Electronic Supplementary Material (ESI) for RSC Advances.

<Supporting Information>

Subtle backbone modifications control the interpenetration of dibenzosuberone-based coordination cages

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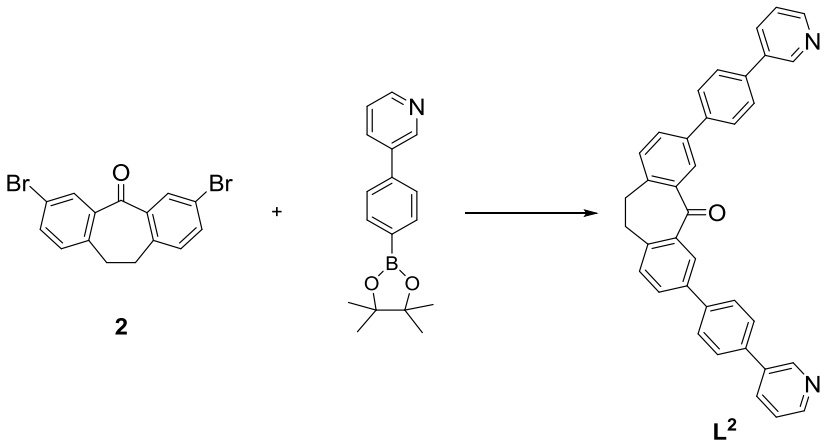
1. **Ligand syntheses**

A) Ligand **L**[2]

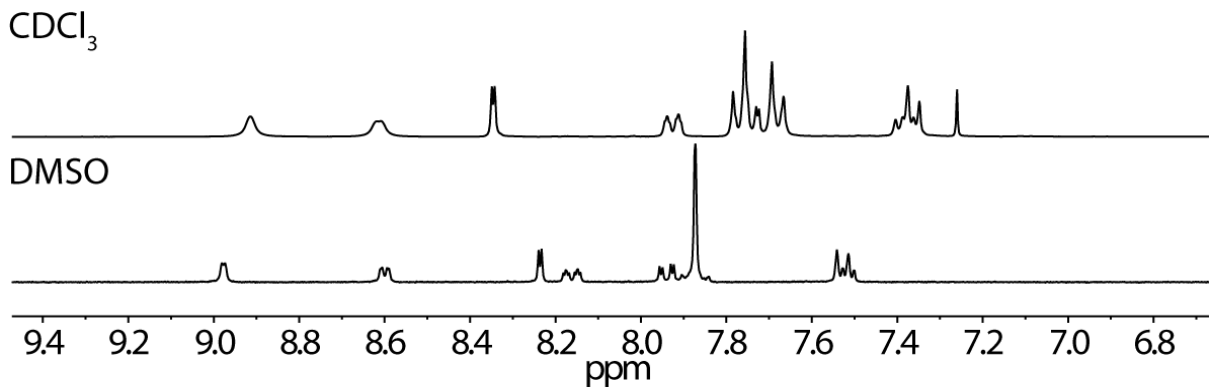


The syntheses of **2**[1] and the pyridine precursor are described in the literature.[2]

