Supporting Information

A Deep Tetranuclear Metallo-Cavitand with Bis(Aryl) Palladium Bridges

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Materials and Methods. ¹H, ¹³C and ¹⁹F NMR spectra were carried out in deuterated solvents on Bruker Avance 400 and 500 Ultrashield spectrometers. Thermogravimetric analysis (TGA) was measured on a Mettler-Toledo TGA/SDTA 851° thermobalance. 5,11,17,23-Tetrakis(1H-imidazo[4,5-f][3,8]phenanthrolin-2-yl)-25,26,27,28-tetra-octyloxy[4]calix[4]arene ¹ and reagent (COD)Pd(C₆F₃Cl₂)₂ were synthesized according to published methods.

Synthesis:

5,11,17,23-Tetrakis(1H-imidazo[4,5-f][3,8]phenanthrolin-2-yl)-25,26,27,28-tetra-octyloxy[4]calix[4]arene ¹ (90 mg, 0.0515 mmol) and (COD)Pd(C₆F₃Cl₂)₂ (127 mg, 0.2060 mmol) were suspended in THF (HPLC grade, 17 ml) and the mixture was stirred at room temperature for 48 hours. The solvent was evaporated; the residue was dissolved in THF (2 ml) and ethyl ether was added (40 ml). A fine solid precipitated. It was kept at -18 °C for further precipitation overnight. The precipitate was filtered, washed with ethyl ether and dried giving 3 as a yellow powder (0.1659 g, 86%).

¹H NMR (500 MHz, THF-d₈) δ = 14.47 (s, 4H; NH), 10.90 (s, 8H; Hₐ), 9.45 (d, 8H, J = 6.3 Hz; Hₐ), 8.84-8.54 (m, 8H; Hₐ), 8.49 (d, 8H, J = 6.3 Hz; Hₐ), 4.93 (d, J = 12.5 Hz, 4H; Hₐ), 4.25 (t, J = 7.3 Hz, 8H; OCH₂), 3.81 (d, J = 12.5 Hz, 4H; Hₐ), 2.37 (m, 8H; CH₂), 1.7-1.35 (m, 40H; CH₂), 1.01 (t, J = 7.4 Hz, 12H; CH₃); ¹³C NMR (DEPTQ-135, 100 MHz, THF-d₈): δ = 158.7, 158.4, 156.4, 156.1, 150.9, 150.5, 148.4, 144.9, 143.3, 134.8, 129.1, 121.8, 118.2, 111.0, 101.9, 74.6, 30.3, 29.0, 28.3, 28.1, 27.9, 24.3, 21.0, 11.7; ¹⁹F NMR (376 MHz, THF-d₈, 220K, -53°C) δ = -89.99 (s, Fₜₜₜ), -90.53 (s, Fₜₜₜ), -91.02 (s, Fₜₜₜ), -91.63 (s, Fₜₜₜ), -120.65 (s, Fₜₜₜ); Anal. Calcd for C₁₆₀H₁₁₂Cl₁₈F₂₄N₁₆O₄Pd₄: C 50.95, H 2.99, N 5.94. Found: C 50.62, H 3.34, N 5.63.
**NMR DATA**

Figure S1. $^1$H NMR (400 MHz) spectrum of 3 in THF-$d_8$ at room temperature
Figure S2. $^{13}$C NMR-DEPTQ-135 (100 MHz) spectrum of 3 in THF-$d_8$ at room temperature
Figure S3. $^1$H, $^1$H-2D COSY spectrum of 3 (400 MHz, THF-$d_8$, r.t.)
Figure S4. $^{1}H,^{19}F$-2D HOESY spectrum of 3 (500 MHz, THF-$d_8$, at -53 °C).

The four ortho fluorine atoms can be assigned as two pointing upwards ($F_{up}$) and two pointing downwards the cavity ($F_{down}$).
**Thermogravimetric Analysis**

TGA conditions: air flow (80 ml/min), heating rate 5 °C/min until 250 °C and 30 °C in the range 250-1100 °C, sample 2.124 mg.

The highest weight loss is observed in the temperature range 250-690 °C where the Pd complex decomposes. Between 690 and 780 °C, a little mass gain is observed, as it has previously been found for other Pd complexes.[3] Decomposition of PdO[4] to Pd metal occurs around 790 °C with a final residue of 12.00%, in good accordance with the chemical formula C_{160}H_{112}Cl_{16}F_{24}N_{16}O_{4}Pd_{4}.

![Thermogravimetric curve of 3](image)

**Figure S5.** Thermogravimetric curve of 3
**Inclusion Complex**

The complex was prepared by mixing equimolecular amounts of host 3 and guest 5 in deuterated THF.

**Figure S6.** $^1$H NMR (400 MHz, THF-$d_8$) spectrum of guest 5 at room temperature
Figure S7. $^1$H NMR (400 MHz, THF-$d_8$, r.t.) spectrum of a 1:1 mixture of compounds 3 (blue) and 5 (red)
Figure S8. Top: $^1$H,$^1$H-2D NOESY (400 MHz, 0.3 ms mixing time, r.t.) spectrum of 3 in THF-d$_8$.

Bottom: Intermolecular contacts scheme.
Figure S9. Variable Temperature $^1$H-NMR of the 5@3 inclusion complex in THF-$d_8$ (1.9 mM).
Host signals in blue, guest signals in red, free guest in green.
Figure S10. Variable Temperature $^{19}$F-NMR of the 5@3 inclusion complex in THF-$d_8$. 
$^1$H NMR Titration Experiments

$^1$H NMR spectroscopic titration experiments for the binding of 5 with 3 were carried out on a Buker Avance 500 Ultrashieded spectrometer at room temperature in THF-$d_8$. In order to maintain the concentration of the host constant along the titration, the experiments were performed adding aliquots of a guest 5 solution ($6.68 \times 10^{-3}$ M), containing host 3 ($1.33 \times 10^{-3}$ M), to a host 3 solution ($1.33 \times 10^{-3}$ M). 20 μL of the guest solution were added to the NMR tube containing the host solution (initial volume = 0.6 mL) and the spectra were recorded after each addition.

**Figure S11.** $^1$H-NMR titration of the 5@3 inclusion complex in THF-$d_8$. Host signals in blue, guest signals in red.
Host NH and Hc protons and guest Hmeta and Hpara protons were monitored. Titration data were analyzed using HypNMR 2006 software with a 1:1 host/guest model giving a binding constant of $2.32 \times 10^3$ for the $\text{5@3}$ inclusion complex.

$K_{11} = 2.32 \times 10^3 \pm 0.0987$

**Figure S12.** Isotherm fitting for Hc (top) and NH (bottom) protons and binding constant of $\text{5@3}$ inclusion complex calculated by HypNMR 2006 software.
References:


