Supporting Information

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1. Synthesis of the cage compounds

According to our previously reported methods,¹ each cage compound [BF₄@Pd₄L₄₋₃][BF₄] was formed in quantitative yield by heating a mixture of the corresponding Ligand (L¹: 1.36 mg, 1.4 µmol; L²: 1.40 mg, 1.4 µmol; L³: 1.45 mg, 1.4 µmol and L⁴: 0.57, 1.4 µmol) and a solution of [Pd(CH₃CN)₄][BF₄]₂ (0.68 µmol, 45 µL of a 15 mM stock solution in CD₃CN) in CD₃CN (450 µL) at 70 °C for 24 h in a closed vial to give a 0.35 mM solution of the double-cage.

2. Titration experiments

The host-guest complexes were formed by titrating a solution of the halide anions (as their tetra-n-butylammonium salts in CD₃CN, 17.5 mM) in steps of 1.0 eq into 500 µL of a 0.35 mM solution of the cages in CD₃CN in an NMR tube. The NMR spectra were recorded immediately after briefly shaking the solution.

Silver ion back-titrations: By addition of Ag(I) ions to the solution containing [2X+BF₄@Pd₄L₄₋₃][BF₄], either AgCl or AgBr were precipitated. For the cage based on dibenzosuberone (L⁴), 28 equiv. of Ag(I) ions were needed for the complete precipitation of AgCl from the host-guest complex with chloride,² whereas the chloride-containing host-guest complexes based on the phenothiazine ligands (L¹-³) show a complete precipitation upon addition of 2 equiv. of Ag(I). For the precipitation of AgBr from the bromide-containing host-guest complexes, only two equiv. of Ag(I) were needed for all examined double-cages.
A. \([\text{BF}_4\text{@Pd}_4\text{L}_1\text{BF}_4]\) 

\[
\begin{align*}
+ 8.0 \text{ eq Cl}^- \\
+ 6.0 \text{ eq Cl}^- \\
+ 4.0 \text{ eq Cl}^- \\
+ 3.0 \text{ eq Cl}^- \\
+ 2.0 \text{ eq Cl}^- \\
+ 1.0 \text{ eq Cl}^- \\
[\text{BF}_4\text{@Pd}_4\text{L}_1\text{BF}_4] \\
\text{Ligand L}^1
\end{align*}
\]

\(\text{ppm}\)

Figure SI-1: \(^1\text{H} \text{NMR} \text{titration (300 MHz, 298 K, CD}_2\text{CN)} \) of \([\text{BF}_4\text{@Pd}_4\text{L}_1\text{BF}_4]\) with \(\text{NBu}_4\text{Cl} \) (17.5 \text{ mm}). Upon addition of two equivalents of Cl\(^-\), \([\text{BF}_4\text{@Pd}_4\text{L}_1\text{BF}_4]\) transforms into \([2\text{Cl}^+\text{BF}_4\text{@Pd}_4\text{L}_1\text{BF}_4]\). Further addition of excess halide results in decomplexation of Pd(II) under release of free ligand 1.
**Figure SI-2:** $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): Precipitation of encapsulated chloride from [2Cl+BF$_4$@Pd$_4$L$_{18}$](BF$_4$)$_5$ with two equivalents of AgBF$_4$ under full recovery of [BF$_4$@Pd$_4$L$_{18}$](BF$_4$)$_7$ (top spectrum as reference).

**Figure SI-3:** ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the host-guest-complex [2Cl+BF$_4$@Pd$_4$L$_{18}$](BF$_4$)$_5$. * = contamination with Br$^-$. 
**Figure S1-4:** $^1$H NMR titration (300 MHz, 298 K, CD$_2$CN) of [BF$_4$@Pd$_4$L$_{18}$](BF$_4$)$_7$ with NBu$_4$Br (17.5 mM). Upon addition of two equivalents of Br$^-$, [BF$_4$@Pd$_4$L$_{18}$](BF$_4$)$_7$ transforms into [2Br+BF$_4$@Pd$_4$L$_{18}$](BF$_4$)$_5$. Further addition of excess halide results in decomplexation of Pd(II) under release of free ligand L$^1$. 

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Figure SI-5: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): Precipitation of encapsulated chloride from $[2\text{Br}+\text{BF}_4\text{Pd}_4\text{L}^1_8]$($\text{BF}_4$)$_5$ with two equivalents of AgBF$_4$ under full recovery of $[\text{BF}_4\text{Pd}_4\text{L}^1_8]$($\text{BF}_4$)$_7$ (top spectrum as reference).