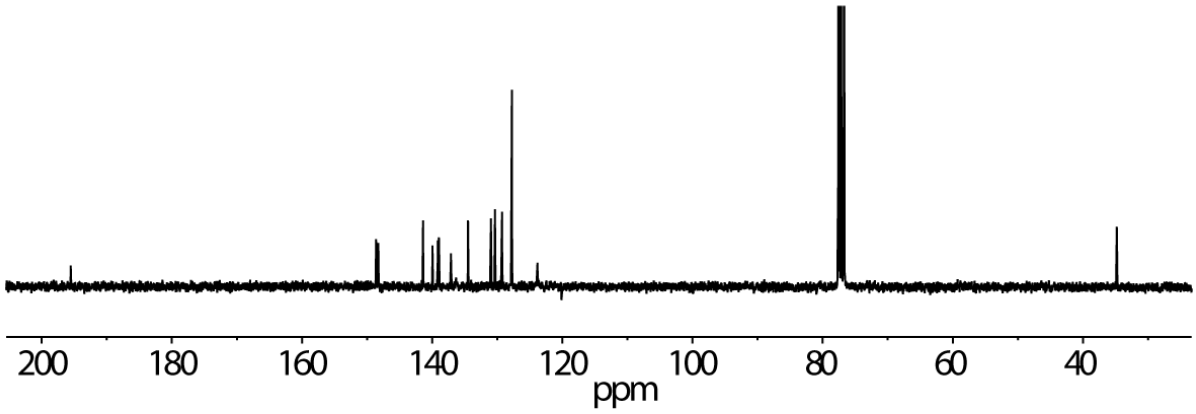
The Suzuki-cross-coupling reaction was performed under nitrogen atmosphere with dibromobenzosuberone (82 mg, 0.22 mmol, 1.0 eq.), 4-(3-pyridinyl)phenylboronic acid pinacol ester (190 mg, 0.67 mmol, 3.0 eq.), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol, 5 mol%) and $K_3PO_4 \cdot H_2O$(163 mg, 0.73mmol, 3eq.) in dioxane (6 mL) for 24 h at 95 °C. The solvent was evaporated under vacuum and the crude residue was purified by column chromatography on silica gel (SiO_2, $CHCl_3$/MeOH = 100:1) and washed with MeOH yielding the clean product (41 mg, 0.080 mmol, 36 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.31 (s, 4H), 7.34 – 7.42 (m, 4H), 7.66 – 7.80 (m, 10H), 7.92 (dt, *J* = 8.1, 1.9 Hz, 2H), 8.35 (d, *J* = 2.1 Hz, 2H), 8.61 (d, *J* = 4.0 Hz, 2H), 8.91 (s, 2H).

^{1}H-NMR (300 MHz, DMSO): δ [ppm] = 3.29 (s, 4H), 7.49 – 7.56 (m, 4H), 7.83 – 7.91 (m, 8H), 7.94 (dd, *J* = 7.9, 2.2, 2H), 8.16 (dt, *J* = 8.1, 2.0, 2H), 8.24 (d, *J* = 2.1, 2H), 8.60 (dd, *J* = 4.8, 1.6, 2H), 8.98 (d, *J* = 1.8, 2H).



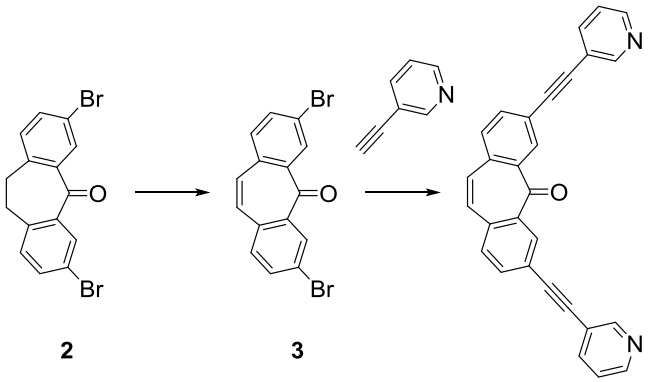
^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 34.79, 123.82, 127.75, 127.81, 129.26, 130.34, 130.96, 134.49, 137.10, 138.96, 139.13, 139.95, 141.41, 148.28, 148.62, 195.54. (the signal of one carbon is missing)



