## Supporting Information

# Influence of Size, Shape, Heteroatom Content and Dispersive Contributions on Guest Binding in a Coordination Cage

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## **Contents:**

1	Gen	eral Information	2
2	<sup>1</sup> H N	IMR spectroscopy	2
3	ESI	- HR mass spectrometry	9
4	X-ra	y data	17
	4.1	Crystal structure of [2Cl+DABCO@Pd <sub>4</sub> L <sub>8</sub> ] <sup>6+</sup>	18
	4.2	Cavity volumes and calculation of packing coefficients (PC)	19
5	Con	nputational Details	20
6	Refe	erences	22

#### **1** General Information

Synthesis of ligand L and the interpenetrated coordination cage  $[2Cl@Pd_4L_8]$  were performed according to a previously reported protocol.<sup>[1]</sup>

NMR measurements were conducted on an Advance-400 instrument from Bruker or a 500 MHz instrument from Varian. ESI mass spectrometric measurements were performed on a maXis instrument from Bruker or an LQT Orbitrap FT spectrometer from Thermo Electron.

## 2 <sup>1</sup>H NMR spectroscopy

#### **General procedure**

To a solution of the halide-activated cage (500  $\mu$ L, 0.30 mM, CD<sub>3</sub>CN) a solution of the neutral guest compound (CD<sub>3</sub>CN, 70 mM, 2-100 eq.) was added. The <sup>1</sup>H NMR spectra were recorded after several days at 23 °C (fixed temperature in an air-conditioned room) to allow full equilibration of the reaction mixture.

NMR data interpretation:

All spectra were referenced to the solvent signal, phase- and baseline-corrected in the usual way. All host-guest systems were found to exhibit slow exchange on the NMR timescale and the association constants could be directly determined from the integral intensities of the free/filled host species in the equilibrated mixture, given the starting concentrations of host and added guest.

The NC $\underline{H}_2$ -signal of the hexyl chain at 4.21 ppm was used as an internal reference for signal integration since no other signals are in its vicinity and it did not show any reaction to the presence and encapsulation of the guest.



For determining the association constant, integral intensities of several protons that point inside the central cavity of the double-cage, in particular proton  $H_{g'}$  and  $H_{a'}$ , were considered. Depending on the guest, these signals were found to undergo characteristic up- or downfield shifts. In cases where signals of encapsulated guests came close to signals of the host-guest complex, COSY and NOESY NMR experiments were employed for an unambiguous signal assignment.



Figure SI 1<sup>-1</sup>H NMR spectra (500 MHz, 296 K, CD<sub>3</sub>CN) of a) empty host [2Cl@Pd<sub>4</sub>L<sub>8</sub>] and different host-guest complexes: [X+2Cl@Pd<sub>4</sub>L<sub>8</sub>] with X= b) cyclopentane c) cyclohexane (8.7 eq.), d) cycloheptane (8.7 eq.), e) cyclooctane (8.7 eq.) f) benzene (8.7 eq.), g) toluene (87 eq.) h) phenol (8.7 eq.), i) norbornadiene (8.7 eq.) j) norbornene (8.7 eq.) and k) norbornane (8.7 eq.). Upon addition of an excess of neutral guest molecule, a new set of signals can be found in the <sup>1</sup>H NMR spectra, which indicates encapsulation inside the central pocket of the interpenetrated coordination cage.



**Figure SI 2**<sup>1</sup>H NMR spectra (500 MHz, 296 K, CD<sub>3</sub>CN) of a) empty host [2Cl@Pd<sub>4</sub>L<sub>8</sub>] and different host-guest complexes: [X+2Cl@Pd<sub>4</sub>L<sub>8</sub>] with X= b) bromocyclopentane c) chlorocyclopentane (8.7 eq.), d) 2-methylthiophene (8.7 eq.), e) thiophene (8.7 eq.), f) tetrahydrothiophene (8.7 eq.), g) furane (8.7 eq.), h) tetrahydrofurane (8.7 eq.), i) cyclobutanone (8.7 eq.), j) cyclopentanone (8.7 eq.), k) cyclohexanone (8.7 eq.) l) 1.4 cyclohexadione (8.7 eq.) and m) cycloheptanone (8.7 eq.). Cyclobutanone does not bind.



