

Pillarplexes: A Metal–Organic Class of Supramolecular Hosts

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S Supporting Information

ABSTRACT: Novel octanuclear NHC complexes of gold(I) and silver(I) form metallocavitan structures with very defined tubular cavities and are able to selectively host linear molecules, exemplarily demonstrating 1,8-diaminooctane as a model guest molecule. The solubility of the host-compounds is easily adjusted by simple anion exchange reactions so that the compounds can be made soluble in water wherein they exhibit a high longtime stability. The gold(I) complex is emissive in aqueous solutions, which enables a determination of the binding constant to the diamine via luminescence quenching. The host–guest interaction was further investigated by isothermal titration calorimetry, NMR spectroscopy, and X-ray crystallography.

Host–guest chemistry is one of the most versatile and applied fields of research utilizing supramolecular interactions.¹ The vast majority of compounds used for this purpose are macrocyclic organic substances, among them tubular-shaped pillar[*n*]arenes and cucurbit[*n*]uriles (Figure 1).² Especially pillar[*n*]arenes have emerged as powerful host-

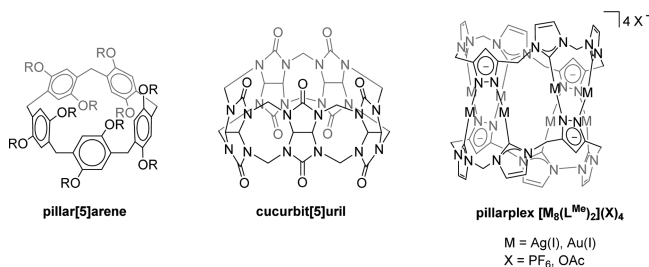


Figure 1. General structures of tubular cavitan compounds capable of noncovalent host–guest interactions: pillar[5]arene,^{2c} cucurbit[5]uril,⁵ and the pillarplex $[M_8(L^{Me})_2](X)_4$.

molecules due to their ready availability and variability, enabling a multitude of applications such as molecular sensing, self-assembly, or rotaxane synthesis.³ However, a general disadvantage of many of these organic cavitan systems is their limited postsynthetic modifiability.⁴

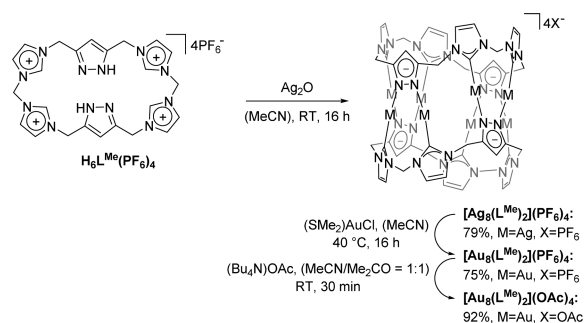
In contrast, metal complexes have hardly been used for this kind of supramolecular chemistry, as the required cavitan structures are not trivially feasible via classical coordination chemistry. Additionally, paramagnetic metal centers, often with unpredictable interactions in multimetallic clusters or sensitivity toward air and moisture, drastically limit their application as

competitive hosts.⁶ Nevertheless, there have been several reports on metallocavitan, -cycles, and -cages that were used for supramolecular purposes.^{6,7}

Organometallic host-systems based on coinage metal complexes could in principal overcome many of these problems. They exhibit crucial advantages such as potential intrinsic photoluminescent properties, straightforward syntheses, and the possibility of postsynthetic modifications while exhibiting a high stability against air and moisture.⁸ We hypothesized that our recently introduced class of calix[4]imidazolylidene[2]-pyrazolates in combination with coordinated silver(I) or gold(I) centers should form complexes consisting of multiple ligands, which are bridged by metal centers since the two tetradentate coordination pockets are not optimal for linear coordination. Ideally, a complex of two oppositely coordinating ligands was envisioned, creating very defined cavitan structures comparable to that of pillar[*n*]arenes.⁹ Hence, we herein report the synthesis of a novel class of macrocyclic, coinage-metal based metallocavitan complexes and their unique properties as photoluminescent host-molecules with an easily tunable solubility and an exclusive selectivity for linear over six-membered aromatic (e.g., phenyl, pyridyl) molecules.