ESI-HRMS ($[C_{37}H_{26}N_2O+H^+]$): found: 515.2100

calc.: 515.2118

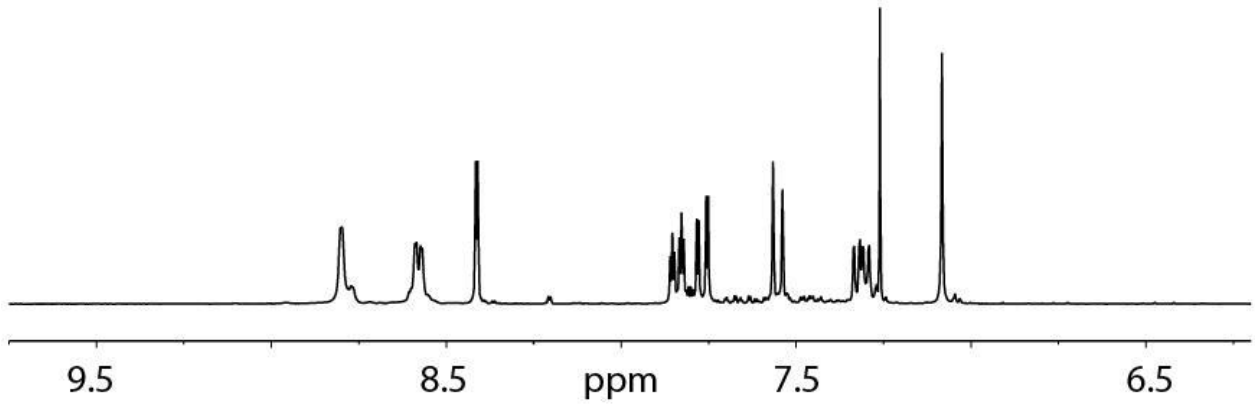
B) Ligand $\mathbf{L^{3a}}$



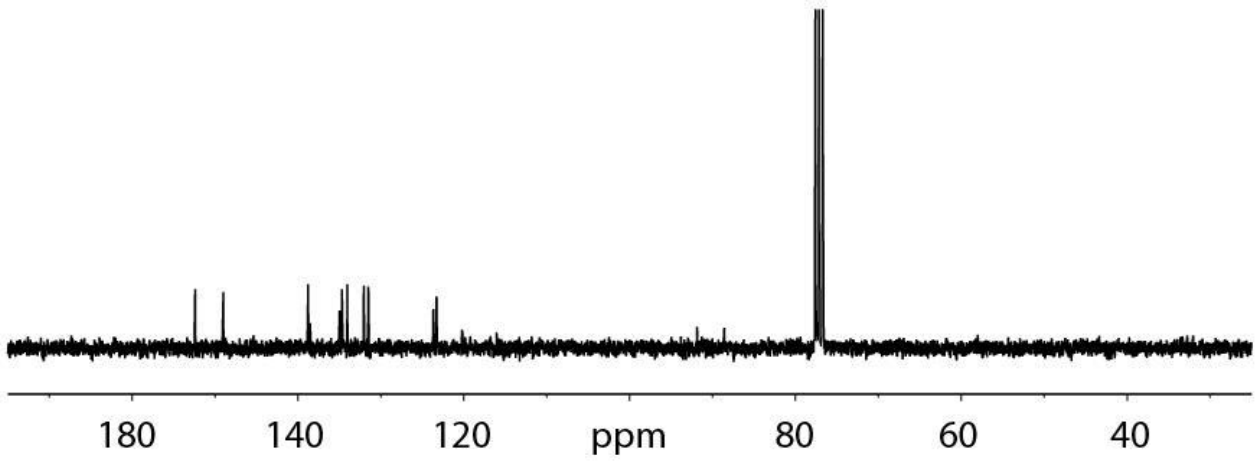
The synthesis of the dibenzosuberone **3** precursor is described in literature.[3]

The Sonogashira-cross-coupling reaction was performed under nitrogen atmosphere with the precursor **3** (50.0 mg, 0.12 mmol, 1.00 eq.), 3-ethynylpyridine (48.0 mg, 0.47 mmol, 3.39 eq.), $PdCl_2(PPh_3)_2$ (4.80 mg, 0,01 mmol, 5.00 mol%) and CuI (2.1 mg, 0.01 mmol, 8.03 mol%) in dry NEt_3 (2 mL) for 23 h at 90 °C. The solvent was evaporated under vacuum and the crude residue was purified by column chromatography on silica gel (SiO_2, $CHCl_3$/MeOH = 50:1 → 15:1). After evaporation of the solvent and washing with acetonitrile the product (20.0 mg, 0.05 mmol, 41 %) was obtained as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.08 (s, 2 H), 7.31 (ddd, *J* = 7.9, 4.9, 0.8 Hz, 2 H), 7.55 (d, *J* = 8.1 Hz, 2 H), 7.77 (dd, *J* = 8.1, 1.8 Hz, 2 H), 7.84 (dt, *J* = 7.9, 1.9 Hz, 2 H), 8.41 (d, *J* = 1.7 Hz, 2 H), 8.58 (dd, *J* = 4.8, 1.4 Hz, 2 H), 8.80 (s, 2 H).



