Supporting Information

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

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Materials and Methods. ^{1}H, ^{13}C and ^{19}F 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^{e} thermobalance. 5,11,17,23-Tetrakis(1*H*-imidazo[4,5-f][3,8]phenanthrolin-2-yl)-25,26,27,28-tetra-octyloxycalix[4]arene **1** [1] and reagent (COD)Pd($C_6F_3Cl_2$)$_2$ [2] were synthesized according to published methods.

Synthesis:

5,11,17,23-Tetrakis(1*H*-imidazo[4,5-f][3,8]phenanthrolin-2-yl)-25,26,27,28-tetra-octyloxycalix[4]arene **1** (90 mg, 0.0515 mmol) and (COD)Pd($C_6F_3Cl_2$)$_2$ (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 ºC for further precipitation overnight. The precipitate was filtered, washed with ethyl ether and dried giving **3** as a yellow powder (0.1659 g, 86%).

^{1}H NMR (500 MHz, THF-d_8) δ= 14.47 (s, 4H; NH), 10.90 (s, 8H; H_a), 9.45 (d, 8H, J = 6.3 Hz; H_b), 8.84-8.54 (m, 8H; H_d), 8.49 (d, 8H, J = 6.3 Hz; H_c), 4.93 (d, J = 12.5 Hz, 4H; H_{ax}), 4.25 (t, J = 7.3 Hz, 8H; OCH_2), 3.81 (d, J = 12.5 Hz, 4H; H_{eq}), 2.37 (m, 8H; CH_2), 1.7-1.35 (m, 40H; CH_2), 1.01 (t, J = 7.4 Hz, 12H; CH_3); ^{13}C NMR (DEPTQ-135, 100 MHz, THF-d_8): 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; ^{19}F NMR (376 MHz, THF-d_8, 220K, -53ºC) δ= -89.99 (s, $F^{ortho}{}_1$), -90.53 (s, $F^{ortho}{}_2$), -91.02 (s, $F^{ortho}{}_3$), -91.63 (s, $F^{ortho}{}_4$), -120.65 (s, F^{para}); Anal. Calcd for $C_{160}H_{112}Cl_{16}F_{24}N_{16}O_4Pd_4$: C 50.95, H 2.99, N 5.94. Found: C 50.62, H 3.34, N 5.63.