Figure SI-6: ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the host-guest-complex $[2\text{Br}+\text{BF}_4\text{Pd}_4\text{L}^1_8]$($\text{BF}_4$)$_5$. * = contamination with Cl$^-$. 

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Figure SI-7: $^1$H NMR titration (300 MHz, 298 K, CD$_3$CN): Competition of two equivalents of bromide with chloride for the binding by $[\text{BF}_4@\text{Pd}_4\text{L}_1^8]$· Signals of $[2\text{Br}+\text{BF}_4@\text{Pd}_4\text{L}_1^8](\text{BF}_4)_5$ and $[2\text{Cl}+\text{BF}_4@\text{Pd}_4\text{L}_1^8](\text{BF}_4)_5$ show almost the same intensity, indicating that a comparable affinity of $[\text{BF}_4@\text{Pd}_4\text{L}_1^8](\text{BF}_4)_5$ for both halide anions. Signals of free ligand $\text{L}^4$ also start to appear.

Figure SI-8: ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the chloride and bromide containing mixture showing equally intense signals for the host-guest-complexes $[2\text{Br}+\text{BF}_4@\text{Pd}_4\text{L}_1^8](\text{BF}_4)_5$, $[\text{Br}+\text{Cl}+\text{BF}_4@\text{Pd}_4\text{L}_1^8](\text{BF}_4)_5$ and $[2\text{Cl}+\text{BF}_4@\text{Pd}_4\text{L}_1^8](\text{BF}_4)_5$.
B. [BF$_4$@Pd$_4$L$_3$$_8$](BF$_4$)$_7$

+ 8.0 eq Cl$^-$

+ 6.0 eq Cl$^-$

+ 4.0 eq Cl$^-$

+ 3.0 eq Cl$^-$

+ 2.0 eq Cl$^-$

+ 1.0 eq Cl$^-$

[BF$_4$@Pd$_4$L$_3$$_8$]

Ligand L$^3$

---

Figure SI-9: $^1$H NMR titration (300 MHz, 298 K, CD$_3$CN) of [BF$_4$@Pd$_4$L$_3$$_8$](BF$_4$)$_7$ with NBu$_4$Cl (17.5 mM). Upon addition of two equivalents of Cl$^-$, [BF$_4$@Pd$_4$L$_3$$_8$](BF$_4$)$_7$ transforms into [2Cl+BF$_4$@Pd$_4$L$_3$$_8$](BF$_4$)$_5$. Further addition of excess halide results in decomplexation of Pd(II) under release of free ligand L$^3$. 
**Figure SI-10:** $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): Precipitation of encapsulated chloride from [2Cl+BF$_4$@Pd$_4$L$_3$](BF$_4$)$_5$ with two equivalents of AgBF$_4$ under full recovery of [BF$_4$@Pd$_4$L$_3$](BF$_4$)$_7$ (top spectrum as reference).

**Figure SI-11:** ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the host-guest-complex [2Cl+BF$_4$@Pd$_4$L$_3$](BF$_4$)$_5$. * = contamination with Br$^-$. 
Figure S1-12: \(^1\)H NMR titration (300 MHz, 298 K, CD\(_3\)CN) of \([\text{BF}_4@\text{Pd}_4\text{L}_8]\) with NBu\(_4\text{Br}\) (17.5 mm). Upon addition of two equivalents of Br\(^-\), \([\text{BF}_4@\text{Pd}_4\text{L}_8]\) transforms into \([2\text{Br}+\text{BF}_4@\text{Pd}_4\text{L}_8]\). Further addition of excess halide results in decomplexation of Pd(II) under release of free ligand L\(^3\).
**Figure SI-13:** $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): Precipitation of encapsulated bromide from [2Br+BF$_4$@Pd$_4$L$_3^8$] with two equiv. of AgBF$_4$ under full recovery of [BF$_4$@Pd$_4$L$_3^8$] (top spectrum as reference).

**Figure SI-14:** ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the host-guest-complex [2Br+BF$_4$@Pd$_4$L$_3^8$].
* = contamination with Cl$^-$. 
Figure SI-15: $^1$H NMR titration (300 MHz, 298 K, CD$_3$CN): Competition of two equivalents of bromide with chloride for the binding by [BF$_4$@Pd$_4$L$_8$]$_8$]([BF$_4$]). Signals of [2Br+BF$_4$@Pd$_4$L$_8$]$_8$ and [2Cl+BF$_4$@Pd$_4$L$_8$]$_8$ show almost the same intensity, indicating that a comparable affinity of [BF$_4$@Pd$_4$L$_8$]$_8$ for both halide anions. Signals of free ligand L$_8$ also start to appear.