^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 80.8, 91.8, 123.2, 123.5, 131.4, 132.0, 133.9, 134.5, 134.6, 134.9, 138.4, 138.8, 148.7, 152.1, 200.0.

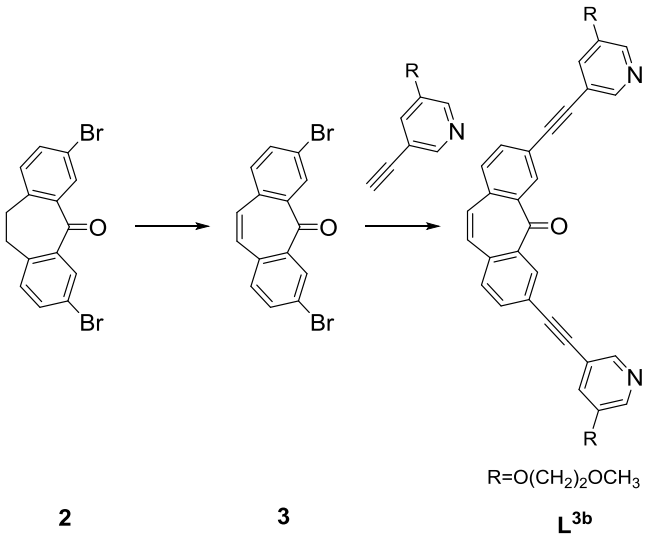


IR (ATR): ν [cm^{-1}] = 513, 620, 703, 744, 805, 828, 857, 893, 911, 932, 976, 1072, 1115, 1190, 1265, 1292, 1384, 1419, 1480, 1547, 1579, 1759, 1901, 2177, 2346, 2879, 2960.

ESI-HRMS ([$C_{29}H_{16}N_2O+H^+$]): found: 408.1265

calc.: 408.1263

C) Ligand $\mathbf{L^{3b}}$:



2 **3** $\mathbf{L^{3b}}$

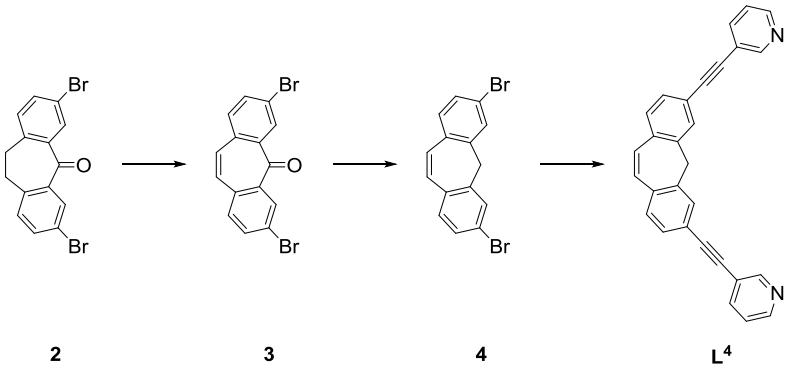
The Sonogashira-cross-coupling reaction was performed under nitrogen atmosphere with **3** (45.0 mg, 0.12 mmol, 1.00 eq.), 3-(2-methoxyethoxy-)ethoxy-5-ethynylpyridine (48.2 mg, 0.27 mmol, 2.20 eq.), $Pd(CN)_2Cl_2$ (2.00 mg, 6.00 µmol, 5.00 mol%), $HP(tBu)_3BF_4$ (4.6 mg, 12.0 µmol, 10.0 mol%) and CuI (1.60 mg, 0.06 µmol, 5.00 mol%) in dry DMF (5 mL) and dry NEt_3 (1 mL) for 24 h at 90 °C. The solvent was evaporated under vacuum and the crude residue was purified by column chromatography on silica gel (SiO_2, $CHCl_3$/MeOH = 20:1 → 10:1). After the evaporation of the solvent the product (41.5 mg, 75.0 µmol, 62 %) was obtained as a yellow solid.

^{1}H NMR (300 MHz, CD_3CN): δ [ppm] = 3.38 (s, 6H), 4.23 - 4.17 (m, 4H), 7.23 (s, 2H), 7.51 (dd, J = 2.8, 1.7 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.85 (dd, J = 8.1 Hz, J^4 = 1.8 Hz, 2H), 8.30 (d, J = 2.8 Hz, 2H), 8.32 (d, J = 1.8 Hz, 2H), 8.38 (d, J = 1.7 Hz, 2H).

