Electronic Supplementary Information

Thermodynamically controlled self-sorting of hetero-bimetallic metallo-supramolecular macrocycles: What a difference a methylene group makes!

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General: All chemicals were of reagent grade quality and used as obtained from commercial suppliers without further purification. Solvents were used as received or - if necessary - dried over 4 Å molecular sieve. Ligand **1**[1] and metal complexes Pd(dppp)OTf$_2$ **2**[2], Pt(dppp)OTf$_2$ **3**[3], Pd(dppe)OTf$_2$ **4**[2] and Pt(dppe)OTf$_2$ **5**[3] were prepared as described in the literature.

Instrumentation and methods: ^{1}H and ^{31}P spectra were recorded with a Bruker ECX 400 instrument. All chemical shifts are reported in ppm with solvent signals taken as internal standards. The electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrometric experiments were performed with a Varian/IonSpec QFT-7 FTICR mass spectrometer equipped with a superconducting 7 Tesla magnet and a micromass Z-spray ESI ion source utilizing a stainless steel capillary with a 0.65 mm inner diameter. The sample solutions were introduced into the source with a syringe pump (Harvard Apparatus) at a flow rate of ca. 2.0 μL·min^{-1}. Parameters were adjusted as follows: Source temperature: 40 °C; temperature of desolvation gas: 40 °C; parameters for capillary voltage, sample and extractor cone voltages are optimized for maximum intensities. No nebulizer gas was used for the experiments. The ions were accumulated in the instrument's hexapole for 2 to 5 s. Next, the ions were transferred into the FTICR analyzer cell by a quadrupole ion guide. The FTICR

cell was operated at pressures below 10^{-9} mbar, and the ions were detected by a standard excitation and detection sequence. For tandem mass spectrometric experiments, the ions of interest were mass-selected and subsequently vibrationally excited with a CO_2 laser in the IR region (infrared multiphoton dissociation (IRMPD), 10.6 μm wavelength) for the time intervals indicated in the Figures to induce fragmentation. The laser power was set to 5 W (20% of the max. 25 W). For each measurement, 10 to 20 scans were averaged to improve the signal-to-noise ratio.

## General procedure for the preparation of Pt or Pd assemblies as their triflate salts

*Preparation of 1:1 mixtures of ligand **1** with metal centres **2** - **5**:*

In separate glass vials, ligand **1** (0.88 mg, 2.46 μmol) was mixed in CD_2Cl_2 (0.25 ml) with metal centres Pd(dppp)OTf₂ **2** (2 mg, 2.46 μmol), Pt(dppp)OTf₂ **3** (2.22 mg, 2.46 μmol), Pd(dppe)OTf₂ **4** (1.98 mg, 2.46 μmol) or Pt(dppe)OTf₂ **5** (2.18 mg, 2.46 μmol) which were suspended in 0.25 ml CD_2Cl_2 each before mixing. The mixtures were stirred at r.t. for 12 h. The solutions were then transferred into NMR tubes for analysis and subsequently investigated with FTICR mass spectrometry.

*Preparation of 1:2 mixtures of ligand **1** with metal centres **2** - **5**:*

In separate glass vials, ligand **1** (0.44 mg, 1.23 μmol) was mixed in CD_2Cl_2 (0.25 ml) with two different metal centres Pd(dppp)OTf₂ **2** (2 mg, 2.46 μmol), Pt(dppp)OTf₂ **3** (2.22 mg, 2.46 μmol), Pd(dppe)OTf₂ **4** (1.98 mg, 2.46 μmol) or Pt(dppe)OTf₂ **5** (2.18 mg, 2.46 μmol) in CD_2Cl_2 (0.25 ml) which were suspended in 0.25 ml CD_2Cl_2 each before mixing. The mixtures were stirred at r.t. for 3 d to reach thermodynamic equilibrium. The solutions were transferred into NMR tubes for analysis and subsequently investigated with FTICR mass spectrometry.