Figure SI-16: ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the chloride and bromide containing mixture showing signals for the host-guest-complexes [2Br+BF$_4$@Pd$_4$L$_8$][BF$_4$]$_5$, [Br+Cl+BF$_4$@Pd$_4$L$_8$][BF$_4$]$_5$, and [2Cl+BF$_4$@Pd$_4$L$_8$][BF$_4$]$_5$. The latter species gives the strongest signal, indicating a preference for chloride binding in this case.
3. Cage Competition experiments

General procedure

A mixture of two different double-cages (250 µL, 0.35 mM in CD$_3$CN per double-cage) in a ratio of 1:1 was used for the competition experiments. This solution was treated with one equivalent of halide (with respect to the whole amount of all contained double-cages, NBu$_3$Cl or NBu$_3$Br, 17.5 mM, 10 µL in CD$_3$CN). The results of the individual competition experiments are printed in the top of the figures.

\[
\text{Cl: } [\text{BF}_4@\text{Pd}_4L^2] > [\text{BF}_4@\text{Pd}_4L^1]\]

Figure SI-17: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between $[\text{BF}_4@\text{Pd}_4L^1]_2(\text{BF}_4)_2$ and $[\text{BF}_4@\text{Pd}_4L^2]_2(\text{BF}_4)_2$ for the binding of the chloride anion shows that the latter one is the better binder. The $[\text{BF}_4@\text{Pd}_4L^1]_2(\text{BF}_4)_2$, $[\text{BF}_4@\text{Pd}_4L^2]_2(\text{BF}_4)_2$, and $[\text{BF}_4@\text{Pd}_4L^1]_2(\text{BF}_4)_2$ spectra are printed as reference.
Figure SI-18: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between [BF$_4$@Pd$_4$L$_{18}^2$](BF$_4$)$_7$ and [BF$_4$@Pd$_4$L$_{18}^1$](BF$_4$)$_7$ for the binding of the bromide anion shows that the latter one is the better binder. The [BF$_4$@Pd$_4$L$_{18}^1$](BF$_4$)$_7$, [2Br$+$BF$_4$@Pd$_4$L$_{18}^1$](BF$_4$)$_5$ and [BF$_4$@Pd$_4$L$_{18}^0$](BF$_4$)$_7$ spectra are printed as reference.
Figure SI-19: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between [BF$_4$@Pd$_4$L$_{18}^3$](BF$_4$)$_7$ and [BF$_4$@Pd$_4$L$_{18}^3$](BF$_4$)$_7$ for the binding of the chloride anion shows that the latter one is the better binder. The [BF$_4$@Pd$_4$L$_{18}^3$](BF$_4$)$_7$, [2Cl+BF$_4$@Pd$_4$L$_{18}^3$](BF$_4$)$_5$, [BF$_4$@Pd$_4$L$_{18}^3$](BF$_4$)$_7$ and [2Cl+BF$_4$@Pd$_4$L$_{18}^3$](BF$_4$)$_5$ spectra are printed as reference. * = impurity.
Figure SI-20: The ESI mass spectrum (FTICR, positive mode, eluent CH$_3$CN) of the host-guest-complexes in the competition experiment of [BF$_4$@Pd$_4$L$_1^1$]$_3$[BF$_4$]$_3$ and [BF$_4$@Pd$_4$L$_1^2$]$_3$[BF$_4$]$_3$ with NBu$_4$Cl clearly shows the higher affinity of the latter cage for chloride binding. * = contamination with Br$^-$. 
**Figure SI-21:** $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between $[\text{BF}_4@\text{Pd}_4 L^3]$ and $[\text{BF}_4@\text{Pd}_4 L^3 ] (\text{BF}_4)_7$ for the binding of the bromide anion shows that the latter one is the better binder. The $[\text{BF}_4@\text{Pd}_4 L^3 ] (\text{BF}_4)_7$, $[\text{BF}_4@\text{Pd}_4 L^3 ] (\text{BF}_4)_5$, $[\text{BF}_4@\text{Pd}_4 L^1 ] (\text{BF}_4)_7$ and $[\text{BF}_4 @ \text{Pd}_4 L^3 ] (\text{BF}_4)_5$ spectra are printed as reference. * = impurity.
**Figure SI-22:** The ESI mass spectrum (FTICR, positive mode, eluent CH₂CN) of the host-guest-complexes in the competition experiment of \([\text{BF}_4@\text{Pd}_4\text{L}^1_8]\)(\text{BF}_4)_7 and \([\text{BF}_4@\text{Pd}_4\text{L}^3_8]\)(\text{BF}_4)_7 with NBu₄Br clearly shows the higher affinity of the latter cage for chloride binding. * = contamination with Cl⁻.
Figure SI-23: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between [BF$_4$@Pd$_4$L$_8^2$][BF$_4$]$_7$ and [BF$_4$@Pd$_4$L$_8^3$][BF$_4$]$_7$ for the binding of the chloride anion shows that the double-cages show comparable affinities. The [BF$_4$@Pd$_4$L$_8^3$][BF$_4$]$_7$, [2Cl+BF$_4$@Pd$_4$L$_8^3$][BF$_4$]$_5$ and [BF$_4$@Pd$_4$L$_8^3$][BF$_4$]$_7$ spectra are printed as reference.
Figure SI-24: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between $[\text{BF}_4@\text{Pd}_4\text{L}_8]^2^+\text{[BF}_4]$ and $[\text{BF}_4@\text{Pd}_4\text{L}_8]^3^+\text{[BF}_4]$ for the binding of the bromide anion shows that the double-cages show comparable affinities. The $[\text{BF}_4@\text{Pd}_4\text{L}_8]^2^+\text{[BF}_4]$, $[2\text{Br+BF}_4@\text{Pd}_4\text{L}_8]^+\text{[BF}_4]$ and $[\text{BF}_4@\text{Pd}_4\text{L}_8]^3^+\text{[BF}_4]$ spectra are printed as reference.
Figure SI-25: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between [BF$_4$@Pd$_4$L$_{18}$] and [BF$_4$@Pd$_4$L$_{18}^+$] for the binding of the chloride anion shows that the latter one is the better binder. The [BF$_4$@Pd$_4$L$_{18}$][BF$_4$], [2Cl+BF$_4$@Pd$_4$L$_{18}$][BF$_4$], [BF$_4$@Pd$_4$L$_{18}^+$][BF$_4$] and [2Cl+BF$_4$@Pd$_4$L$_{18}^+$][BF$_4$]$_3$ spectra are printed as reference. * = impurity.
\[ \text{Br: } [BF_4@Pd_4L^1_{8}] > [BF_4@Pd_4L^1_{8}] \]

