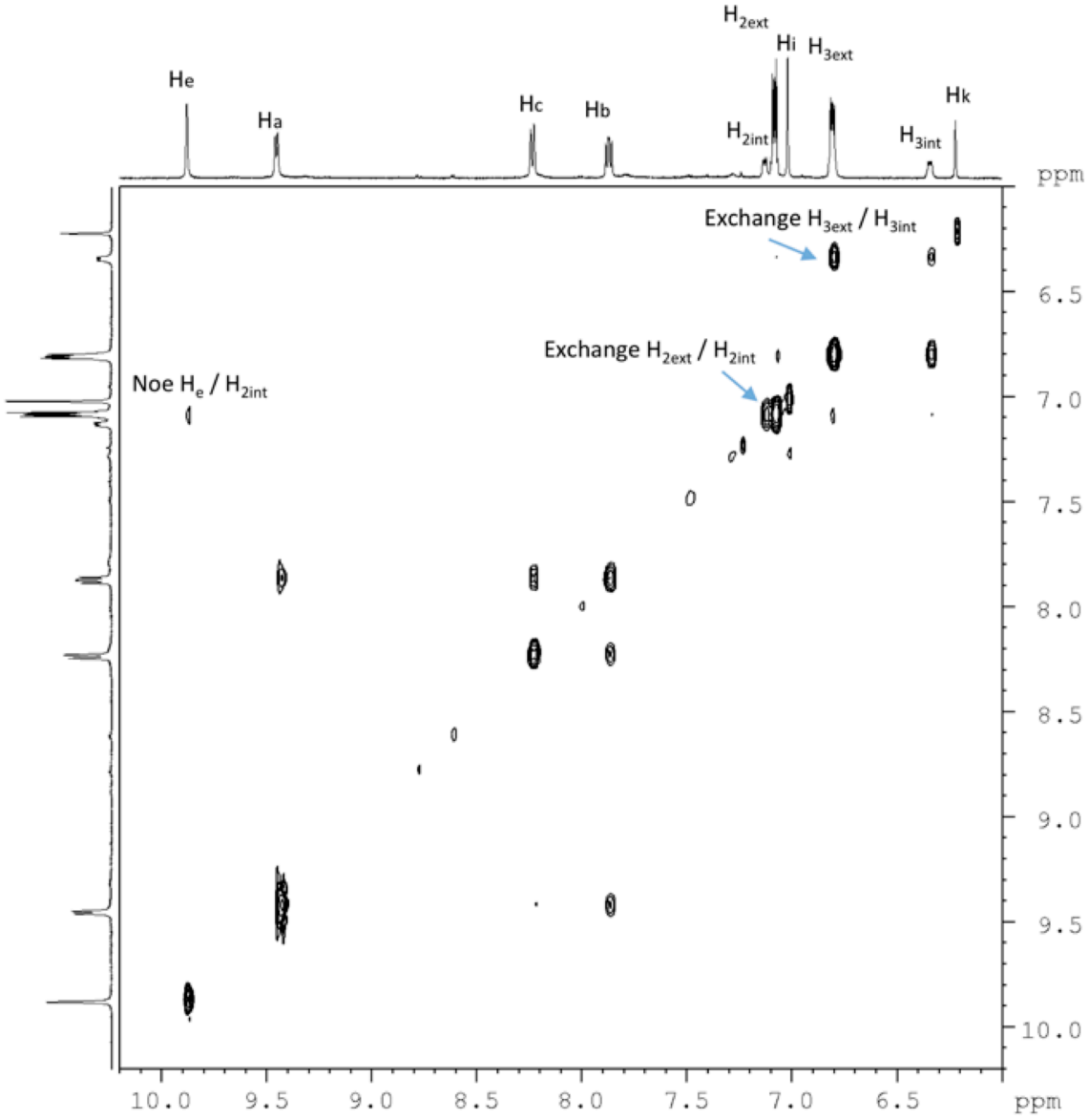


**Figure S5**. 2 D NOESY spectrum of $[Au(bdt)_2 \subset Pt_2\mathbf{L}_4][Au(bdt)_2]_3$ (**2**) recorded in DMSO.




## Computational Details

Properties of the host-guest complex were calculated by density functional theory (DFT), using the popular B3LYP method[1,2] as well as the more recent M06 method[3] and several basis sets for comparison: 3-21G[4] and cc-pVDZ[5] for main group atoms, CEP-121G basis and effective core potential[6] for the metals, and LANL2DZ[7] for all atoms. The suffix "-D3" added to the method (e.g., "B3LYP-D3") indicates the inclusion of Grimme's 3-parameter correction[8] to model dispersion effects. Initial energy and natural bond analysis (NBO)[9] calculations were carried out using the Gaussian 09 package[10], whereas energy decomposition analysis (EDA)[11] was performed using Gamess. [12] In all cases, the fixed X-ray geometry or a truncation of that geometry was used.