The reaction of $H_6L^{Me}(PF_6)_4$ with an excess of silver(I) oxide in acetonitrile cleanly affords the octanuclear complex $[Ag_8(L^{Me})_2](PF_6)_4$ in high yields after workup (Scheme 1). Nuclear magnetic resonance spectroscopy suggests a highly symmetric coordination motif where each metal is coordinated linearly by two ligands as was also found for similar NHC ligand motifs.¹⁰ The results obtained from mass spectrometry and

Scheme 1. Synthesis of $[Ag_8(L^{Me})_2](PF_6)_4$, Transmetalation with $(SMe_2)AuCl$, and Subsequent Anion Exchange with $(Bu_4N)OAc$ To Afford $[Au_8(L^{Me})_2](PF_6)_4$ and $[Au_8(L^{Me})_2](OAc)_4$



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elemental analysis confirm the composition of an M_8L_2 -type compound with four hexafluorophosphate anions. Subsequently, we synthesized the gold(I) complex $[Au_8(L^{Me})_2](PF_6)_4$ via transmetalation employing $(SMe_2)AuCl$ as precursor. $[Au_8(L^{Me})_2](PF_6)_4$ is emissive as a solid in the blue region of the visible spectrum with an emission wavelength of $\lambda_{max} = 430$ nm and quantum yields of 40% ($\lambda_{ex} = 335$ nm), which are comparable to reported photoluminescent gold(I) NHC complexes (see SI).^{10d,11} The tubular structure of the complex should in principle be of perfect size to host small or linear molecules, respectively. Thus, we performed NMR titration experiments with 1,8-diaminooctane as a model guest. When following the addition of aliquots of $[Au_8(L^{Me})_2](PF_6)_4$ in CD_3CN to a solution of 1,8-diaminooctane in CD_3CN via 1H NMR spectroscopy a strong highfield shift of the CH_2 -protons of the amine was observed, depending on the amount of host added (Figure 2). To determine the type of host-guest interaction we performed a Job-Plot analysis, which resulted in an 1:1 stoichiometry of $[Au_8(L^{Me})_2](PF_6)_4$ and 1,8-diaminooctane (see SI).

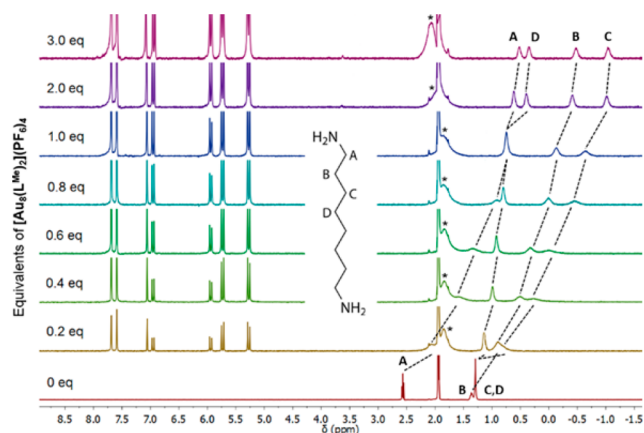


Figure 2. 1H NMR titration (400 MHz, 298 K) of $[Au_8(L^{Me})_2](PF_6)_4$ in CD_3CN into a 7 mM solution of 1,8-diaminooctane in CD_3CN . The asterisk marks the water signal. The signals between 5 and 8 ppm are assigned to $[Au_8(L^{Me})_2](PF_6)_4$ (see SI). Electronic shielding by the cavity of $[Au_8(L^{Me})_2](PF_6)_4$ (host) leads to a highfield shift of the protons (A–D) of 1,8-diaminooctane (guest). The assignment of the protons of 1,8-diaminooctane was verified by 2D-COSY NMR spectroscopy at -40 °C (see SI). A K_d value of 24.0 ± 5.4 μM was calculated.

The NMR titration experiments allowed for the calculation of the dissociation constant via line fitting of the guest's signal positions at varying amounts of $[Au_8(L^{Me})_2](PF_6)_4$ present in the solution (see SI). A value of $K_d = 24.0 \pm 5.4$ μM was determined, comparable to that observed for the analogous guest with a functionalized pillar[5]arene in a 1:1 mixture of MeCN/ H_2O .^{4a} Upon crystallization of $[Au_8(L^{Me})_2](PF_6)_4$ in the presence of 1,8-diaminooctane single crystals of the supramolecular complex suitable for X-ray measurements were obtained (Figure 3, left). The expected eight gold atoms are situated between two of the pyrazolato/imidazolylidene hybrid ligands in a way that the metal ions are bound to one nitrogen and one carbon donor atom each. This leads to a staggered arrangement of the two ligand molecules by 90° relative to each other. The structural prerequisite of the ligand leads to several close Au–Au contacts between 2.987(1) and 3.005(1) Å, that are all well below the sum of the van der Waals radii of 3.80 Å.¹² Due