**Figure SI 3**<sup>1</sup>H NMR spectra (500 MHz, 296 K, CD<sub>3</sub>CN) of a) empty host [Cl@Pd\_L<sub>8</sub>] and after the addition of different neutral guest molecules: b) tetrahydropyrane (18.9 eq.) c) 1;3 dioxane (8.7 eq.), d) 1,4 dioxane (1.8 eq.), e) piperazine (1.8 eq.), f) DABCO (1.8 eq.), g) pyrazine (1.8 eq.), h) 2,3 dimethylpyrazine (87 eq.), i) 2,5 dimethylpyrazine (87 eq.), and j) pyridine (8.7 eq). Addition of guest molecules a-g and j results in the formation of the host guest complex [X+Cl@Pd₄Ls]. In contrast, the neutral guest molecules 2,5dimethylpyrazine and 2,3-dimethylpyrazine are not encapsulated inside the interpenetrated coordination cage, due to the steric bulk of the methyl groups.



hexylthiophene (18.9 eq.), d) adamantane (18.9 eq.), e) adamantone (18.9 eq.), f) azulene (18.9 eq.), g) coumarine (18.9 eq.), h) hexafluorobenzene (18.9 eq.), i) naphthalene **Figure SI 4**<sup>1</sup> H NMR spectra (400 MHz, 296 K, CD<sub>3</sub>CN) of [Cl@Pd<sub>4</sub>L<sub>8</sub>] and after the addition of various neutral guest molecules: a) hexane (18.9 eq.), b) ferrocene (18.9 eq.), c) 3-(18.9 eq.), j) isooxazol and k) butyrolactone (87 eq.) and I) decalin (mixture of cis and trans isomer, 18.9 eq.). No change in chemical shift could be observed after the addition of the neutral guest molecules and an equilibration time of 7-14 days. The shifting of proton signal f, is due to association of the guest molecule to the interpenetrated coordination cage from the outside.



Figure SI 5<sup>-1</sup>H NMR spectra (500 MHz, 296 K, CD<sub>3</sub>CN) of [Cl@Pd<sub>4</sub>L<sub>8</sub>] and after the addition of various neutral guest molecules: a) chlorobenzene (8.7 eq.) b) benzoquinone (8.7 eq.), c) 2,3-dimethylpyrazine (87 eq.), d) 2,5-dimethylpyrazine (18.9 eq.), e) trans 1,3 pentadiene (8.7 eq.), f) pyrrole (8.7 eq.), g) pyrazole (8.7 eq.), h) imidazole (8.7 eq.), i) 1-methylimidazole (8.7 eq.), j) pyrrolidine (8.7 eq.) and k) ethylenediamine (8.7 eq.). No evidence of encapsulation of the neutral guests a-g was found after the equilibration time of 14 days, confirmed by no change in chemical shift in the <sup>1</sup>H NMR spectrum. In contrast, addition of neutral guest h-j resulted in the partial decomplexation of the interpenetrated coordination cage [Cl@Pd4L8] and the release of free ligand L (illustrated in the <sup>1</sup>H NMR spectra in blue). The change in chemical shift of proton signal f, is due to association of the guest molecule from the outside of the interpenetrated coordination cage.

**Table SI 1** Experimental and computed binding free enthalpies, volumes and packing coefficients for all tested guests. a) volume of the neutral guest was gained from Spartan via EDF2/6-31G\* computation b) The packing coefficient (PC) was calculated as the quotient of  $V_{guest}/V_{cavity}$ \*100. The volume of the cavity was calculated using VOIDOO (details see below under 4.2).

