# Supporting Information

Versatile Formation of [2]Catenane and [2]Pseudorotaxane Structures; Threading and Noncovalent Stoppering by a Self-Assembled Macrocycle

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^{1}H NMR spectra:

1) Pseudorotaxane formation ($\downarrow$, 500 MHz) by the addition of γ-CD to the macrocyclic complex **M** (2 mM) derived from Pd(en) in D_2O, according to the equivalents of γ-CD added (a) 0 equiv, (b) 0.4 equiv, (c) 0.8 equiv, (d) 1.2 equiv, (e) 1.5 equiv.
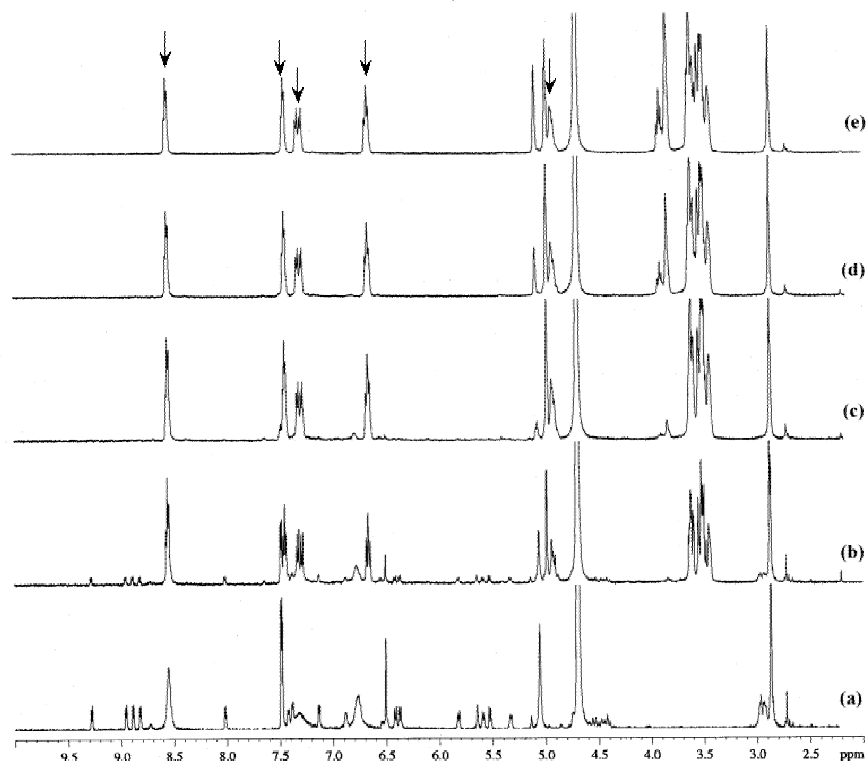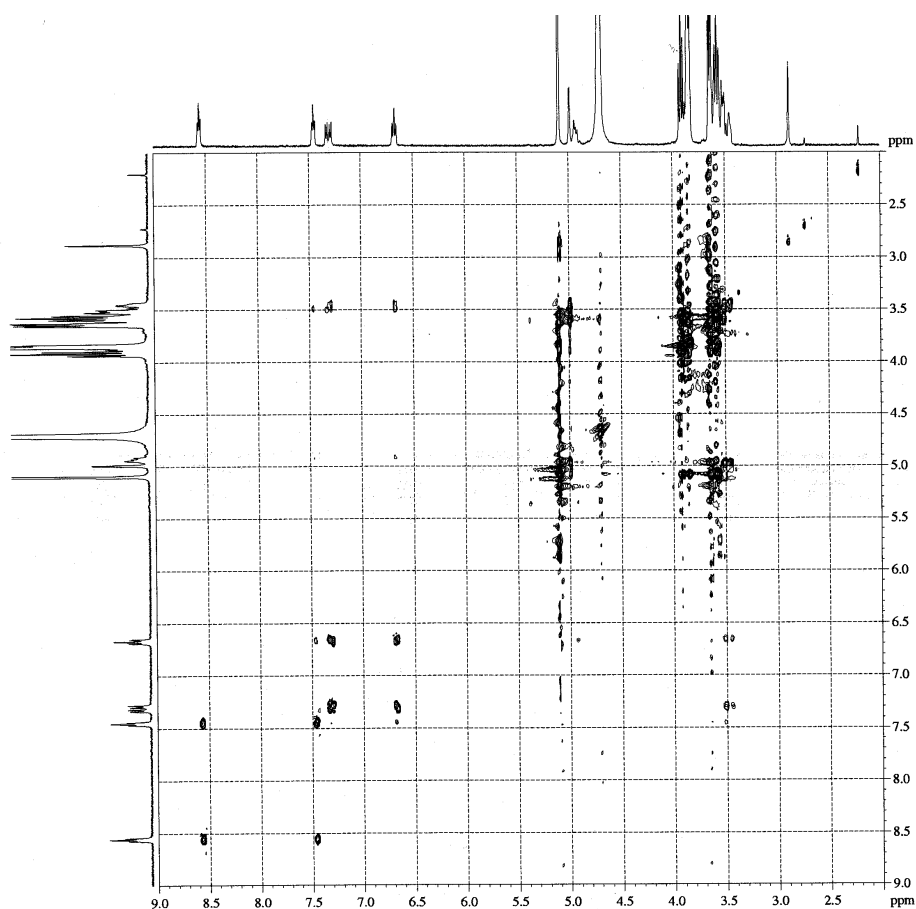