\[
\begin{align*}
&\text{[2Br+BF}_4@\text{Pd}_4\text{L}^1_{8}] \\
&\text{[BF}_4@\text{Pd}_4\text{L}^1_{8}] \\
&\text{mixture} \\
&\text{[2Br+BF}_4@\text{Pd}_4\text{L}^4_{8}] \\
&\text{[BF}_4@\text{Pd}_4\text{L}^4_{8}] \\
\end{align*}
\]

Figure SI-26: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between [BF$_4@Pd_4L^1_{8}$(BF$_4$)]$_7$ and [BF$_4@Pd_4L^1_{8}$(BF$_4$)]$_7$ for the binding of the bromide anion shows that the latter one is the better binder. The [BF$_4@Pd_4L^1_{8}$(BF$_4$)]$_7$, [2Br+BF$_4@Pd_4L^1_{8}$(BF$_4$)]$_5$, [BF$_4@Pd_4L^4_{8}$(BF$_4$)]$_7$ and [2Br+BF$_4@Pd_4L^4_{8}$(BF$_4$)]$_5$ spectra are printed as reference. * = impurity.
Figure SI-27: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between [BF$_4$@Pd$_4$L$_8^2$](BF$_4$)$_7$ and [BF$_4$@Pd$_4$L$_8$](BF$_4$)$_7$ for the binding of the chloride anion shows that the latter one is the better binder. The [BF$_4$@Pd$_4$L$_8^2$](BF$_4$)$_7$, [2Cl+BF$_4$@Pd$_4$L$_8^4$](BF$_4$)$_5$ and [BF$_4$@Pd$_4$L$_8^4$](BF$_4$)$_7$ spectra are printed as reference.
Figure SI-28: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between $[\text{BF}_4\text{Pd}_4\text{L}_2^8]$ and $[\text{BF}_4\text{Pd}_4\text{L}_4^8]$ for the binding of the bromide anion shows that the latter one is the better binder. The $[\text{BF}_4\text{Pd}_4\text{L}_2^8][\text{BF}_4]^5$, $[\text{BF}_4\text{Pd}_4\text{L}_4^8][\text{BF}_4]^5$ and $[\text{BF}_4\text{Pd}_4\text{L}_4^8][\text{BF}_4]^7$ spectra are printed as reference.
Figure SI-29: \(^1\)H NMR titration (500 MHz, 298 K, CD\(_3\)CN): A competition experiment between [BF\(_4\)@Pd\(_4\)L\(_3\)](BF\(_4\))\(_7\) and [BF\(_4\)@Pd\(_4\)L\(_4\)](BF\(_4\))\(_7\) for the binding of the chloride anion shows that the latter one is the better binder. The [BF\(_4\)@Pd\(_4\)L\(_3\)](BF\(_4\))\(_7\), [2Cl+BF\(_4\)@Pd\(_4\)L\(_3\)](BF\(_4\))\(_5\), [BF\(_4\)@Pd\(_4\)L\(_4\)](BF\(_4\))\(_7\) and [2Cl+BF\(_4\)@Pd\(_4\)L\(_4\)](BF\(_4\))\(_5\) spectra are printed as reference. * = impurity.
Figure SI-30: $^1$H NMR titration (500 MHz, 298 K, CD$_3$CN): A competition experiment between $[\text{BF}_4@\text{Pd}_4L^3_8](\text{BF}_4)_7$ and $[\text{Br}+\text{BF}_4@\text{Pd}_4L^4_8](\text{BF}_4)_5$ for the binding of the chloride anion shows that the latter one is the better binder. The $[\text{BF}_4@\text{Pd}_4L^3_8](\text{BF}_4)_7$, $[\text{Br}+\text{BF}_4@\text{Pd}_4L^4_8](\text{BF}_4)_5$, $[\text{BF}_4@\text{Pd}_4L^3_8](\text{BF}_4)_7$ and $[\text{Br}+\text{BF}_4@\text{Pd}_4L^4_8](\text{BF}_4)_5$ spectra are printed as reference. $^*$ = impurity.
4. $^1$H,$^1$H-NOESY correlations