NMR DATA

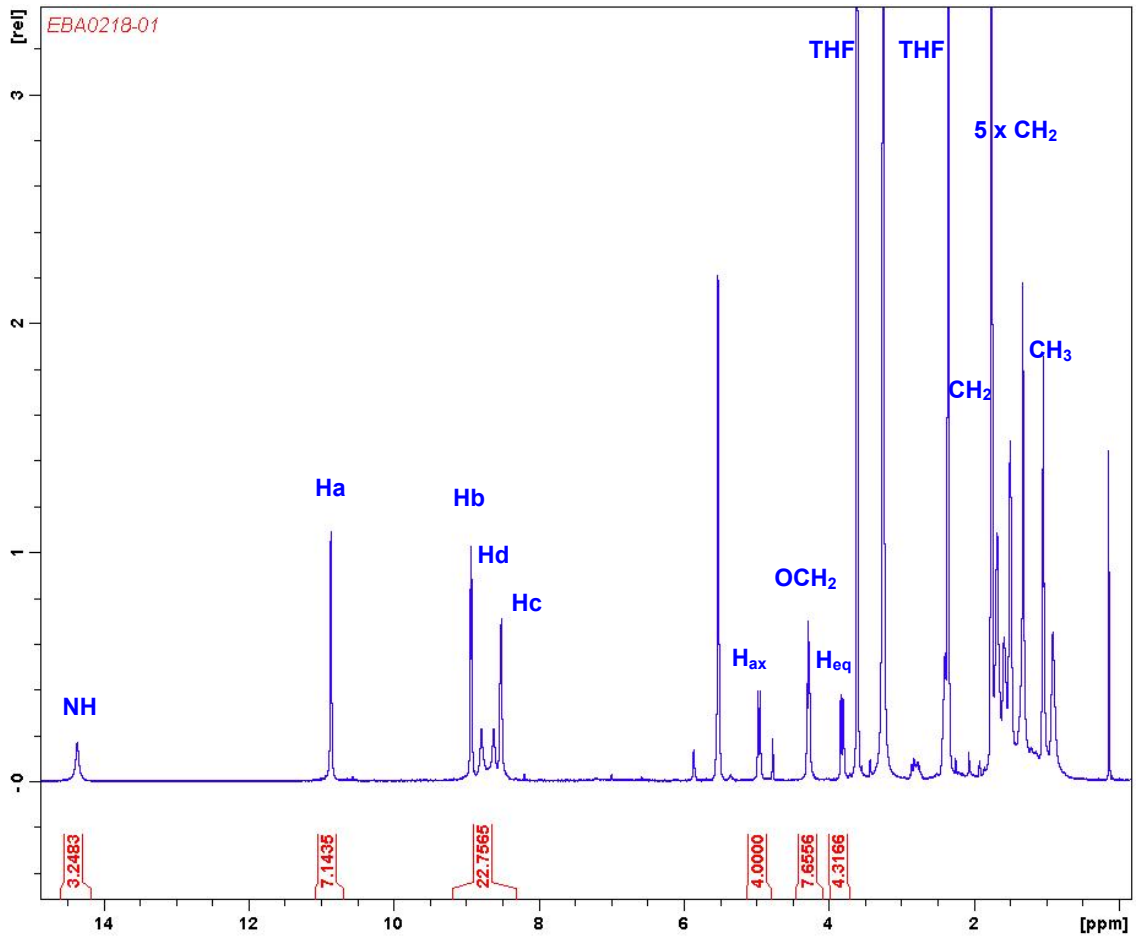


Figure S1. ^{1}H NMR (400 MHz) spectrum of **3** in THF-d_8 at room temperature

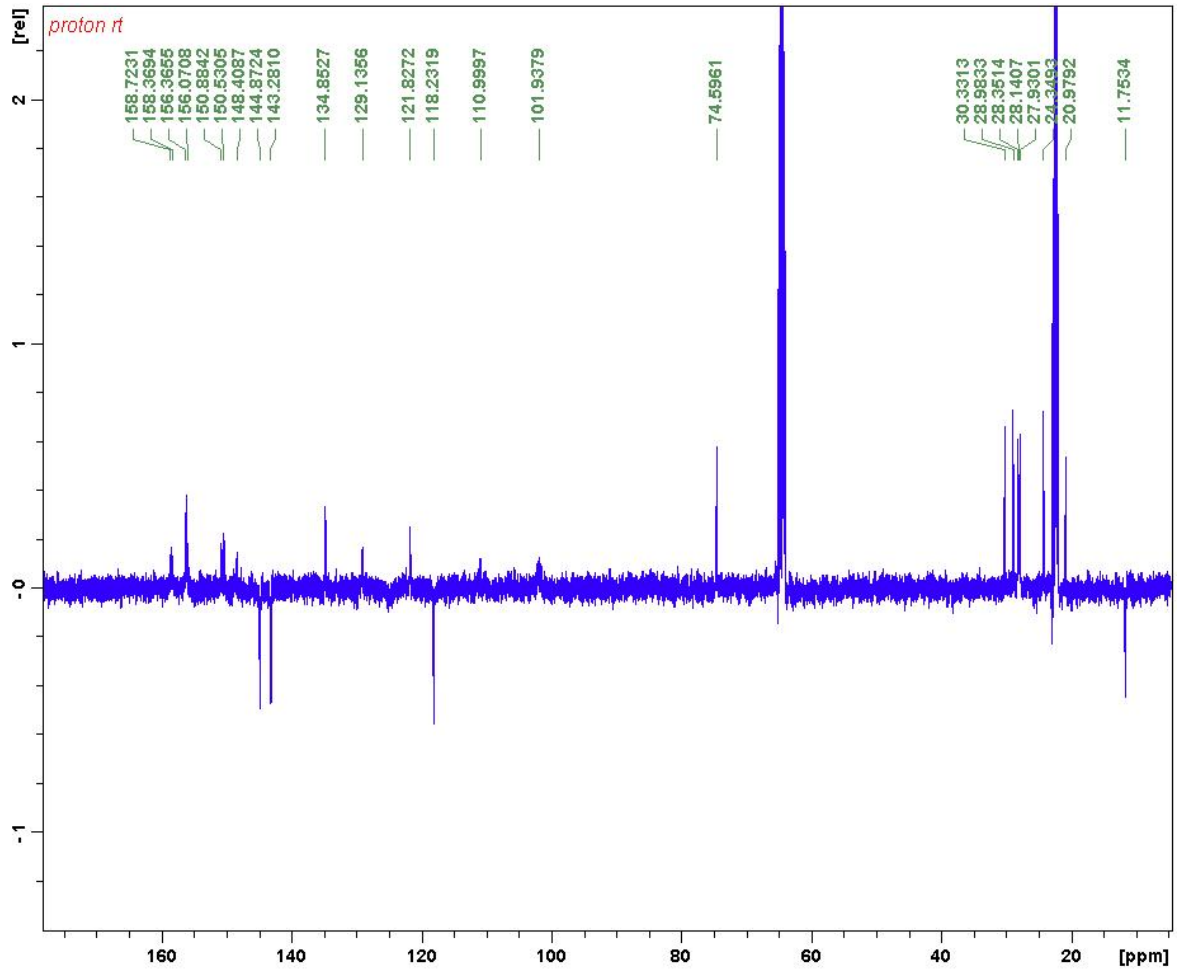


Figure S2. ^{13}C NMR-DEPTQ-135 (100 MHz) spectrum of **3** in THF-d_8 at room temperature