2) Pseudorotaxane formation ($\downarrow$, 300 MHz) by the the addition of γ-CD to the macrocyclic complex **M'** (0.1 mM) derived from Pd(1,2-diaminocyclohexane) in D_2O, according to the equivalents of the γ-CD added (a) 0 equiv, (b) 4 equiv.
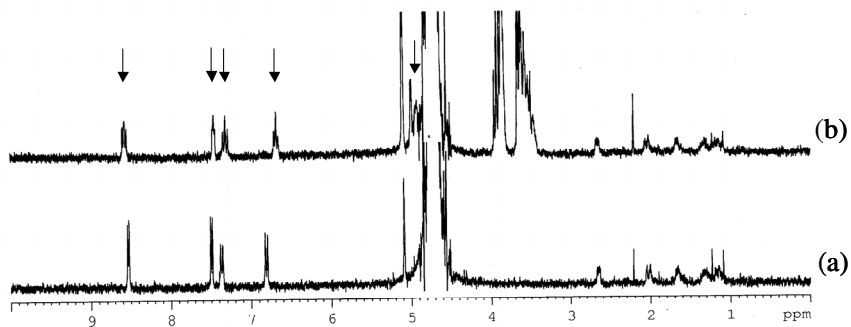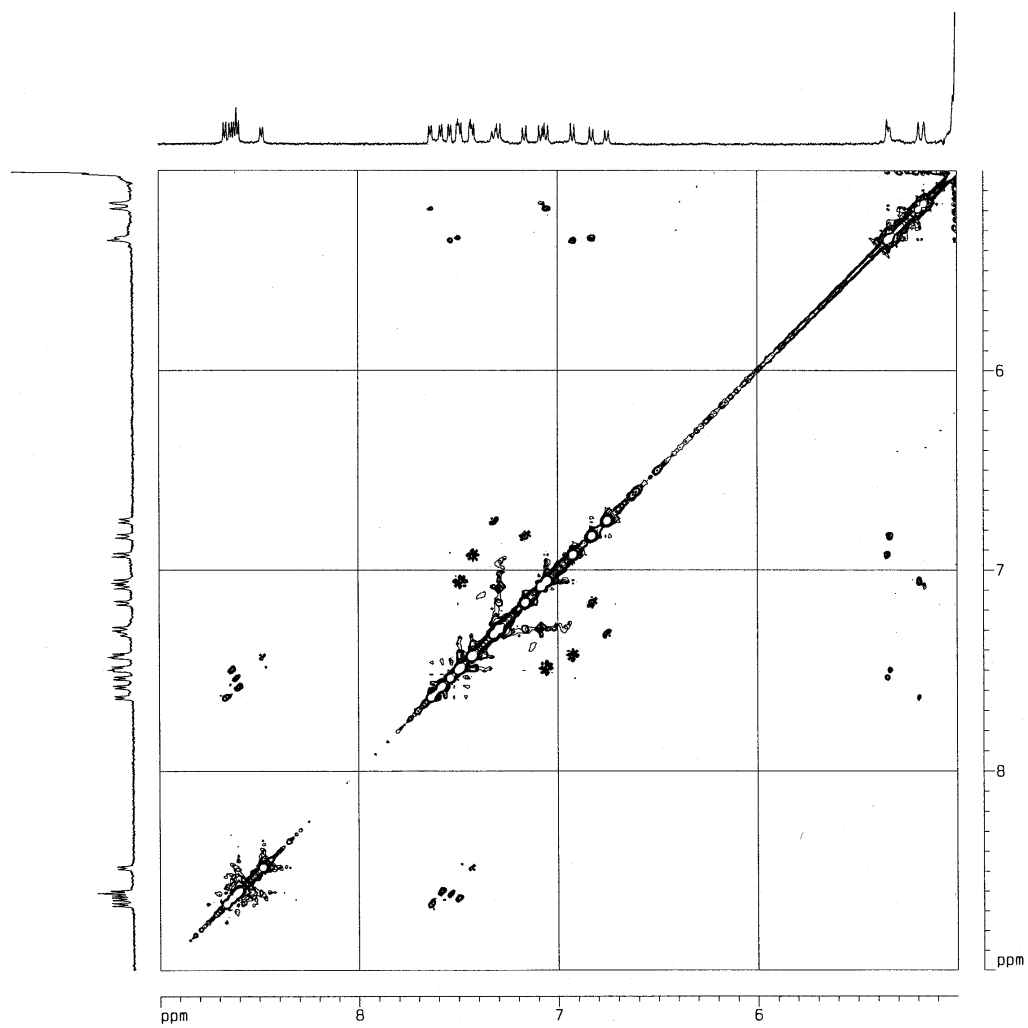
HH COSY spectrum (600 MHz, D_2O) of the aromatic regions of the macrocyclic part in the [2]catenane structure and the free macrocyclic Pd (II) complex **M** (↓), respectively.
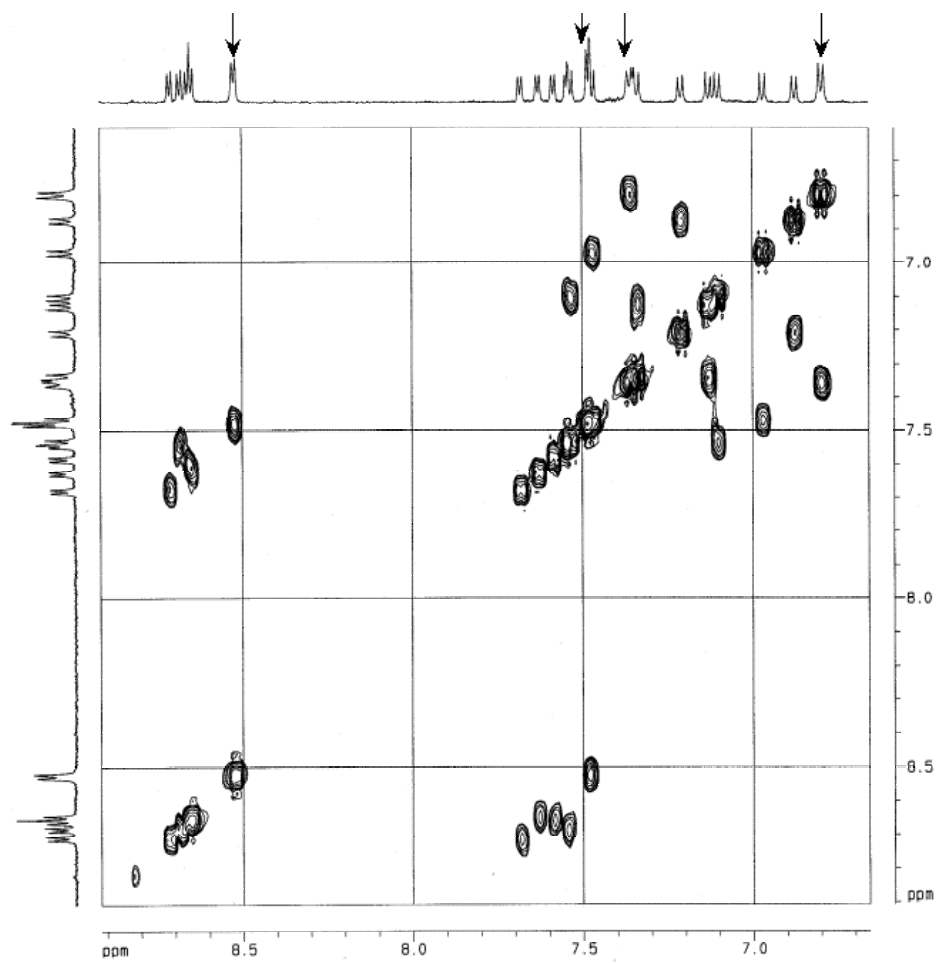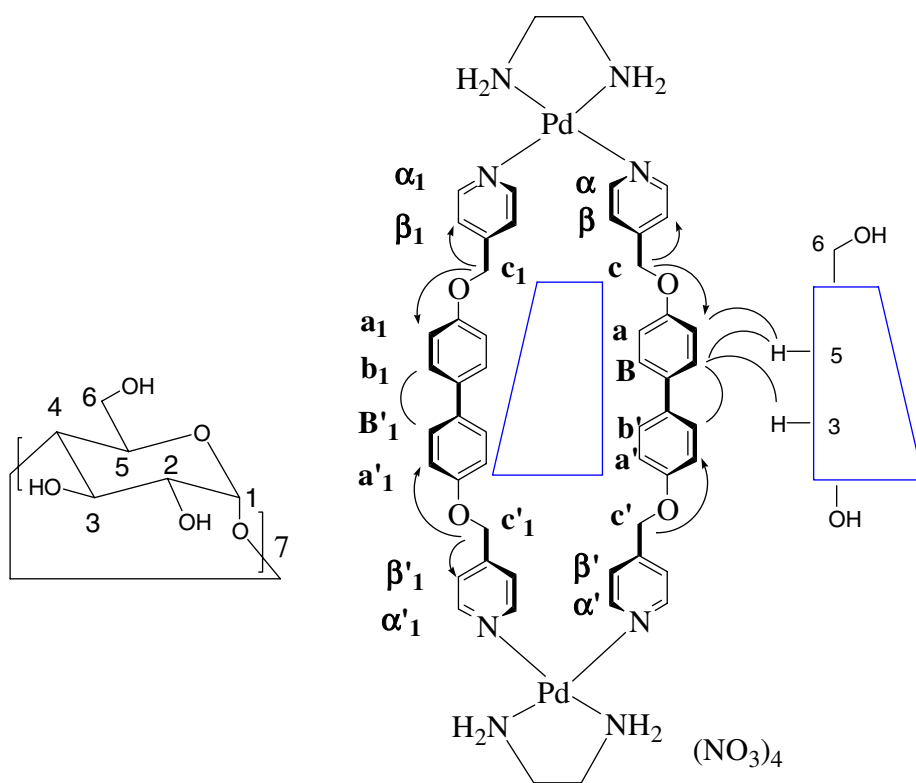
2D ROESY spectra of the [2]pseudorotaxane structure: the two-dimensional rotating frame Overhauser experiment (ROESY) was performed according to the pulse sequence: -90° - D0 - spin-lock - FID (D1 is relaxation delay and D0 is the incremental delay). The experiment was performed in phase-sensitive mode using time-proportional phase increment (TPPI), and a full-regulated power was used for excitation (1 db attenuation). The attenuation employed for the cw spin-lock field was 22.5 db. The solvent was presaturated before the start of the main sequence by slightly modifying the standard Bruker pulse program. A spin-lock time of 800 ms was used when the experiment was carried out. The experimental parameters used were S1 = 2 s, Δd0 = 3 μs, SW = 11.1 ppm. In the F1 domain, TD1 = S1 = 512 data points. In the F2 domain, TD = SI = 1K data points. NS = 128 and DS = 4. The data were processed with a sine-bell window function shifted by π/2 in both domain and phased so that the ROE cross-peaks were anti-phase with the diagonal (HOHAHA cross-peaks appear in phase with the diagonal). Automated base-line correction was applied in both frequency domain and maximum spectral clarity was achieved by the careful subtraction of typical "background" noise from all the row and column data after Fourier transformation.