On the basis of the NOESY spectra of the coordination cages with different anions ($X = Cl^\text{-}$, $Br^\text{-}$) bound in the outer pockets, the NOESY signal intensities can be correlated with proton-proton distances. The data obtained from the crystal structure of [BF$_4$@Pd$_4$L$_4$](BF$_4$)$_7$ was used to calculate the distances within the structures of [2Cl+BF$_4$@Pd$_4$L$_4$](BF$_4$)$_5$ and [2Br+BF$_4$@Pd$_4$L$_4$](BF$_4$)$_5$ according to our previously published method.$^{[3]}$

The relative integral $I_{rel}$ of an NOE signal depends on the interatomic distance $d$ ($a = \text{proportionality factor}$).

$$I_{rel} = a \cdot d^{-6}$$

To calculate the atomic distances, the interatomic distance $d$ has to be written as a function of the measured integral.

$$d = a \cdot I_{rel}^{-1/6}$$

To obtain reliable distances, the experimental conditions for the measurement of all NOESY spectra were held as constant as possible. Each individual proton-proton crosspeak in the NOESY spectrum of [BF$_4$@Pd$_4$L$_4$](BF$_4$)$_7$ was compared to the corresponding crosspeak for [2X+BF$_4$@Pd$_4$L$_4$](BF$_4$)$_5$ with $X = Cl^\text{-}$, $Br^\text{-}$. To minimize the error, one of the diagonal signal’s integral was set to $I = 1$. The two crosspeak signal intensities $I_1$ and $I_2$ were averaged. The distances $d_x$ in [2X+BF$_4$@Pd$_4$L$_4$](BF$_4$)$_5$ were calculated according to the following equation:

$$d_x = d_{BF_4} \cdot \frac{I_{rel,X}^{-1/6}}{I_{rel,BF_4}^{-1/6}}$$

All signals used for the correlation show contribution of two protons to the observed integral $I_{rel}$, so the NOE signal integrals could not be directly compared to the distances in the crystal structure. Artificial distances $d'$ were calculated from the two contributing distances $d_1$ and $d_2$ using the following equation.

$$d' = (d_1^{-6} + d_2^{-6})^{-1/6}$$

An analogous distance $d'^\ast$ was extracted from a series of molecular models and compared to the artificial distances $d'$.

Errors for the distances $\Delta d_x$ were calculated using the integral-dependent maximum error. The integral error $\Delta I_{rel}$ was obtained from the standard deviation of the two averaged integral values and the contribution of the noise as an absolute part $\Delta I_{rel,\text{noise}} = 0.0004$ obtained from the noise level of the NOESY spectra.