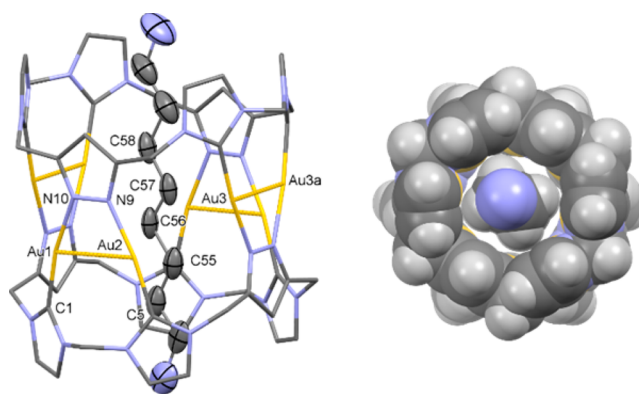


Figure 3. Left: Solid-state molecular structure of the cation of $[Au_8(L^{Me})_2](PF_6)_4$ shown in capped sticks with one molecule 1,8-diaminooctane cocrystallized within the cavity. Ellipsoids are shown at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity. Right: Top view of the host-guest complex in the space filling model (N-bound H atoms were not refined). Counterions and solvent molecules are omitted for clarity. Selected geometrical parameters: Au1–Au2 3.004(1) Å, Au3–Au3a 2.990(1) Å, C1–Au1 1.97(2) Å, C5–Au2 1.99(2) Å, N10–Au1 2.08(2) Å, N9–Au2 2.02(1) Å, C1–Au1–N10 169.2(7)°, C5–Au2–N9 171.6(7)°, C55–C56–C57–C58 180°.

to the structural resemblance to the well-established class of organic pillar[n]arenes in terms of their cavity-shape and host-guest interaction properties we chose to name the M_8L_2 -type compounds “pillarplexes”.^{2c} The overall structure of the cationic complex resembles a tube with a slight constriction in the plane of the gold atoms in a hyperboloid fashion. The diamine guest can be envisioned as possessing a stretched all anti conformation, which is necessary to penetrate the cavity (Figure 3). This observation can be rationalized by visualizing the space-filling model of the supramolecular assembly (Figure 3, right).

The height of the metallocavitand amounts to approximately 11.7 Å, its inner diameter to 4.3 Å. Hence, the penetrable cavity is significantly longer, but narrower than that of pillar[5]arene (height 7.8 Å, inner diameter 4.7 Å)¹³ suggesting a higher selectivity toward linear molecules. Indeed, upon addition of 1,1'-dioctadecyl viologen bromide to a solution of $[Au_8(L^{Me})_2](PF_6)_4$ the signal position of the protons bound to the pyridinium rings do not alter their positions in the 1H NMR spectrum, whereas the peaks of the protons of the alkyl chains are strongly highfield shifted (see SI). Hence, it can be concluded that the pyridyl moieties of viologens are not able to access the cavity of $[Au_8(L^{Me})_2](PF_6)_4$ in contrast to that of pillar[5]arene or cucurbit[6]uril.^{2c,5} Upon addition of *p*-phenylenediamine to a solution of $[Au_8(L^{Me})_2](PF_6)_4$ no highfield shift of the potential guest's aromatic protons were observed either, further indicating that six-membered arenes are size-excluded by the cavity of the metallocavitand (see SI). These results are in accordance to the solid state structure, proving that the pillarplex has a crucially smaller cavity compared to its organic congeners. The fact that the pillarplexes exhibit an exclusive selectivity for linear over six-membered aromatic molecules is unique, as all of the organic host-compounds include either both (pillar[n]arenes, cucurbit[n]urils ($n \geq 6$) and cyclodextrins) or neither of both (cucurbit[5]uril, see Table 1).