The host-guest complexation energies were calculated with counterpoise corrections[13] in an effort to compensate for basis set superposition error (BSSE). Briefly, BSSE results from the use of a larger number of basis functions to represent the complex than the number of basis functions used for the individual monomers. This discrepancy causes the energy of the complex to be

artificially lower in comparison to the monomers and tends to overestimate binding energies. The counterpoise correction partially addresses this problem by finding the energies of the monomers using the basis set of the entire complex and using these energies to estimate the magnitude of the error.

These energies are predicted to be quite similar among different basis sets and between the B3LYP and M06 methods, which suggests that these basis sets are adequate for calculating the energetics. The interior gold guest is predicted to be more strongly bound than the exterior guest, by 12—18 kcal/mol in the absence of dispersion and by 42—47 kcal/mol when dispersion is included. This seems reasonable, given that the interior guest has more near-atom interactions available and also the possibility of p-stacking interactions between the central methoxyphenyl ring of each arm and the phenyl rings of the guest.

The overall interaction energy of the two guests with the host is greater than the sum of the individual interaction energies, indicating that each guest encourages the host to accept a second guest.

**Table S1. Counterpoise-corrected host-guest interaction energies (kcal/mol).**

| DFT method | basis set | # functions[a] | [host-int] + [ext][b] | [host-ext] + [int][b] | [host] + [ext] + [int][b] |
|---|---|---|---|---|---|
| B3LYP | LANL2DZ | 1376 | -122.4 | -140.5 | -299.6 |
| B3LYP | cc-pVDZ,CEP-121G | 2308 | -122.4 | -134.9 | -294.1 |
| B3LYP-D3 | LANL2DZ | 1376 | -145.2 | -192.7 | -374.4 |
| B3LYP-D3 | 3-21G,CEP-121G | 1452 | -146.2 | -189.5 | -372.3 |
| B3LYP-D3 | cc-pVDZ,CEP-121G | 2308 | -145.2 | -187.1 | -368.9 |
| M06-D3 | cc-pVDZ,CEP-121G | 2308 | -142.1 | -191.8 | -370.2 |

[a] Total number of contracted basis functions for the entire complex. A larger number of basis functions generally implies a better basis set.

[b] [host-int] + [ext] represents the energy change upon formation of the entire complex from inserting a gold guest molecule into the complex of $Pt_2$ metallacage host containing the interior guest; [host-ext] + [int] is DE for inserting the interior guest to form the entire complex; [host] + [ext] + [int] is DE for formation of the entire complex from the host and both guest molecules initially separated.

Most of the interaction energies given in Table S1 are theoretical *gas-phase* binding energies. The binding energy in polar solvent is expected to be lower because the separated ions (particularly the +4 metallocage) will be more strongly stabilized by solvent interactions than the combined +2 complex. However, the effect of the counterions would also have to be incorporated into that calculation, and therefore we have not attempted to model the solution-phase in the present results.

The B3LYP/cc-pVDZ,CEP-121G NBO analysis yields a set of atom-by-atom interaction energies, labeled $E^{(2)}$ calculated by second-order perturbation theory. These values represent individual donor-acceptor interaction energies, including charge-transfer contributions. Summing $E^{(2)}$ values over all of the interactions from atoms of the host to atoms of a guest, we can roughly estimate the total donor-acceptor interaction energy. Those results for this complex are summarized in Table S2. For both the interior and exterior guests, the dominant contribution to these energies

arises from the guest acting as a donor to the organic component of the host cage.

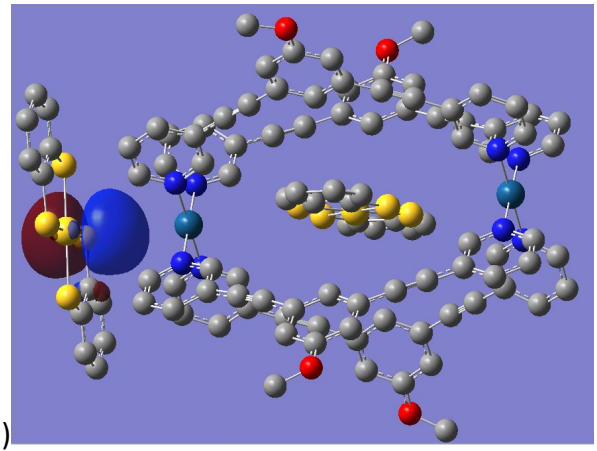
**Table S2. Donor-acceptor interaction energies (kcal/mol) from NBO analysis.**

| **donor-acceptor**[a] | **exterior guest** | **interior guest** |
|---|---|---|
| $Pt_a$ - guest | -4.6 | -0.2 |
| $Pt_b$ - guest | 0 | -0.2 |
| cage - guest | -11.3 | -2.9 |
| guest - $Pt_a$ | -9.3 | -5.9 |
| guest - $Pt_b$ | 0 | -6.1 |
| guest - cage | -24.6 | -36.8 |
| **total** | **-49.8** | **-52.1** |