				ΔG <sup>296</sup> <sub>exp.</sub> /	$\Delta G_{calc.}$
Guest	M/g∙mol	V/A <sup>3a</sup>	PC/% <sup>b</sup>	kJ∙mol <sup>−1</sup>	kJ∙mol <sup>-1</sup>
1,3 Dioxane	88.1	93.2	47.2	-12.3	
1,4 cyclohexadione	117.4	117.5	58.4	-8.8	
1,4 Dioxan	88.1	93.8	47.3	-25.4	
2-methylthiophene	98.2	104.9	52.2	-10.8	
benzene	78.1	99.0	49.5	-17.4	-34.9
bromocyclopentane	149.0	113.6	56.8	-11.5	
chlorocyclopentane	104.6	109.2	54.2	-12.6	
cycloheptane	98.2	129.5	64.5	-19.3	
cycloheptanone	112.2	132.2	65.8	-13.6	
cyclohexane	80.7	111.8	55.9	-20.2	-18.9
cyclohexanone	98.2	114.5	57.1	-13.4	
cyclooctane	112.2	147.2	73.6	-15.6	
cyclopentane	70.1	95.2	47.5	-12.8	-19.5
cyclopentanone	84.1	97.8	48.7	-10.5	
DABCO	112.2	126.4	63.8	-27.1	-31.0
furane	68.1	77.7	38.9	-6.1	1.4
norbornadiene	92.1	113.2	56.2	-20.2	-28.4
norbornane	96.2	120.1	60.1	-19.9	
norbornene	94.2	116.3	58.2	-19.2	
phenol	94.1	106.1	53.0	-12.8	-13.1
piperazine	86.1	100.1	50.7	-22.8	
pyrazine	80.1	86.3	43.5	-21.8	
pyridine	79.1	92.6	46.5	-12.3	
tetrahydopyrane	86.1	102.8	51.6	-17.2	
tetrahydrofurane	72.1	86.0	43.1	-14.3	
tetrahydrothiophene	88.2	95.6	47.6	-16,9	
thiophene	84.1	86.5	43.1	-13.4	
toluene	92.1	117.2	58.4	-7.5	

**Table SI 2** Comparison of Gibbs free energies  $\Delta G$  (kJ·mol<sup>-1</sup>) for binding of the guests benzene and cyclohexane from solvents acetonitrile and acetone. Samples were equilibrated at 296 K over several days in sealed NMR tubes. Differences between upper/lower and left/right values, respectively, are printed as bold numbers.

	benzene		cyclohexane
acetonitrile	-17.5	-2.8	-20.3
	13.1	-2.1	15.2
acetone	-4.4	-0.7	-5.1

Based on the assumption that solvent release from the pocket plays a minor role and the host-guest contribution to the free enthalpy of binding is largely independent of the solvent, differences in  $\Delta G^{296}$  between encapsulation from different solvents represent differences in desolvation contributions. The data shows that both benzene and cyclohexane are more easily encapsulated from acetonitrile than from acetone, owing to the better match in polarity between the neutral guests and the latter solvent. Double mutant cycle analysis indicates that the formal transfer of apolar cyclohexane (Reichardt polarity index = 0.006; see: Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, 3rd ed., 2003) from acetonitrile (0.460) to acetone (0.355) is energetically favoured over the transfer of more polar benzene (0.111) between the same solvents.

#### 3 ESI – HR mass spectrometry



Figure SI 6 ESI mass spectrum of [2Cl+norbornane@Pd<sub>4</sub>L<sub>8</sub>].







Figure SI 8 ESI mass spectrum of [2Cl+norbornadiene@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 9 ESI mass spectrum of [2Cl+phenol@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 10 ESI mass spectrum of [2Cl+toluene@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* were assigned to  $[2Cl@Pd_4L_8]$ .