To exploit the facile tunability of the solubility of the Au_8 complex via simple anion exchange we substituted the hexafluorophosphates with acetate anions resulting in the highly water-soluble (~ 1 g mL^{-1}) complex $[Au_8(L^{Me})_2](OAc)_4$

Table 1. Comparison of the Cavity Dimensions of Different Host-Compounds and Suitable Guest Molecules for Each Class

	cucurbit[5]uril ¹⁴	pillarplex [Au ₈ (L ^{Me}) ₂](PF ₆) ₄	pillar[5]arene ¹³	α -cyclodextrine ¹⁵	cucurbit[6]uril ¹⁴
shape	pumpkin	hourglass	pillar	bucket	pumpkin
inner diameter (Å)	4.4 (portal: 2.4)	4.3 (portal: 4.8)	4.7	4.7	5.8 (portal: 3.9)
height (Å)	9.1	11.7	7.8	7.9	9.1
includable guests (<i>n</i> -alkyl or aryl ^a)		<i>n</i> -alkyl	<i>n</i> -alkyl, aryl	<i>n</i> -alkyl, aryl	<i>n</i> -alkyl, aryl

^aAryl in this context represents molecules containing six-membered, aromatic substituents, e.g., phenyl and pyridyl.

(Scheme 1). Similar to its hexafluorophosphate congener, the acetate complex is photoluminescent in the blue region as a solid with an emission wavelength of $\lambda_{\max} = 455$ nm and a quantum yield of 40% ($\lambda_{\text{ex}} = 335$ nm). Subsequently, we set out to investigate the host–guest behavior of the pillarplex in water. Upon titration of aliquots of a solution of [Au₈(L^{Me})₂](OAc)₄ in D₂O to a solution of 1,8-diaminooctane in D₂O a set of strongly highfield shifted signals emerges (see SI). In contrast to [Au₈(L^{Me})₂](PF₆)₄ in CD₃CN the exchange in D₂O is slow compared to the NMR time scale indicating a tighter binding of the guest in the case of [Au₈(L^{Me})₂](OAc)₄. Likewise, the stoichiometry of the interaction in aqueous solution is 1:1 as determined by a NMR-spectroscopic Job–Plot titration in D₂O (see SI).

For a quantitative determination of the binding constant we made use of the intrinsic photoluminescent properties of the metallocavitand. Whereas no photoluminescence was observed for [Au₈(L^{Me})₂](PF₆)₄ in acetonitrile solution, most likely due to quenching by the solvent, a distinct emission peak at $\lambda_{\max} = 445$ nm is found for [Au₈(L^{Me})₂](OAc)₄ in water. Inspired by reports of fluorescence quenching experiments with functionalized pillar[5]arenes and linear amines by Stoddart et al.^{4a} we performed similar experiments with [Au₈(L^{Me})₂](OAc)₄ and were able to observe a decline of the emission signal depending on the amount of 1,8-diaminooctane present in solution (Figure 4). The decrease was of enough significance to perform a

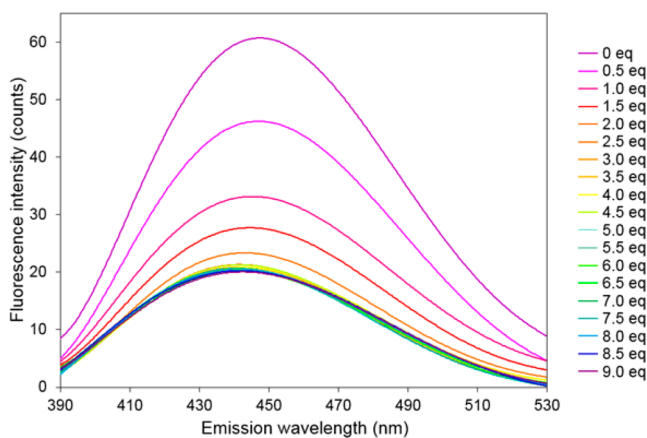


Figure 4. Luminescence quenching experiment (142 μM , H₂O, $\lambda_{\text{ex}} = 335$ nm, $\lambda_{\text{em}} = 445$ nm). The luminescence of [Au₈(L^{Me})₂](OAc)₄ was recorded in solutions with different amounts of 1,8-diaminooctane present. A K_{d} value of $11.9 \pm 1.9 \mu\text{M}$ was calculated for the process.

quantitative analysis. The determined dissociation constant of $11.9 \pm 1.9 \mu\text{M}$ after line fitting of the data is in good accordance with the results obtained for [Au₈(L^{Me})₂](PF₆)₄. The K_{d} is approximately half of the value, which can be explained by the different polarities of the solvents and the hydrophobicity of the alkyl chain of 1,8-diaminooctane that is more pronounced in

aqueous than in acetonitrile solution suggesting a stronger propensity for the guest to diffuse into the host's cavity.