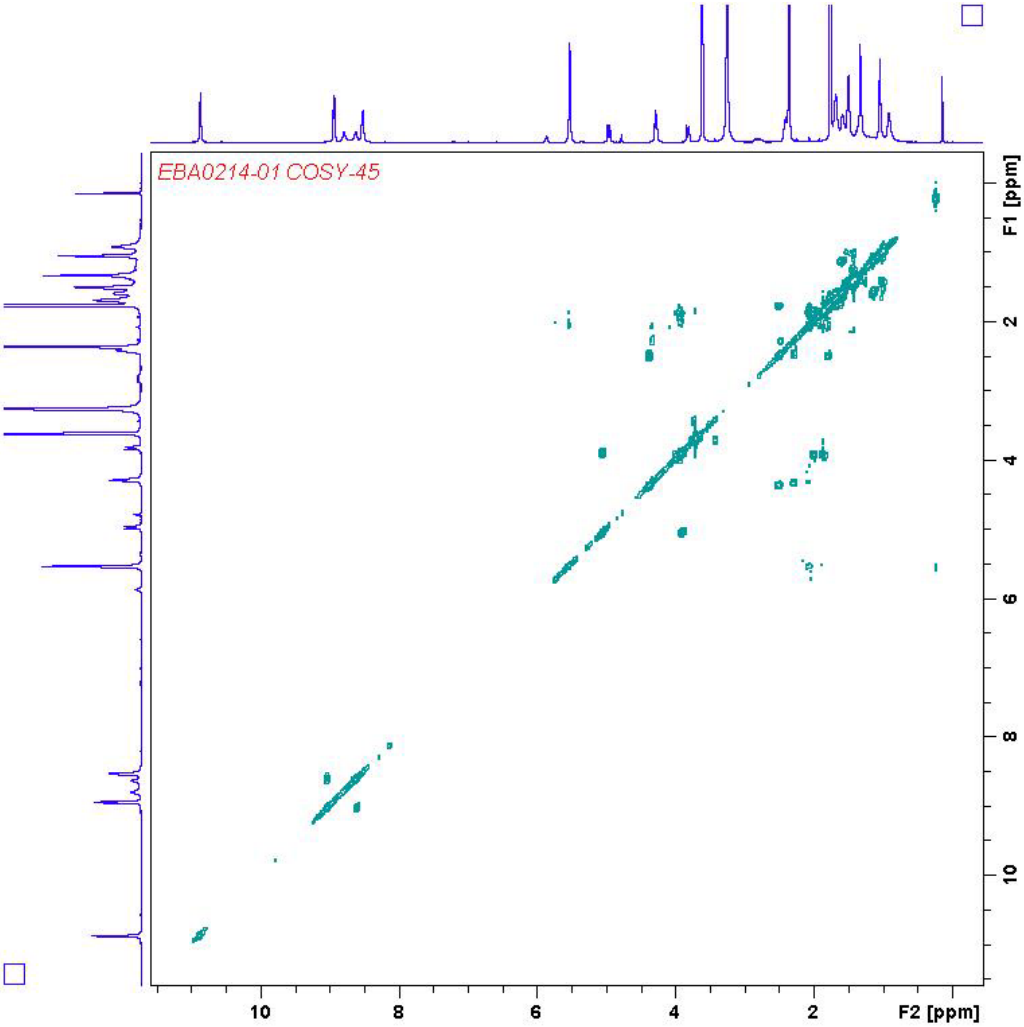


Figure S3. ^{1}H,^{1}H-2D COSY spectrum of **3** (400 MHz, THF-d_8, r.t.)

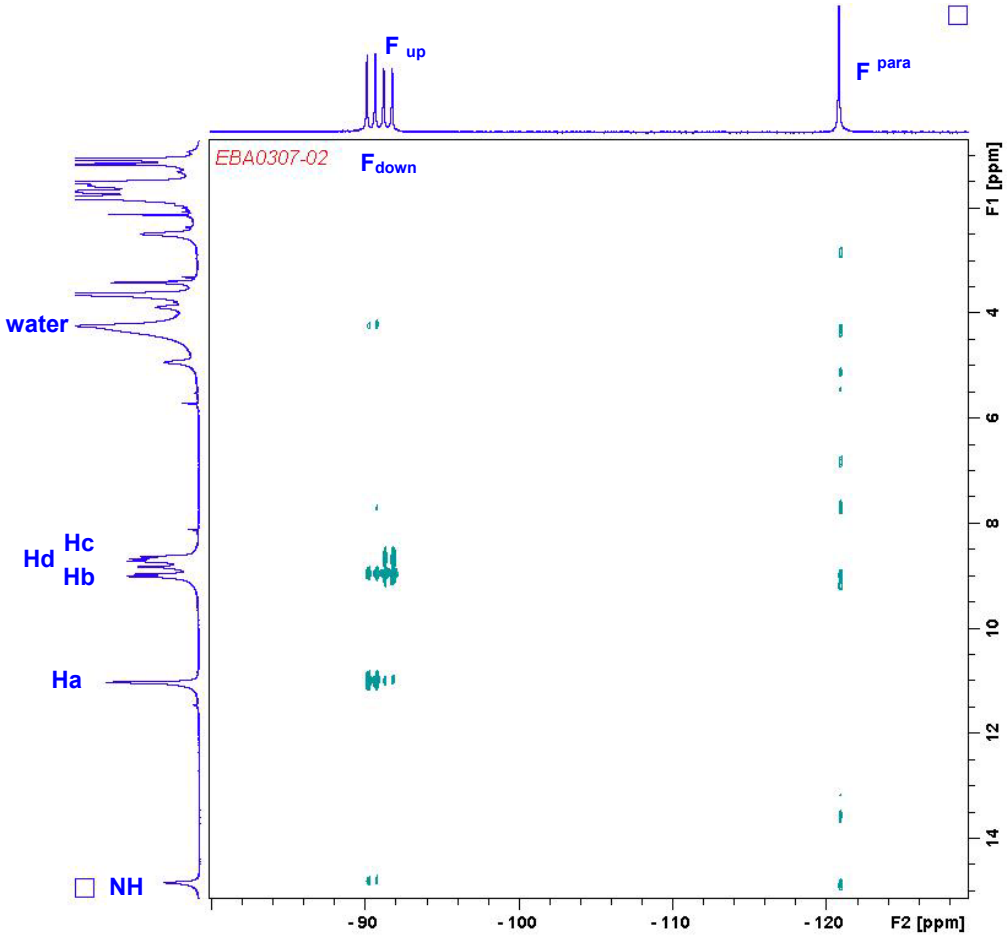


Figure S4. $^{1}H,^{19}F$-2D HOESY spectrum of **3** (500 MHz, THF-*d*8, at -53 ºC). The four *ortho* fluorine atoms can be assigned as two pointing upwards (F_{up}) and two pointing downwards the cavity (F_{down})

Thermogravimetric Analysis

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

The highest weight loss is observed in the temperature range 250-690 ºC where the Pd complex decomposes. Between 690 and 780 ºC, 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 ºC with a final residue of 12.00%, in good accordance with the chemical formula $C_{160}H_{112}Cl_{16}F_{24}N_{16}O_4Pd_4$.