2D NOESY spectra (600 MHz, D$_2$O) of the [2]Catenane structure;

The proposed assignments of the [2]Catenane structure for the cross-peaks arising from through-space correlations; Strong interactions (**arrow**) and weak interactions (**line**).

Selective 1D NOE spectra (600 MHz) in D_2O at 298 K;

(a) ^{1}H NMR spectrum of [2]Catenane structure (irradiations of **B** and **B'$_1$** protons), (b) irradiations of **B** protons, (c) irradiations of **B'$_1$** protons.; the enhancements (↑) by irradiations (↓).
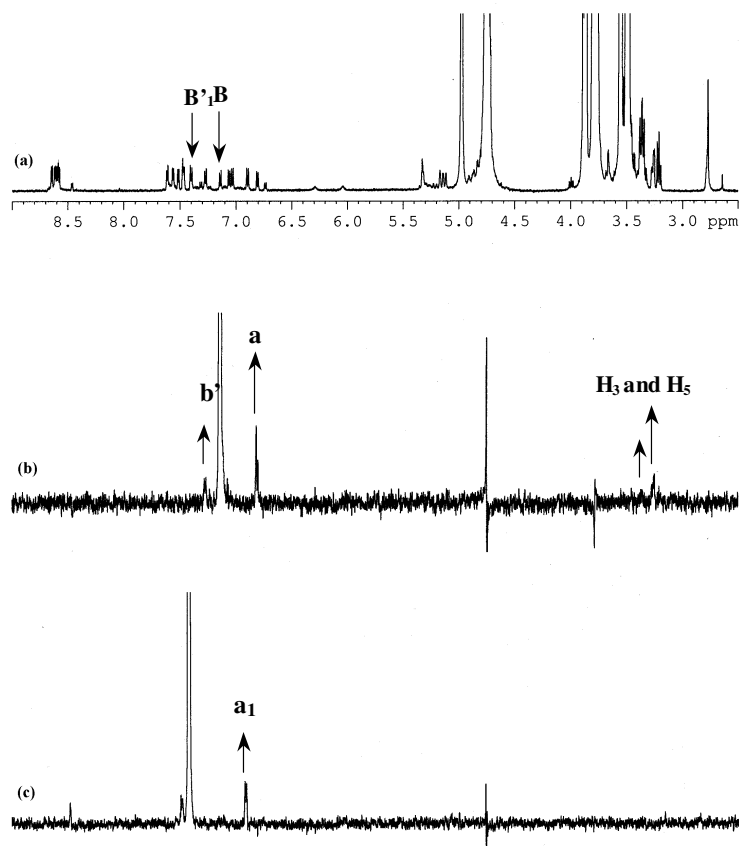
Partial ^{1}H NMR Spectrum (500 MHz, D_2O) of [2]Catenane Structure
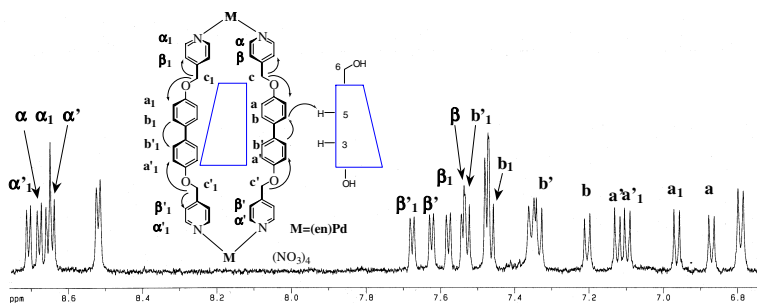
CSI-MS spectrum of the [2]pseudorotaxane structure:

The isotope patterns of $[M+\gamma\text{-CD-3(NO}_3)]^{3+}$ and $[M+\gamma\text{-CD-2(NO}_3)]^{2+}$ Fragment ions.