ESI-HRMS ($[C_{35}H_{28}N_2O_5+H^+]$): found: 557.2065

calc.: 557.2071

D) Ligand $\mathbf{L^4}$



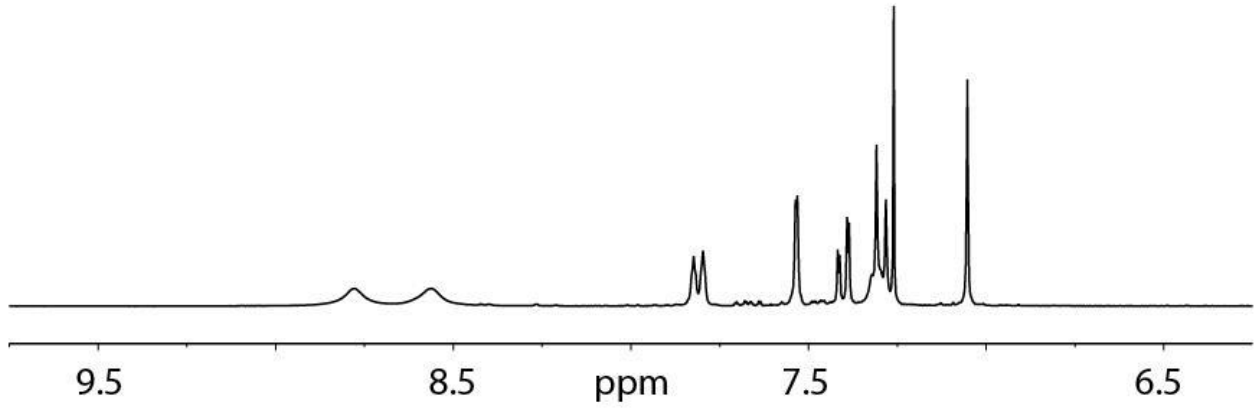
2 **3** **4** $\mathbf{L^4}$

The synthesis of the dibenzocycloheptatriene derivate **4** is described in the literature.[3]

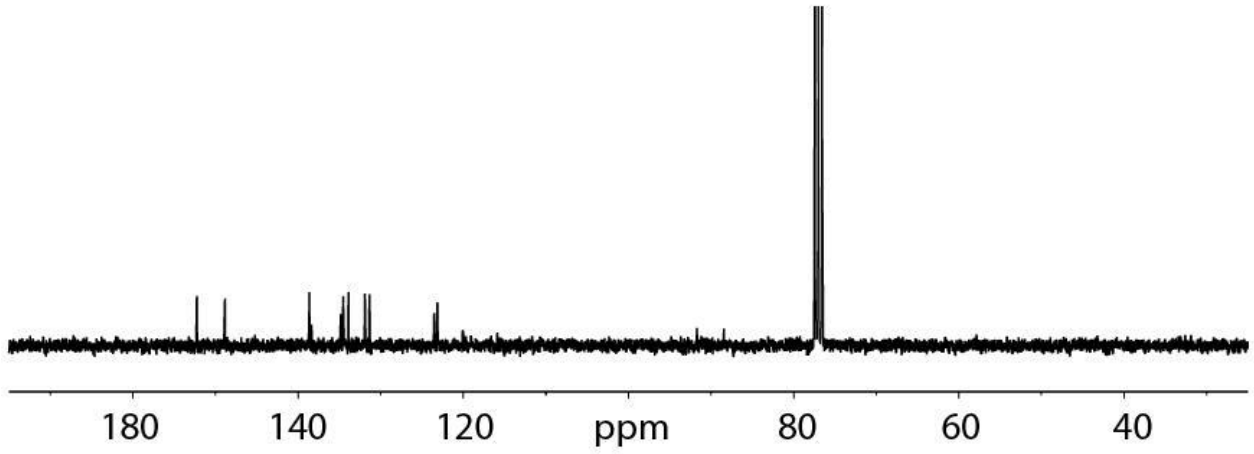
The Sonogashira-cross-coupling reaction was performed under nitrogen atmosphere with the precursor **4** (25.0 mg, 0.07 mmol, 1.00 eq.), 3-ethynylpyridin (24.8 mg, 0.24 mmol, 3.39 eq.), $PdCl_2(PPh_3)_2$ (2.50 mg, 3.00 µmol, 5.00 mol%) and CuI (1.20 mg, 0.01 mmol, 8.87 mol%) in dry NEt_3 (2 mL) for 23 h at 90 °C. The solvent was evaporated under vacuum and the crude residue was