$$\Delta d_x = \left| \frac{\partial d_x}{\partial I_{rel,BF_4}} \cdot \Delta I_{rel,BF_4} \right| + \left| \frac{\partial d_x}{\partial I_{rel,X}} \cdot \Delta I_{rel,X} \right|$$

$$\Delta d_x = \left| \frac{1}{6} \cdot d_{BF_4} \cdot \frac{I_{rel,X}^{-7/6}}{I_{rel,BF_4}^{-1/6}} \cdot \Delta I_{rel,BF_4} \right| + \left| \frac{1}{6} \cdot d_{BF_4} \cdot \frac{I_{rel,X}^{-1/6}}{I_{rel,BF_4}^{-5/6}} \cdot \Delta I_{rel,X} \right|$$
A series of models for [2X+BF₄@Pd₄L₈]₅(BF₄)₅ was generated by applying different values of the translation Δd on the crystal structure of [BF₄@Pd₄L₈]₅(BF₄)₅. In order to identify a suitable model representing the real solution structure of [2X+BF₄@Pd₄L₈]₅(BF₄)₅, the deviations of these distances from those obtained from the NOESY correlation were quantified by calculation of the Q-factor for each model.

\[
Q = \left( \frac{\sum_{i=1}^{N} (d_{i}^{\text{exp}} - d_{i}^{\text{calc}})^2}{\sum_{i=1}^{N} (d_{i}^{\text{exp}})^2} \right)^{1/2}
\]

A perfect agreement of the model and the experiment would result in \( Q = 0 \).

**Table 1:** NOE signal intensities and proton distances for [BF₄@Pd₄L₈]₅(BF₄)₅ and [2C+BF₄@Pd₄L₈]₅(BF₄)₅

<table>
<thead>
<tr>
<th>[3BF₄@Pd₄L₈]</th>
<th>NOE</th>
<th>Crystal Structure</th>
<th>Protons</th>
<th>l₁</th>
<th>l₂</th>
<th>l</th>
<th>Δl</th>
<th>d₁</th>
<th>d₂</th>
<th>d₃</th>
</tr>
</thead>
</table>
g -> f'        | 0.0155 | 0.0108 | 0.0132 | 0.0033 | 4.948 | 5.340 | 5.405 |
g -> e'        | 0.0027 | 0.0025 | 0.0026 | 0.0001 | 5.817 | 6.419 | 4.559 |
f' -> a        | 0.0377 | 0.0324 | 0.0351 | 0.0037 | 3.017 | 3.320 | 2.800 |
e' -> a        | 0.0239 | 0.0269 | 0.0254 | 0.0021 | 3.377 | 3.716 | 3.135 |

<table>
<thead>
<tr>
<th>[2C+BF₄@Pd₄L₈]</th>
<th>NOE</th>
<th>Correlation</th>
<th>Protons</th>
<th>l₁</th>
<th>l₂</th>
<th>l</th>
<th>Δl</th>
<th>d'</th>
<th>Δ/</th>
<th>(best fit) d₁</th>
<th>(best fit) d₂</th>
<th>(best fit) d₃</th>
</tr>
</thead>
</table>
g -> f'        | 0.0339 | 0.0298 | 0.0319 | 0.0029 | 4.664 | 0.252 | 4.220 | 4.674 | 3.926 |
g -> e'        | 0.0064 | 0.0058 | 0.0061 | 0.0004 | 3.955 | 0.123 | 5.860 | 5.194 | 4.863 |
f' -> a        | 0.0187 | 0.0248 | 0.0218 | 0.0043 | 3.032 | 0.149 | 2.934 | 3.245 | 2.728 |
e' -> a        | 0.0173 | 0.0128 | 0.0151 | 0.0032 | 3.420 | 0.152 | 3.274 | 3.623 | 3.045 |

<table>
<thead>
<tr>
<th>[2Br+BF₄@Pd₄L₈]</th>
<th>NOE</th>
<th>Correlation</th>
<th>Protons</th>
<th>l₁</th>
<th>l₂</th>
<th>l</th>
<th>Δl</th>
<th>d'</th>
<th>Δ/</th>
<th>(best fit) d₁</th>
<th>(best fit) d₂</th>
<th>(best fit) d₃</th>
</tr>
</thead>
</table>
g -> f'        | 0.0148 | 0.0147 | 0.0148 | 0.0001 | 5.303 | 0.204 | 4.801 | 5.205 | 4.432 |
g -> e'        | 0.0045 | 0.0044 | 0.0045 | 0.0001 | 4.169 | 0.041 | 5.690 | 6.304 | 5.295 |
f' -> a        | 0.0271 | 0.0223 | 0.0247 | 0.0034 | 2.968 | 0.123 | 2.985 | 3.291 | 2.773 |
e' -> a        | 0.0202 | 0.0176 | 0.0189 | 0.0018 | 3.293 | 0.101 | 3.686 | 3.343 | 3.105 |

Table 1 shows that the best model for [2Cl+BF₄@Pd₄L₈]₅(BF₄)₅ is found at an inner Pd-Pd distance of \( d(\text{Pd-Pd}) = 9.65 \, \text{Å} \). This is a change of 0.80 Å compared to [BF₄@Pd₄L₈]₅(BF₄)₅, where \( d(\text{Pd-Pd}) \) is 8.85 Å.