Figure SI 11 ESI mass spectrum of [2Cl+benzene@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* could be assigned to [2Cl@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 12 ESI mass spectrum of [2Cl+cyclooctane@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 13 ESI mass spectrum of [2Cl+cycloheptane@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 14 ESI mass spectrum of [2Cl+cyclohexane@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 15 ESI mass spectrum of [2Cl+cylopentane@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* could be assigned to  $[2Cl@Pd_4L_8]$ .







**Figure SI 17** ESI mass spectrum of [2Cl+cyclohexanone@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* could be assigned to  $[2Cl@Pd_4L_8]$ .



Figure SI 18 ESI mass spectrum of  $[2Cl+cyclopentanone@Pd_4L_8]$ . Signals highlighted with \* could be assigned to  $[2Cl@Pd_4L_8]$ .



Figure SI 19 ESI mass spectrum of [2Cl+tetrahydrofuran@Pd<sub>4</sub>L<sub>8</sub>].



**Figure SI 20** ESI mass spectrum of [2Cl+tetrahydrothiophene@Pd<sub>4</sub>L<sub>8</sub>]. \*:  $[Pd_4L_8]$  cage; • Encapsulation of the oxidation product of tetrahydrothiophene C<sub>4</sub>H<sub>8</sub>SO.



Figure SI 21 ESI mass spectrum of [2Cl+thiophene@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* correspond to  $[2Cl@Pd_4L_8]$ .



**Figure SI 22** ESI mass spectrum of [2Cl+2-methylthiophene@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* could be assigned to [2Cl@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 23 ESI mass spectrum of [2Cl+chlorocyclopentane@Pd<sub>4</sub>L<sub>8</sub>]; \* = [2Cl@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 24 ESI mass spectrum of [2Cl+bromocyclopentane@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* correspond to [2Cl@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 25 ESI mass spectrum of  $[2Cl+pyridine@Pd_4L_8]$ . Signals highlighted with \* correspond to  $[2Cl@Pd_4L_8]$ .



Figure SI 26 ESI mass spectrum of [2Cl+pyrazine@Pd<sub>4</sub>L<sub>8</sub>]. Signals highlighted with \* correspond to [2Cl@Pd<sub>4</sub>L<sub>8</sub>].











Figure SI 29 ESI mass spectrum of [2Cl+1,3-dioxane@Pd<sub>4</sub>L<sub>8</sub>] (\*= [2Cl@Pd<sub>4</sub>L<sub>8</sub>].



Figure SI 30 ESI mass spectrum of [2Cl+tetrahydropyran@Pd<sub>4</sub>L<sub>8</sub>].

## 4 X-ray data

### 4.1 Crystal structure of [2Cl+DABCO@Pd<sub>4</sub>L<sub>8</sub>]<sup>6+</sup>

Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of ethanol into a 0.3 mM solution of the interpenetrated coordination cage in acetonitrile.

X-ray data were collected at 80(2) K at the DESY beamline P11<sup>[2]</sup> using a radiation wavelength of 0.5636 Å. Data integration and reduction were undertaken using the XDS.<sup>[3]</sup> The structure was solved by intrinsic phasing/direct methods using SHELXT<sup>[4]</sup> and refined with SHELXL<sup>[5]</sup> using 24 cpu cores for full-matrix least-squares routines on F<sup>2</sup> and ShelXle<sup>[6]</sup> as a graphical user interface. Hydrogen atoms were included as invariants at geometrically estimated positions. Techniques commonly applied for macromolecular structures were employed to generate a molecular model and increase robustness of the refinement. Stereochemical restraints for the acridone (residue class ACR) ligands and DABCO

(residue class DAB) guest of the structure were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1.2-distances (DFIX) and 1.3-distances (DANG), as well as restraints for planar groups (FLAT). Both BF<sub>4</sub><sup>-</sup> counter ions sit on a special position and were treated with similarity restraints (SADI) for 1.2 and 1.3 distances. All non-hydrogen atoms other than Boron atoms (of the BF4- counterions) were refined anisotropically. The refinement of ADP's for non-hydrogen atoms was enabled by using the rigid bond restraint (RIGU) in the SHELXL<sup>[5]</sup> program. SIMU restraints were additionally employed. Due to high flexibility of terminal hexyl chains, non-crystallographic symmetry (NCS) restraints for similarity of 1.4 distances in between both acridone (ACR) ligands were employed. SADI restraints were employed for to ensure similarity in between 1.2 distances of hexyl chain carbon atoms.