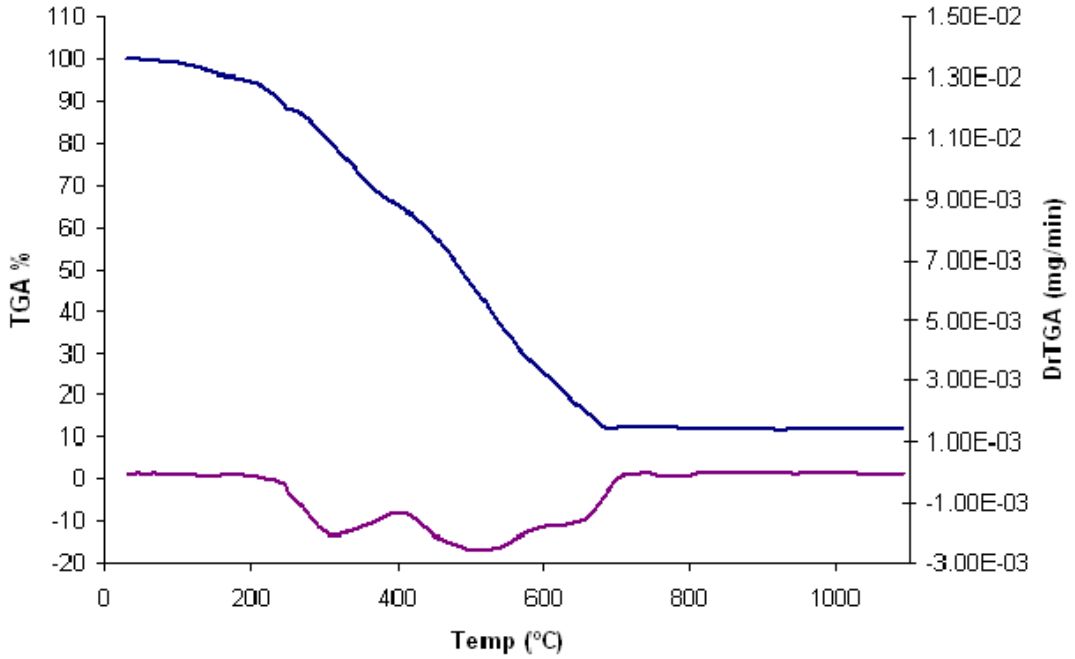


Figure S5. Thermogravimetric curve of **3**

Inclusion Complex

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

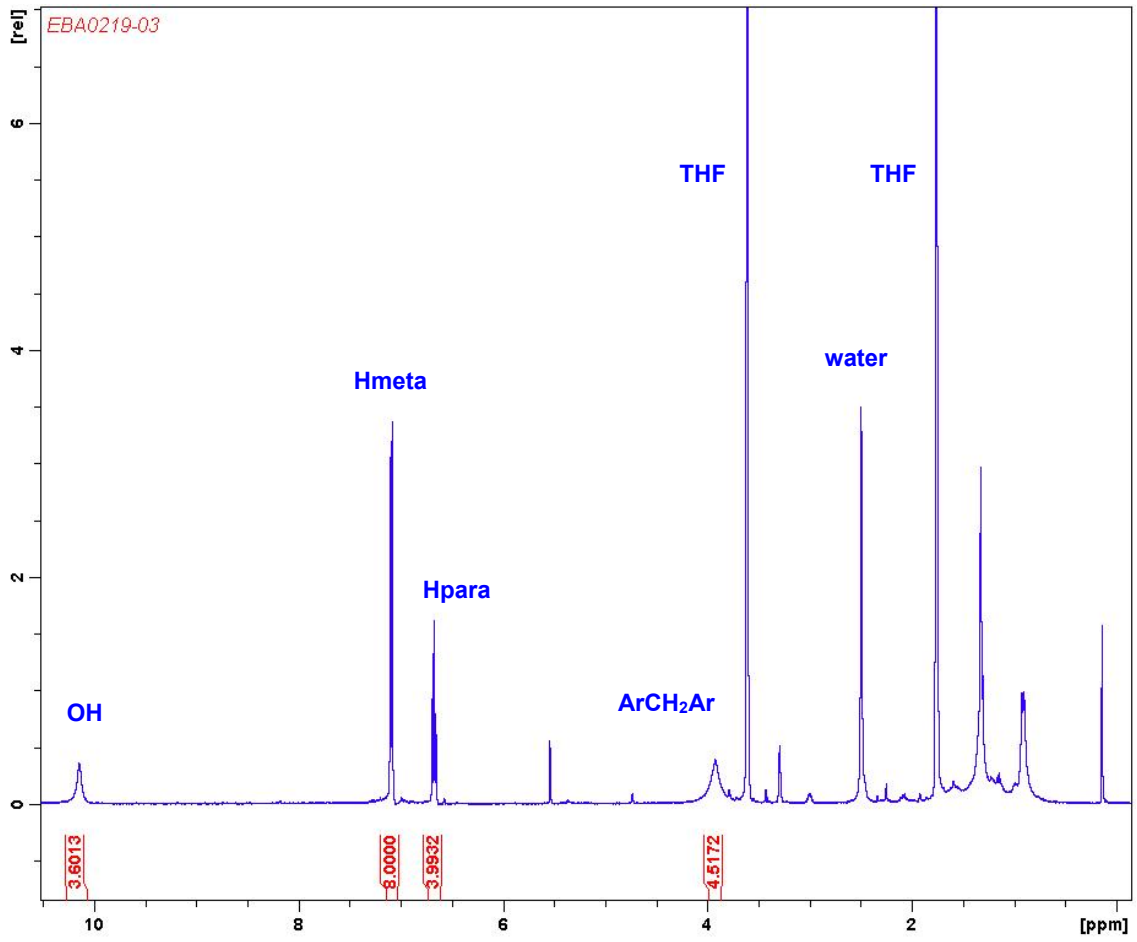


Figure S6. ^{1}H NMR (400 MHz, THF-d_8) spectrum of guest **5** at room temperature