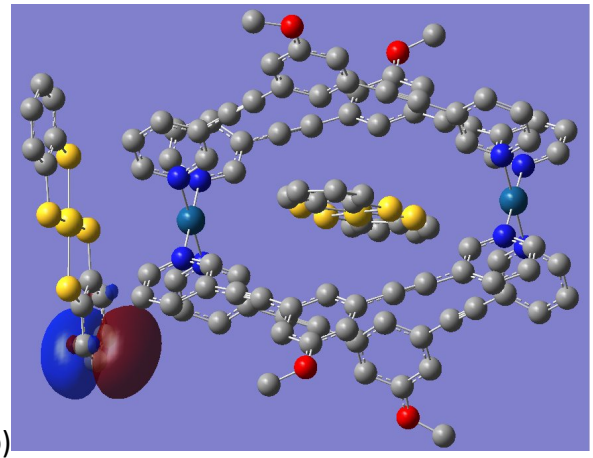
[a] $Pt_a$ is the Pt atom adjacent to the exterior guest; $Pt_b$ is opposite the exterior guest; cage consists of the remaining organic component of the host compound.

The possibility of a metal-metal host-guest interaction exists for this complex, but the Pt atoms appear to be too distant from the guest molecules to account for more than about a quarter of the total interaction energy. Looking specifically for Pt-Au interactions, we find that in the case of the exterior guest, most of the energy contribution involving the neighboring Pt atom is ascribed to direct Pt-Au interaction, whereas for the interior guest the Pt atoms interact roughly equally with the Au atom and with the associated S atoms. In either case, however, Pt-Au bonding appears to be a relatively small contribution to the stabilization of these guests. Instead, most of the donor-acceptor stabilization is provided by the nearest-neighbour interactions, especially the electropositive hydrogen atoms on the host aryl groups as the acceptors and the guest sulfur atoms and aryl carbons as donors.

This is consistent in part with the NBO orbital analysis, which predicts the highest energy occupied MOs to be π-type orbitals on each of the four sulfur atoms of the exterior guest molecule, conjugated into the aryl π-system (Fig. S6a). The next highest energy occupied orbitals are the π-bonding orbitals from the two guest phenyl groups (Fig. S6b), which may also act as donor orbitals. The lowest unoccupied orbitals are Pt d orbitals, but candidate acceptor orbitals at the host appear at slightly higher energy (Fig. S6c).

(a) 

(b)



(c)

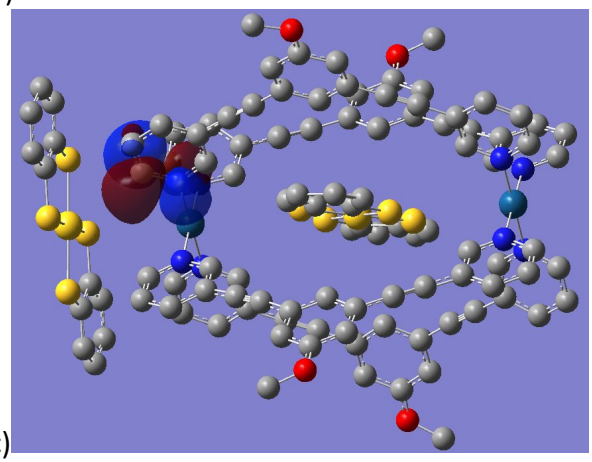


**Figure S6.** Selected NBO molecular orbitals calculated at the B3LYP/cc-pVDZ,CEP-121G level: (a) the HOMO, a possible donor orbital from the guest S atom; (b) HOMO-4, a possible donor orbital from the guest aryl group; (c) LUMO+8, a possible acceptor orbital.

The importance of S and aryl guest interactions with the host phenyl hydrogens is also consistent with a very crude analysis of the electrostatic interactions between the host and guests based on the approximate formal charges on each atom assigned by the Mulliken method.[14] It should be emphasized that Mulliken charges are extremely sensitive to computational parameters such as basis set, and the energy values we obtain from them are not likely to be accurate. However, it is reasonable to expect that qualitative conclusions about the relative interaction strengths may be drawn from these values. For the exterior guest, average nearest neighbor (guest S)-(host H) distance is 3.21 A, and the average nearest neighbor (guest C)-(host H) distance is 2.95 A. For the interior guest, the nearest neighbor average nearest neighbor (guest S)-(host H) distance is 2.87 A. With partial charges of -0.03e to -0.20e on the electronegative atoms and up to 0.2 on the H atoms, the Coulomb potential energy between the host and guest may account for 40—50 kcal/mol of the total binding energy for the exterior guest and 20—30 kcal/mol for the interior guest.

To more accurately divide the host-guest binding energy into distinct contributions, a thorough energy decomposition analysis (EDA) is desirable. Unfortunately, these are much more resource-intensive calculations than the energy calculations, and a complete EDA of these interactions is prohibitive for a host molecule of this size. Efforts to develop a suitable model for this energy analysis are ongoing. At present, we can only say that both guest molecules appear to be stabilized by a combination of dispersion, donor-acceptor interaction, and electrostatics, each contribution being of magnitude in the tens of kcal/mol. The interior guest appears to be stabilized largely by the dispersion interaction, whereas electrostatic interactions may play a larger

role in stabilizing the exterior guest. Overall, the interior guest is predicted to be more strongly bound to the cage by roughly 40—50 kcal/mol.

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