**Figure SI 31** The asymmetric unit of the  $[2CI+DABCO@Pd_4L_8]^{6+}$ , with all non-hydrogen atoms shown as ellipsoids at the 50% probability level. <u>*Color scheme:*</u> C: gray; N: blue; O: red; Cl: yellow; Pd: orange, H: white, F: green, B: salmon.

Table SI 3 Crystal data and structure	e refinement for	[2Cl+DABCO@Pd₄L <sub>8</sub> ] <sup>6+</sup>
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CCDC number	1557039
Identification code	sl324a_sq
Empirical formula	$C_{270}H_{228}B_3CI_2F_{12}IN_{26}O_8Pd_4\\$
Formula weight	4848.60
Temperature	80(2) K
Wavelength	0.5636 Å
Crystal system	tetragonal
Space group	P4/ncc
	a = 22.064(3) Å; α= 90°.
Unit cell dimensions	b = 22.064(3) Å; β= 90°.
	c = 62.075(12) Å; γ = 90°.
Volume	30219(10) Å <sup>3</sup>

Z	4
Density (calculated)	1.066 Mg/m <sup>3</sup>
Absorption coefficient	0.224 mm <sup>-1</sup>
F(000)	9952
Crystal size	0.200 x 0.200 x 0.020 mm <sup>3</sup>
Theta range for data collection	0.520 to 17.631°.
Index ranges	-23<=h<=23, -23<=k<=23, -66<=l<=66
Reflections collected	249159
Independent reflections	9732 [R(int) = 0.0622]
Completeness to theta = 17.631°	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	9732 / 1644 / 790
Goodness-of-fit on $F^2$	1.632
Final R indices [I>2sigma(I)]	R1 = 0.0950, wR2 = 0.3564
R indices (all data)	R1 = 0.1132, wR2 = 0.3840
Largest diff. peak and hole	1.664 and -0.790 e.Å <sup>-3</sup>

#### 4.2 Cavity volumes and calculation of packing coefficients (PC)

Crystallographically determined structure of  $[2Cl+DABCO@Pd_4L_8]^{6+}$  was symmetry expanded and the DABCO guests molecule as well as Chloride counter ions were removed. Resulting inner cavities were calculated with VOIDOO,<sup>[7]</sup> using a primary grid and plot grid spacing of 0.1 Å and 40 cycles of volume refinement with the default water size probe radius of 1.4 Å. Molecular visualization was done using PyMol.<sup>[8]</sup>

For the benzene containing cage a volume of 201.66  $Å^3$  was calculated, while for the DABCO structure a volume of 200.84  $Å^3$  was obtained. Thus, the averaged volume of the central cavity is 201.25  $Å^3$ . This value was used to calculate the packing coefficient in Table SI 1.



**Figure SI 32** Visualization of the central cavity of the interpenetrated coordination cage (based on [2Cl+DABCO@Pd<sub>4</sub>L<sub>8</sub>]). The cavity boundaries of the central pocket of the interpenetrated coordination structure are depicted as blue solids. <u>*Color scheme:*</u> C: gray; N: blue; O: red; Cl: yellow; Pd: orange, H: white.