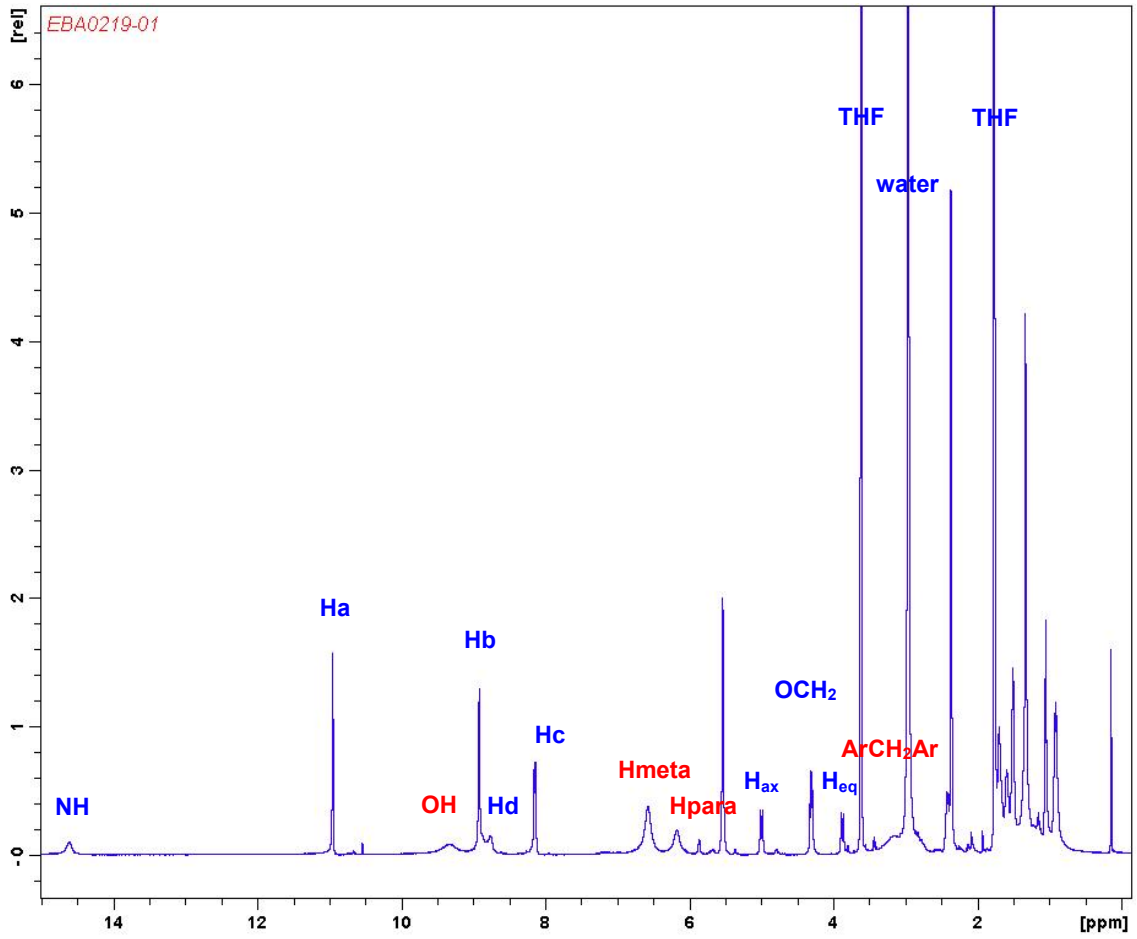


Figure S7. ^{1}H NMR (400 MHz, THF-d_8, r.t.) spectrum of a 1:1 mixture of compounds **3** (blue) and **5** (red)

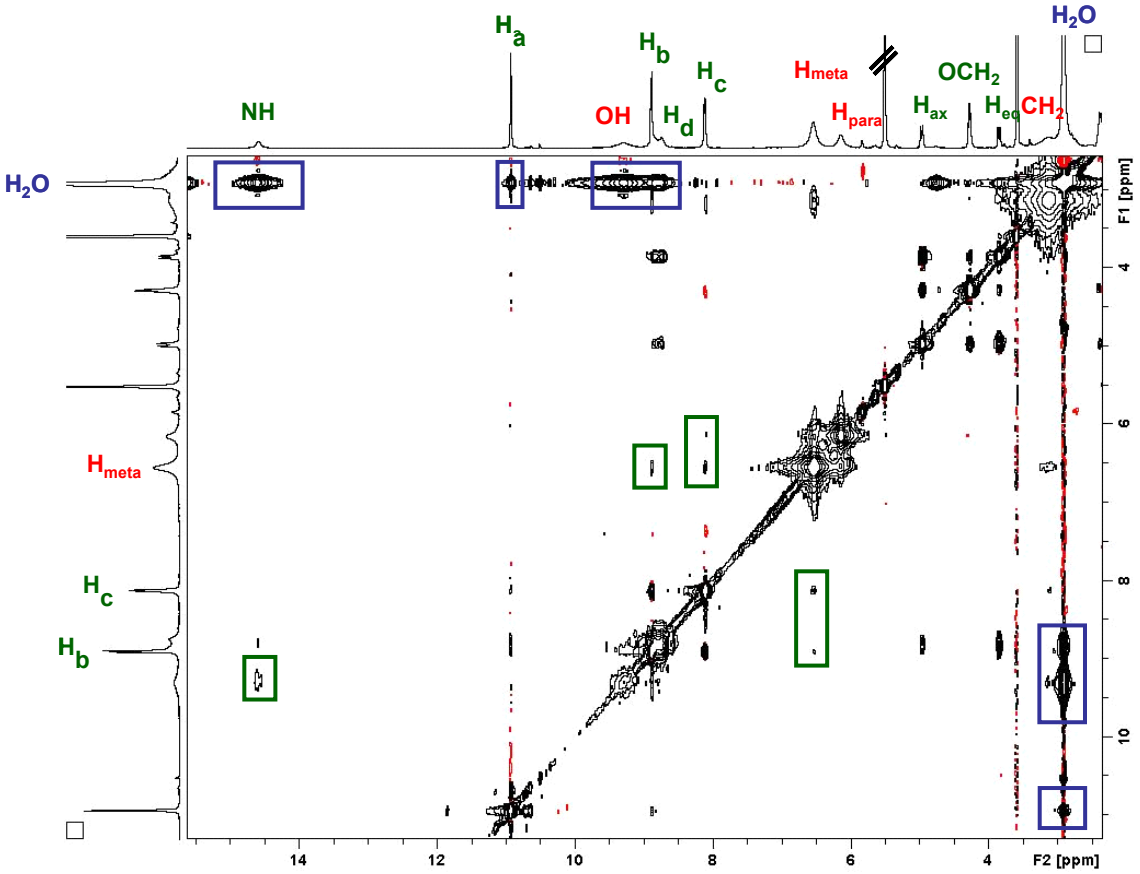
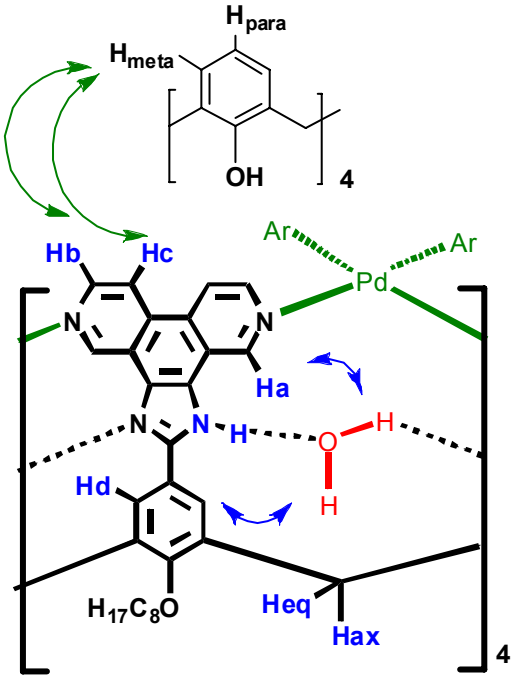