The best model for [2Br+BF₄@Pd₄L₈]₅(BF₄)₅ is found at an inner Pd-Pd distance of \( d(\text{Pd-Pd}) = 9.05 \, \text{Å} \). This is a change of 0.20 Å compared to [BF₄@Pd₄L₈]₅(BF₄)₅, where \( d(\text{Pd-Pd}) \) is 8.85 Å.
5. Calculations of the NMR shifts after binding of halide anions

General procedure

Relative NMR chemical shifts $\Delta \delta$ of the protons $H_a$ and $H_{a'}$ were calculated using the GIAO method as implemented in Gaussian ‘09.\[^3\] A fragment of the double cage structure containing one inner Pd(II) ion and two BF$_4^-$ anions was used for the calculations (s. Fig. SI-31). In order to reduce computational costs, the hexyl substituents were truncated to leave methyl groups. The DFT computation was performed on the B3LYP/LANL2DZ level of theory using the default solvation model (IEFPCM) with the solvent acetonitrile. The rather small basis set was used as a compromise between computational costs and the large system size including a transition metal cation. For comparison, a smaller fragment (only one ligand backbone, two neighboring pyridines, one BF$_4^-$ anion, but without the palladium(II) cation) was calculated with a larger basis set (6-311G-(d,p)) and resulted in similar trends for the $\Delta \delta$ values (not shown).

Figure SI-31: Fragment used for the computation of relative NMR chemical shifts by Gaussian ‘09.

The results of the relative NMR chemical shift computations of the protons $H_a$ and $H_{a'}$ for all four coordination cages $[\text{BF}_4@\text{Pd}_4\text{L}_8^n](\text{BF}_4)_2$ with $n = 1-4$ and the experimental values (s. also Tab. 1) are shown in Fig. SI-32. The $\Delta \delta$ value is the difference between the shifts of the $H_a$ and $H_{a'}$ protons of $[\text{BF}_4@\text{Pd}_4\text{L}_8^n](\text{BF}_4)_2$ and $[2X+\text{BF}_4@\text{Pd}_4\text{L}_8^n](\text{BF}_4)_2$ with $X = \text{Cl}^-$, Br$^-$. 
Figure SI-32: Results of the computation of relative NMR chemical shifts for a) [BF₄@Pd₄L₁₈], b) [BF₄@Pd₄L₂₈], c) [BF₄@Pd₄L₃₈] and d) [BF₄@Pd₄L₄₈]. The horizontal lines assign the experimental differences between the shifts of the cages [BF₄@Pd₄Lₙ₈] with n = 1, 3, 4 and the cages [2X+BF₄@Pd₄L₉₈] with X = Cl⁻, Br⁻. No experimental values could be obtained for [BF₄@Pd₄L₂₈] since the compound shows very broad signals in the ¹H NMR.

Table SI-2: Summary of the differences in chemical shifts of the protons Hₐ and Hₐ' upon anion binding.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Δshift Hₐ in ppm</th>
<th>Δshift Hₐ' in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-1.57</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>[BF₄@Pd₄L₁₈]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BF₄@Pd₄L₂₈]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BF₄@Pd₄L₃₈]</td>
<td>-1.01</td>
<td>0.68</td>
</tr>
<tr>
<td>[BF₄@Pd₄L₄₈]</td>
<td>-0.70</td>
<td>0.44</td>
</tr>
<tr>
<td>Br</td>
<td>-0.94</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>[BF₄@Pd₄L₁₈]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BF₄@Pd₄L₂₈]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BF₄@Pd₄L₃₈]</td>
<td>-0.62</td>
<td>0.44</td>
</tr>
<tr>
<td>[BF₄@Pd₄L₄₈]</td>
<td>-0.49</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Table SI-3: Summary of the Pd-Pd distances in the coordination cages. In cases of \([\text{BF}_4@\text{Pd}_4L_{18}^1]\), \([\text{BF}_4@\text{Pd}_4L_{18}^2]\) and \([\text{BF}_4@\text{Pd}_4L_{18}^3]\) the distances are obtained from the X-ray structure.\(^{[1a,1b]}\) The values for \([\text{BF}_4@\text{Pd}_4L_{18}^4]\) are taken from the DFT-calculated structure.\(^{[1b]}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(Pd-Pd)(_{\text{monocage}}) in Å</th>
<th>d (Pd(<em>{\text{outer}})-Pd(</em>{\text{inner}})) in Å</th>
<th>d (Pd(<em>{\text{inner}})-Pd(</em>{\text{inner}})) in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{BF}_4@\text{Pd}<em>4L</em>{18}^1])</td>
<td>17.62</td>
<td>8.77</td>
<td>8.85</td>
</tr>
<tr>
<td>([\text{BF}_4@\text{Pd}<em>4L</em>{18}^2])</td>
<td>16.77</td>
<td>8.16</td>
<td>8.63</td>
</tr>
<tr>
<td>([\text{BF}_4@\text{Pd}<em>4L</em>{18}^3])</td>
<td>16.55</td>
<td>8.42-8.52</td>
<td>8.03</td>
</tr>
<tr>
<td>([\text{BF}_4@\text{Pd}<em>4L</em>{18}^4])</td>
<td>16.34</td>
<td>8.09</td>
<td>8.25</td>
</tr>
</tbody>
</table>
6. Model calculations for the double-cage systems