purified by column chromatography on silica gel (SiO_2, $CHCl_3$/MeOH = 50:1 → 15:1). After the evaporation of the solvent the product (16.0 mg, 0.04 mmol, 57 %) was obtained as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.76 (s, 2 H), 7.06 (s, 2 H), 7.30 (d, J = 7.9 Hz, 2 H), 7.32 (s, 2 H), 7.40 (dd, J = 7.9, 1.6 Hz, 2 H), 7.54 (d, J = 1.3 Hz, 2 H), 7.81 (d, J = 7.9 Hz, 2 H), 8.57 (s, 2 H), 8.78 (s, 2 H).



^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 41.1, 87.3, 92.7, 122.7, 123.2, 128.3, 129.5, 131.2, 131.8, 135.7, 137.6, 148.4, 152.1. (the signals of two quaternary carbons are missing)



IR (ATR): ν [cm^{-1}] = 512, 543, 555, 626, 700, 722, 749, 803, 825, 845, 861, 896, 920, 948, 1019, 1039, 1093, 1120, 1165, 1186, 1261, 1329, 1407, 1431, 1472, 1497, 1560, 1579, 1599, 2920, 3026.

ESI-HRMS ([$C_{29}H_{18}N_2$+H^+]): found: 394.1477

calc.: 394.1470

2. **Self-assembly of coordination cages**

a) $[Pd_2\mathbf{L^2}_4](BF_4)_4$

Cage compound $[Pd_2\mathbf{L^2}_4](BF_4)_4$ was obtained in quantitative yield by heating a mixture of ligand $\mathbf{L^2}$ (0.693 mg, 1.34 µmol, 2.0 eq.) and $[Pd(CH_3CN)_4(BF_4)_2]$ (0.689 µmol, 45.9 µL of a 15 mM stock solution in d_6-DMSO) in d_6-DMSO (0.500 mL) at 70 °C for 24 h in a closed vial.

^{1}H NMR (300 MHz, DMSO): δ [ppm] = 3.19 (s, 16H), 7.47 (d, J = 8.0 Hz, 8H), 7.84 – 8.00 (m, 48H), 8.43 (d, J = 2.0 Hz, 8H), 8.48 (d, J = 8.1 Hz, 8H), 9.37 (d, J = 5.5 Hz, 8H), 9.62 (d, J = 2.1 Hz, 8H).

b) $[BF_4@Pd_4\mathbf{L^2}_8](BF_4)_7$

The double cage compound was obtained by heating a mixture of the ligand $\mathbf{L^2}$ (0.728 mg, 1.41 µmol) and a solution of $[Pd(CH_3CN)_4(BF_4)_2]$ (0.717 µmol, 47.8 µL of a 15 mM stock solution in CD_3CN) in CD_3CN (0.500 mL) at 70°C for 24 h in a closed vial.

^{1}H NMR (300 MHz, CD_3CN): δ [ppm] = 3.00 – 3.19 (m, 32H), 6.88 (d, J = 8.1 Hz, 16H), 7.05 – 7.10 (m, 8H), 7.21 (s, 8H), 7.42 (d, J = 7.9 Hz, 8H), 7.54 – 7.58 (m, 8H), 7.61 (d, J = 8.2 Hz, 16H), 7.74 – 7.86 (m, 40H), 8.00 (s, 8H), 8.02 – 8.05 (m, 16H), 8.06 – 8.09 (m, 8H), 8.39 (d, J = 7.9 Hz, 8H), 9.09 (d, J = 5.7 Hz, 8H), 9.51 (d, J = 6.7 Hz, 8H), 9.78 (s, 8H), 9.99 (s, 8H).

c) $[Pd_2\mathbf{L^{3a}}_4](BF_4)_4$

Cage compound $[Pd_2\mathbf{L^{3a}}_4](BF_4)_4$ was obtained by heating a mixture of ligand $\mathbf{L^{3a}}$ (0.62 mg, 1.52 µmol, 2.0 eq.) and $[Pd(CH_3CN)_4(BF_4)_2]$ (0.75 µmol, 50.0 µL of a 15 mM stock solution in CD_3CN) in CD_3CN (0.500 mL) at 23 °C in a closed vial. NMR signals assignable to the monomeric cage were recorded after a reaction time of about 10 minutes. Longer reaction times or heating the sample lead to the formation of an insoluble precipitate and the vanishing of all NMR signals.