Figure S8. Top: ^{1}H,^{1}H-2D NOESY (400 MHz, 0.3 ms mixing time, r.t.) spectrum of **3** in THF-d_8. **Bottom:** intermolecular contacts scheme.



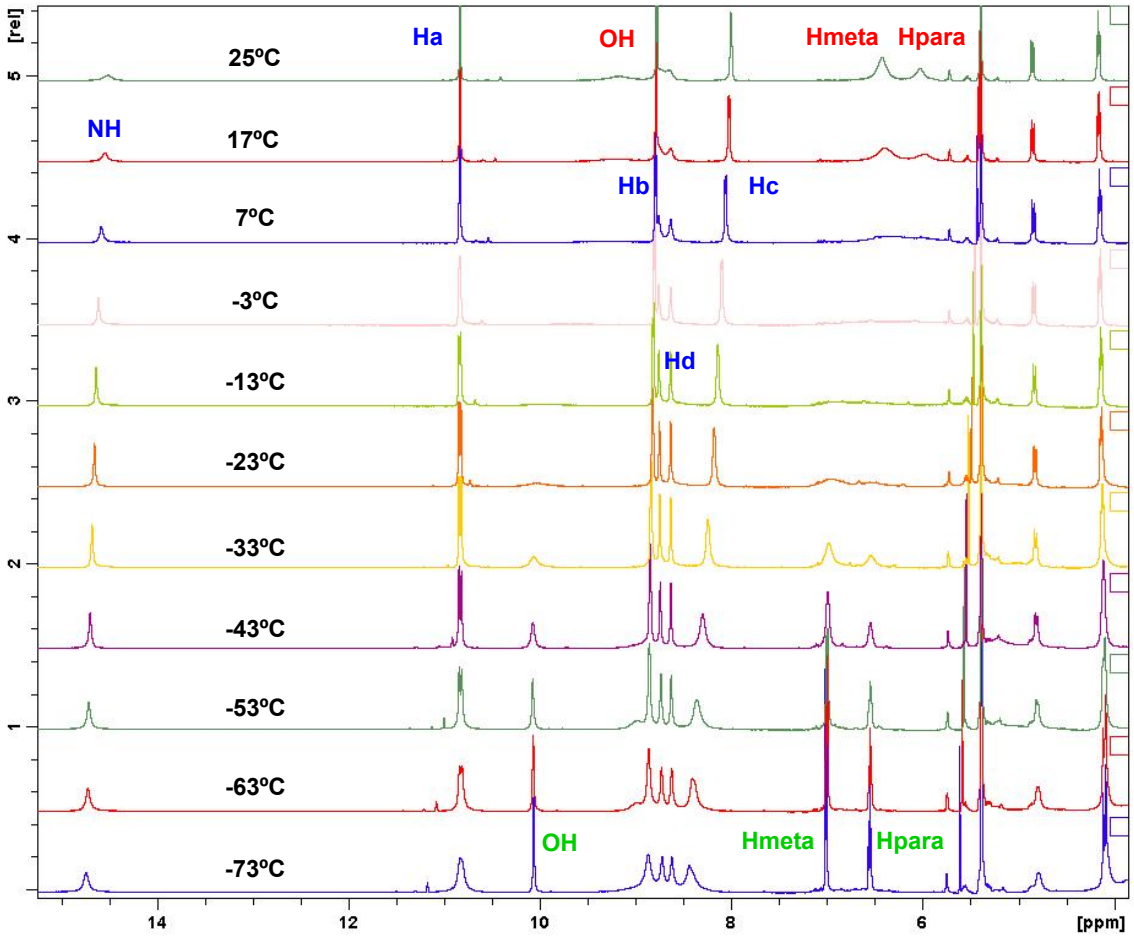


Figure S9. Variable Temperature ^{1}H-NMR of the **5@3** inclusion complex in THF-d_8 (1.9 mM). Host signals in blue, guest signals in red, free guest in green.