In order to calculate optimal $\Delta d$ and $R$ (denoted as $d(N,N) = d(Pd,Pd)$ in the main text) values for the cage systems interacting with halide anions in the outer pockets, we applied the push-and-pull model adopted in our previous study of L4. The fitting range for the anion $Cl^-$ was expanded up to 10.5 Å, $BF_4^-$ to 9.8 Å, and the same distance range as in $Cl^-$ was adopted for $Br^-$. The scheme in Fig. SI-33 shows our simplified model for the host-guest interactions. The only variable for a fixed $R$ is the distance $r_2$ in the inner pocket. The interaction energies are computed by splitting the total potential into three separate terms, each being calculated at the DF-MP2/cc-pVTZ level of theory (cc-pVTZ-PP for Pd, in combination with the ECP28MDF pseudopotential). Each subsystem consists of two Pd(II) complexes with four pyridines, with the anion being placed in the middle of the two planes. The distance $r$ between the two planes is varied and the interaction energy calculated. In the case of $BF_4^-$, since the anion is not perfectly spherical, the structure was optimized, keeping the planes fixed. The optimisations were carried out at the BP86/def2-SVP level of theory with the ORCA program package. The wave function calculations were carried out with Molpro2010.1.

The potential profiles were calculated for each of the three different anions and were then fitted to a linear combination of gaussian functions through the use of the OGOLEM program. In the case of the halides, 7 Gaussian functions were used. For $BF_4^-$ only 4 Gaussians were applied to avoid overfitting of the profile. The results are shown in Figs. SI-34.

![Fig. SI-33: Push-and-pull model for anion binding. The three pockets are represented by three different subsystems. The total potential is given by $V=V_1+V_2+V_3$, which upon fixing the distance $R$, is dependent on a single variable (in our case, the distance $r_2$).](image-url)
Table SI-4: Calculated Pd\textsubscript{inner}-Pd\textsubscript{inner} distances used for Fig. 5.

<table>
<thead>
<tr>
<th></th>
<th>( L^1 )</th>
<th>( L^2 )</th>
<th>( L^3 )</th>
<th>( L^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF( 4^- )</td>
<td>9.17±0.17</td>
<td>8.39±0.14</td>
<td>8.20±0.20</td>
<td>8.09±0.25</td>
</tr>
<tr>
<td>Br( - )</td>
<td>9.80±0.09</td>
<td>9.46±0.32</td>
<td>9.28±0.33</td>
<td>9.01±0.41</td>
</tr>
<tr>
<td>Cl( - )</td>
<td>9.80±0.06</td>
<td>9.78±0.18</td>
<td>9.63±0.26</td>
<td>9.07±0.33</td>
</tr>
</tbody>
</table>

The theoretical error bars are based on a 1 kcal/mol tolerance for each given minimum. The estimated errors for the distance are computed as the average deviation of the upper and lower values. The distances for BF\( 4^- \) and Cl\( - \) in \( L^4 \) are the same as featured in a previous work. The error bar for the Cl\( - \) distance has been reviewed based on a new parameterization of the BF\( 4^- \) inner pocket potential.
Fig. SI-34: a) DF-MP2 interaction energy profile (in kJ/mol) for BF$_4^-$ interacting with two Pd(II)(pyridine)$_4$ planes. b) DF-MP2 interaction energy profile (in kJ/mol) for Br$^-$ interacting with two Pd(II) planes. c) DF-MP2 interaction energy profile (in kJ/mol) for Cl$^-$ interacting with two Pd(II) planes.
References