To verify the results obtained from the luminescence quenching experiment we conducted host–guest titrations followed by isothermal titration calorimetric analysis (Figure 5). The stoichiometry of the interaction between

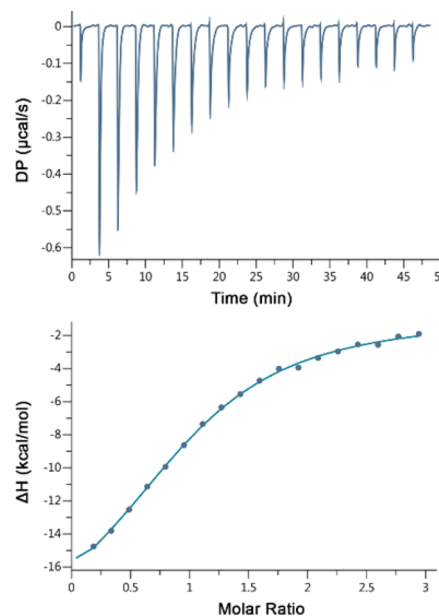


Figure 5. Microcalorimetric titration of [Au₈(L^{Me})₂](OAc)₄ with 1,8-diaminooctane in water at 25 °C. Top: Raw data for the 19 sequential injections (2 μL per injection) of a solution of 1,8-diaminooctane (200 μM) into a solution of [Au₈(L^{Me})₂](OAc)₄ (30 μM). Bottom: “Net” heat effects obtained by subtracting the dilution heat from the reaction heat, which was fitted by using the “one set of sites” binding model [$\chi^2 = 0.015 \text{ kcal}^2 \text{ mol}^{-2}$; $N(\text{sites}) = 0.986 \pm 0.017$; $K_{\text{d}} = 7.45 \pm 0.36 \mu\text{M}$; $\Delta G = -7.0 \text{ kcal mol}^{-1}$; $\Delta H = -20.2 \pm 0.4 \text{ kcal mol}^{-1}$; $\Delta S = -44.3 \text{ cal mol}^{-1}$].

[Au₈(L^{Me})₂](OAc)₄ and 1,8-diaminooctane was confirmed to be 1:1 as previously determined via the Job–Plot analysis. The uptake of the linear amine is solely enthalpy-driven ($\Delta H = -20.2 \pm 0.4 \text{ kcal mol}^{-1}$) as the entropic changes are not in favor of the formation of the supramolecular complex ($\Delta S = -44.3 \text{ cal mol}^{-1}$). The main contributions to the enthalpic term in this case are the occurrence of suitable noncovalent contacts between host and guest as well as the reduction of unfavorable interactions of the alkyl chain in aqueous solution upon diffusion into the cavity of [Au₈(L^{Me})₂](OAc)₄. The negative entropic term is mainly caused by the required all-anti alignment of the alkyl chain that is a crucial prerequisite for the formation of the host–guest complex (see Figure 3). For the dissociation constant a value of $K_{\text{d}} = 7.5 \pm 0.4 \mu\text{M}$ was determined, which is in good accordance with the result obtained by the luminescence quenching experiment.

In conclusion we have established a novel class of organo-metallic host-compounds that are highly selective for linear molecules. Additionally, the solubility of these metallocavitand complexes is easily tunable by simple anion exchange reactions so that these compounds can in principal be applied for supramolecular recognition in a plethora of solvents. The behavior of the octanuclear gold(I) pillarplexes toward 1,8-diaminooctane as model guest substance was investigated for $[\text{Au}_8(\text{L}^{\text{Me}})_2](\text{PF}_6)_4$ in acetonitrile and for $[\text{Au}_8(\text{L}^{\text{Me}})_2](\text{OAc})_4$ in water. The acetate complex was found to be emissive in aqueous solutions, which enabled the determination of dissociation constants via luminescence quenching experiments that could be confirmed by ITC experiments. The obtained data suggest higher affinities toward the guest molecule than those determined for the related organic pillar[5]arenes.^{4a} Based on the results we are currently aiming toward a widespread spectrum of further modifications and applications of these tremendously versatile and stable metallocavitands.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08571.

Experimental details and spectroscopic and crystallographic data (PDF)
CCDC 1498661 (CIF)

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Notes

The authors declare no competing financial interest.

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