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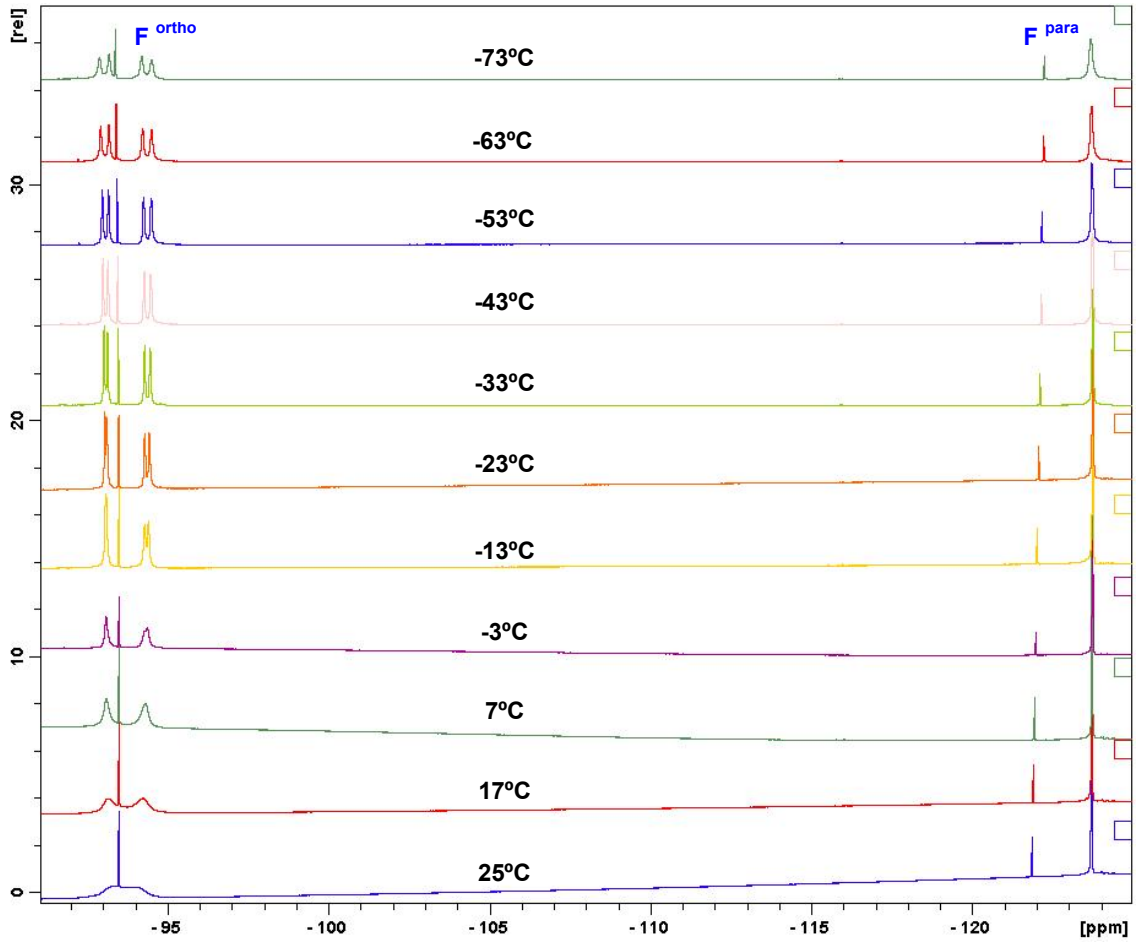

Figure S10. Variable Temperature ^{19}F-NMR of the **5@3** inclusion complex in THF-d_8.

^{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 x 10^{-3} M), containing host **3** (1.33 x 10^{-3} M), to a host **3** solution (1.33 x 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.