#### 5 Computational Details

The host, guest and combined host-guest geometries were optimized with RI-BP86,<sup>9,10</sup> the def2-SVP<sup>11,12</sup> orbital basis and the corresponding J-basis<sup>13</sup> using the TURBOMOLE package.<sup>14</sup> For the Pd atoms the ECP-28MWB pseudopotential<sup>15</sup> was used. The host structure was taken from X-ray crystallography results at a distance of 10.16 Å between the palladium atoms. To lower the number of atoms and make the system computationally more feasible the host was reduced to the pocket region. This was done by cutting out the top and bottom palladium-pyridine planes and saturating with hydrogens as shown in Fig. SI 33. Only the hydrogens were optimized. The guest molecules were manually inserted into the pocket. Different conformations were used as starting structures for optimizations whereby the host was kept fixed. Out of this conformational sampling, the most stable structures were selected.

For the obtained minimum structures single point DF-SCS-LMP2<sup>16-19</sup> calculations were performed. The Dunning cc-pVTZ<sup>20</sup> orbital basis set was used in combination with the cc-pVTZ-PP<sup>21</sup> basis and ECP28MDF<sup>21</sup> pseudopotential for Pd (this basis will be referred to as VTZ). The density fitting basis used were the corresponding defaults (for the cc-pVTZ<sup>22,23</sup>) except for calculations with Pd where the JKFIT and MP2FIT def2-TZVPP<sup>24,25</sup> basis set was used. The orbitals were localized by the Pipek-Mezey scheme.<sup>26</sup> The corresponding orbital domains were determined with a Boughton-Pulay criterion<sup>27</sup> at a threshold of 0.985. To speed up the calculations we made use of the multipole-approximation<sup>28</sup> for very-distant pairs (r=10 Bohr) and local fitting.<sup>16</sup> The parameters were chosen by taking test calculations of the host pocket and increasing the distance parameter between 8 and 12 Bohr. All calculations were carried out with a development version of Molpro2015.1.<sup>29</sup>

According to the locality of the orbitals we were able to build fragments (guest plus host) to determine the dispersion contributions<sup>30</sup> at the SCS-LMP2/VTZ level of theory, stabilizing the guest molecules.

To build a bridge between theory and experiment we computed the binding affinities. A computational protocol was devised, making use of the aforementioned geometries. Solvent effects (acetonitrile) were included by D-COSMO-RS<sup>31</sup> at the RI-BP86/def2-TZVP<sup>32-34</sup> level in a supermolecular approach(Turbomole) -  $\Delta E_{solv}$ . Ambient pressure (1 bar) and temperature (298.15 K) were used in all solvent corrections and thermodynamic corrections. Thermochemistry corrections were computed with the RRHO-approach.<sup>35</sup> The frequencies were computed at the RI-BP86/def2-SVP level for guests@host and a truncated Hessian containing only the guest molecules' 2nd derivatives was weighted and diagonalized. Those values are compared to the free guest-molecule, building  $\Delta E_{ZPVE}$ ,  $\Delta H$ (0->T) and  $\Delta S$ . Furthermore, a correction to the solvation energies was added, accounting for the missing translational degrees of freedom in solution, based on the Ardura *et al.* equation for bimolecular reactions<sup>36</sup> ( $\Delta G_{trans}$ ). Final electronic energies were calculated at the SCS-LMP2/cc-pVTZ level of theory.

The total free energy of binding was then calculated as:

 $\Delta G = \Delta E(SCS-LMP2/VTZ) + \Delta E_{solv} + \Delta E_{ZPVE} + \Delta H(0 \rightarrow T) - T\Delta S + \Delta G_{trans}$ 



**Figure SI 33** right: double cage structure, left: model used for the cage system in the calculations. The ligands were truncated (C-C bonds replaced by C-H) and the bottom and lower planes were removed. The chlorides in the inner pockets were kept in order to neutralize part of the charge.



**Figure SI 34** DID (Dispersion Interaction Density) plots of some selected guests inside the cavity (colour coding: red = strong; blue = weak interacting regions): a) cyclopentane, b) cyclohexane, c) pyridine, d) norbornadiene, e) phenol, f) 1,4-dioxane, g) DABCO, h) 2-methylthiophene, i) benzene.

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