^{1}H NMR (500 MHz, CD_3CN): δ [ppm] = 7.22 (s, 8H), 7.62 (ddd, J = 8.1, 5.9, 0.7 Hz, 8H), 7.71 (d, J = 8.1 Hz, 8H), 7.88 (dd, J = 8.1 Hz, 1.8, 8H), 8.20 (dt, J = 8.1, 1.6 Hz, 8H), 8.42 (d, J = 1.8 Hz, 8H), 8.70 (dd, J = 5.6, 1.3 Hz, 8H), 8.95 (d, J = 1.8 Hz, 8H).

d) $[BF_4@Pd_4\mathbf{L^{3b}}_8](BF_4)_7$

The double cage compound was obtained by heating a mixture of the ligand $\mathbf{L^{3b}}$ (0.88 mg, 1.53 µmol) and a solution of $[Pd(CH_3CN)_4(BF_4)_2]$ (0.75 µmol, 50.0 µL of a 15 mM stock solution in CD_3CN) in CD_3CN (0.500 mL) at 70 °C for 24 h in a closed vial.

^{1}H NMR(500 MHz, CD_3CN):δ [ppm] = 2.93 – 4.30 (-$OCH_2CH_2OCH_3$, 56H), 6.67 (dd, J = 8.0, 1.8 Hz, 4H), 6.94 (dd, J = 2.7, 1.3 Hz, 4H), 7.02 (s, 4H), 6.97 (s, 4H), 7.17 (dd, J = 8.2 Hz, 4H), 7.60 (d, J = 1.8 Hz, 4H), 7.65 (d, J = 8.1 Hz, 4H), 7.77 (dd, J = 2.5, 1.8 Hz, 1H), 7.84 (d, J = 8.0, 1.3 Hz, 4H), 7.95 (d, J = 1.8 Hz, 4H), 8.73 (d, J = 2.6 Hz, 4H), 9.20 (d, J = 1.2 Hz, 4H), 9.65 (d, J = 2.6 Hz, 4H), 10.01 (d, J = 1.2 Hz, 4H).

e) $[Pd_2\mathbf{L^4}_4](BF_4)_4$

Cage compound $[Pd_2\mathbf{L^4}_4](BF_4)_4$ was obtained in quantitative yield by heating a mixture of ligand $\mathbf{L^4}$ (0.61 mg, 1.55 µmol) and $[Pd(CH_3CN)_4(BF_4)_2$ (0.831 µmol, 55.4 µL of a 15 mM stock solution in CD_3CN) in CD_3CN (0.554 mL) at 70 °C for 24 h in a closed vial.

^{1}H NMR (500 MHz, CD_3CN): δ [ppm] = 3.79 (s, 8H), 7.12 (s, 8H), 7.39 (d, J = 8.0 Hz, 8H), 7.49 (dd, J = 8.0, 1.7 Hz, 8H), 7.55 - 7.58 (m, 8H), 7.64 (d, J = 1.6 Hz, 8H), 8.20 (dt, J = 8.2, 1.6 Hz, 8H), 8.44 – 8.50 (m, 8H), 8.75 (d, J = 1.8 Hz, 8H).

3. **Calculation details**

Input structures are based on manual modifications of the X-ray structural data of the previously reported double-cage $[BF_4@Pd_4\mathbf{L^1}_8](BF_4)_7$.[1] For structure manipulation, the Spartan '08 software package was used.[4] PM6 and DFT calculations were performed using the program Gaussian '09.[5] Semiempiric gas phase calculations were performed on the PM6 level of theory.[6] DFT calculations used the def2 basis sets[7] and dispersion corrected M06[8] or ωB97XD functionals.[9]

4. **Literature**

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