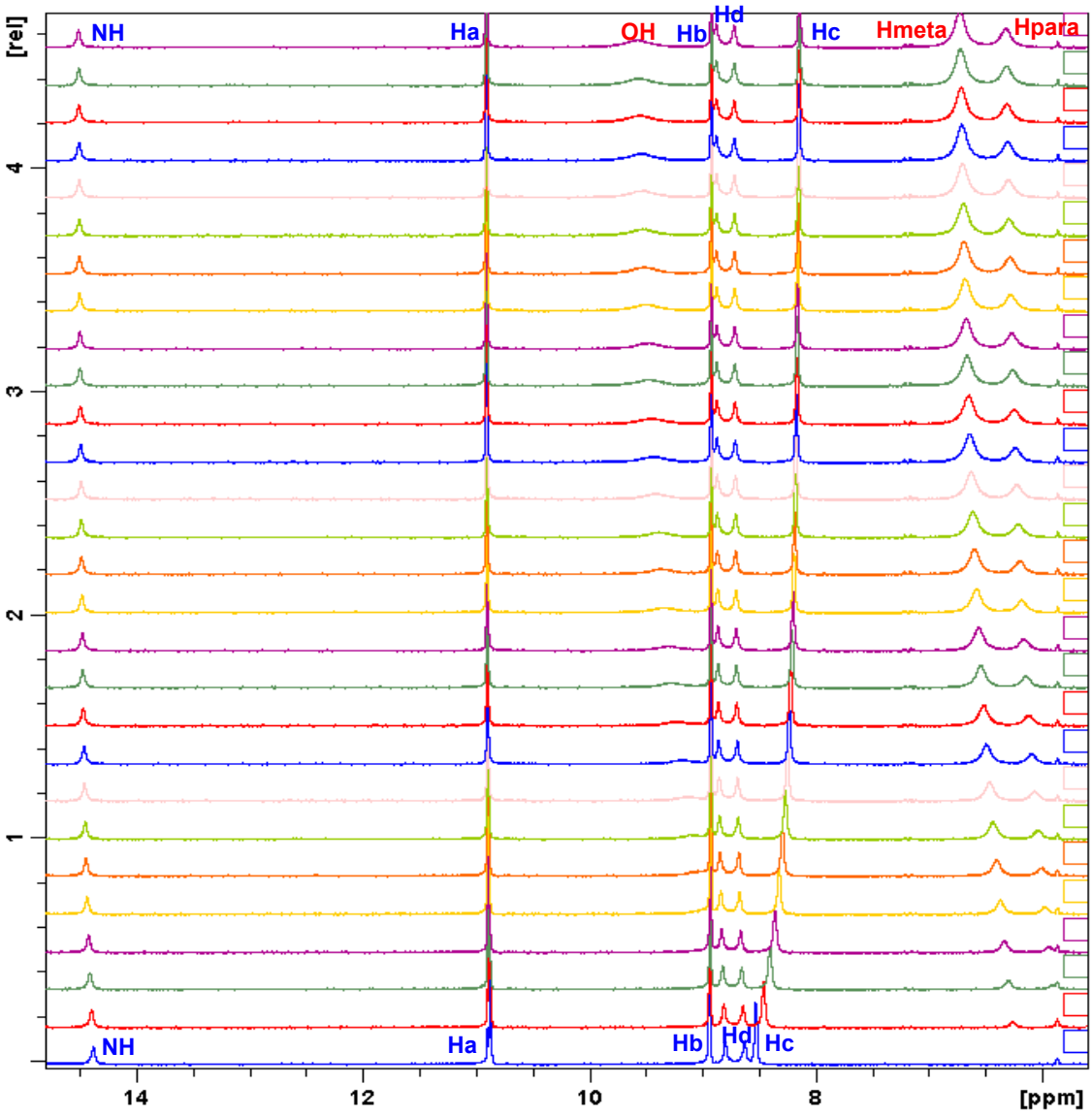

Figure S11. ^{1}H-NMR titration of the **5@3** inclusion complex in THF-d_8. Host signals in blue, guest signals in red.

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 x 10^3 for the **5@3** inclusion complex.

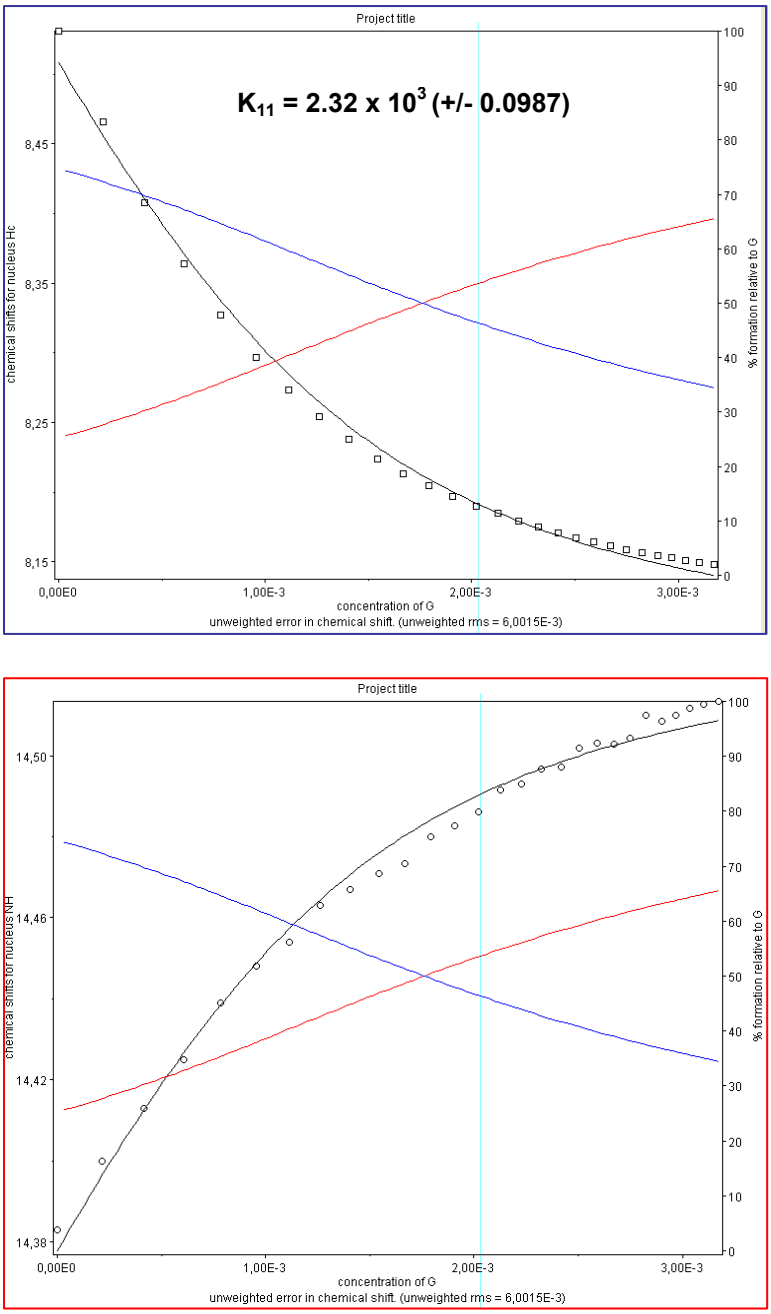

Figure S12. Isotherm fitting for Hc (top) and NH (bottom) protons and binding constant of **5@3** inclusion complex calculated by HypNMR 2006 software.

References:

[1] E. Botana, E. Da Silva, P. Ballester, J. Benet-Buchholz, J. de Mendoza, *Angew. Chem. Int. Ed.* 2007, **46**, 198.

[2] P. Espinet , J. M. Martínez-Ilarduya, C. Pérez-Briso, A. L. Casado, M. A. Alonso, *J. Organomet. Chem*. 1998, **551**, 9.

[3] J. Pérez, J. L. Serrano, J. M. Galiana, F. L. Cumbrera, A. L. Ortiz, G. Sánchez and J. García *Acta Crystallographica Section B* 2007, **63**, 75.

[4] P. Fortazzi, G. Groppi *Catalysis Today* 1999, **54**, 165.