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3. F. Fochi, P. Jacopozzi, E. Wegelius, K. Rissanen, P. Cozzini, E. Marastoni, E. Fisicaro, P. Manini, R. Fokkens and E. Dalcanale, *J. Am. Chem. Soc.* 2001, **123**, 7539-7552.
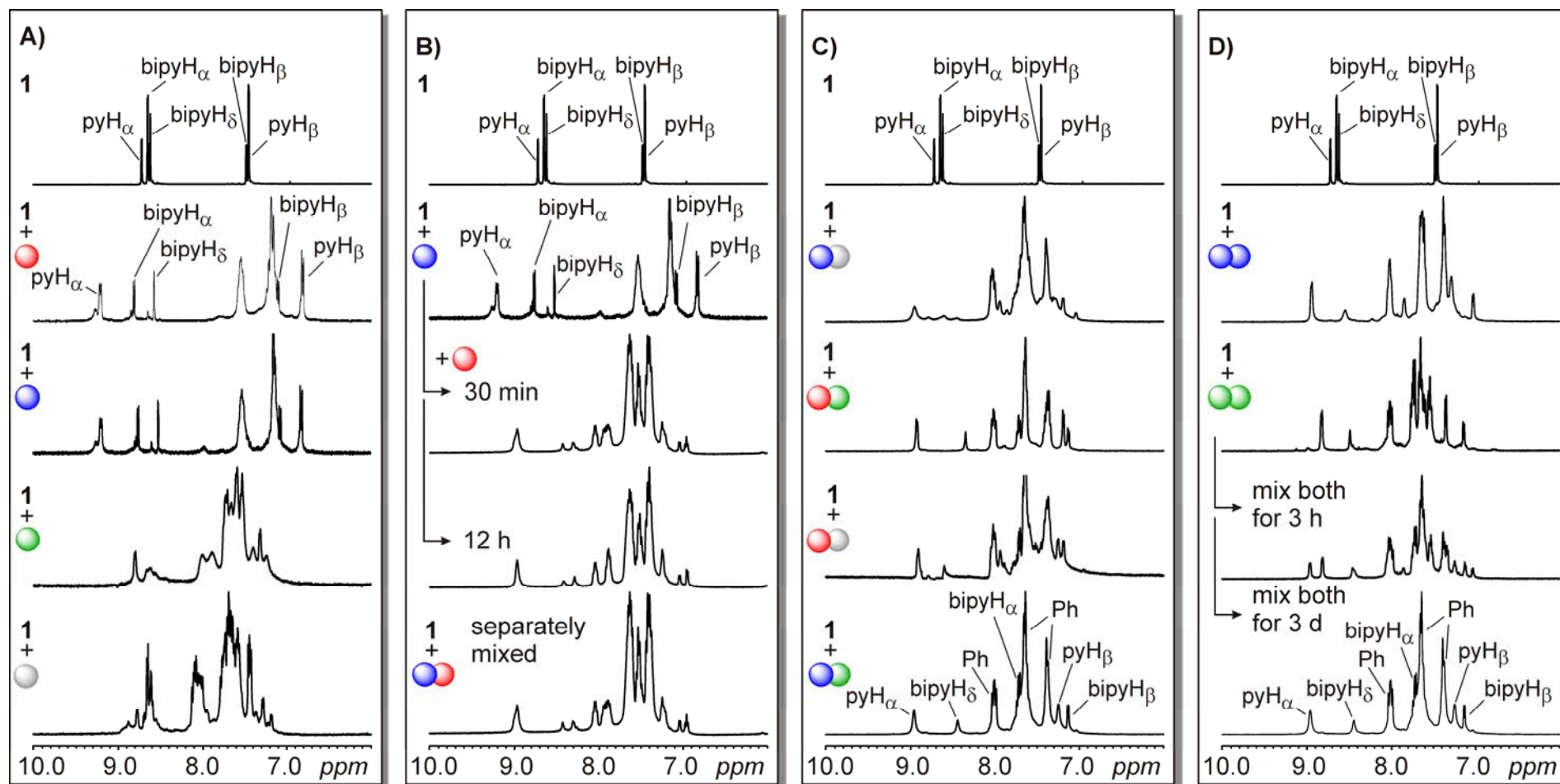
Figure S1. Room-temperature ^{1}H NMR spectra in CD$_2$Cl$_2$ (same sequence as the ^{31}P NMR spectra shown in Figure 1 in the main text): A) separate 1:1 mixtures of **1** and **2 - 5**, respectively. B) 1:1 mixture of **1** and **3** (top), to which 1 eq. of **2** is added (recorded after 30 min and 12 h (center)), and **1** added to a 1:1 mixture of **2** and **3** directly. C) mixtures of **1** with pairwise mixtures of **2 - 5** (1:1:1 each) showing the self-sorting based on the anchillary ligands. D) Heterobimetallic self-sorting of metal corners between two preformed homometallic 4:2 (M:L) macrocycles.
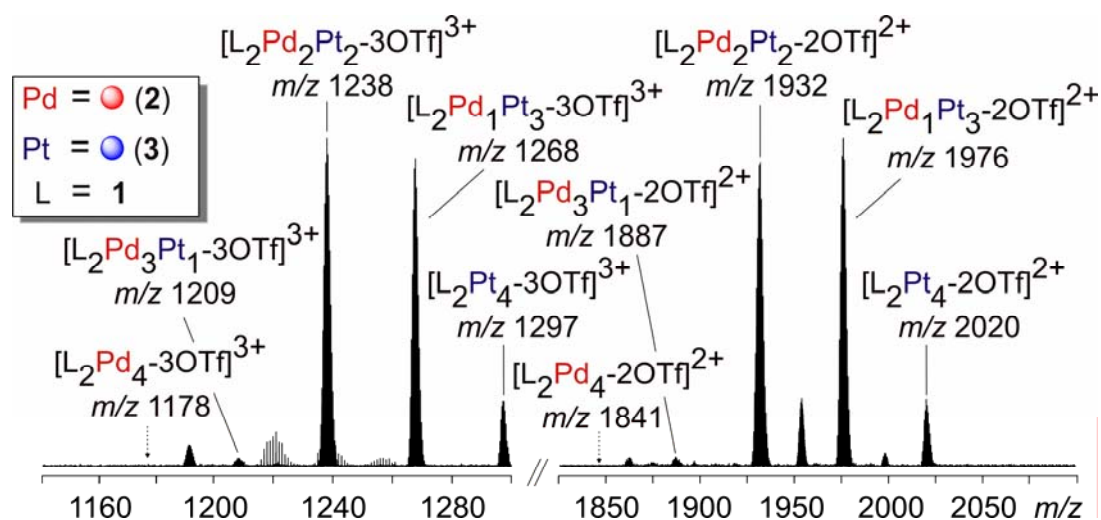
Figure S2. ESI mass spectrum of the mixture of ligand **1** after combination with metal centres **2** and **3** and stirring for 12 h. In this mixture, the two (dppp)M(II) (M = Pd, Pt) complexes compete with each other for both binding sites. Since both bear the same ancillary ligand, no self-sorting can occur. In this case, a distribution of both metal centers over both binding sites is observed implying that stoichiometries other than $M_{bpy}:M_{py}:L = 2:2:2$ can form. The ESI mass spectra shown here nicely confirm this conjecture. The different complexes are observed in their +2 (right) and +3 (left) charge states. The lower abundance of Pd-rich complexes may result either from different ESI response factors or from a faster fragmentation of the kinetically less inert Pd complexes.

The heterobimetallic metallo-macrocycle **7** shown in Figure 2 in the main text bears the kinetically more inert Pt centres at the pyridine coordination sites. Thus one might expect the preferential loss of a (dppe)Pd(II) ion from the bipyridine sites. The chelate effect, however, compensates for that and structure-indicative fragments are formed as described in the main text. The second heterobimetallic metallo-macrocycle **6** fragments differently (Figure S3). It bears the kinetically more labile Pd centres at the pyridine sites so that both effects, the more inert Pt-N bond and the chelate effect now cooperate to keep the (dppe)Pt(II) fragment at the bipyridine sites. Consequently, the loss of a singly charged (dppp)Pd(II) fragment leaves the doubly charged $M_{bpy}:M_{py}:L = 2:1:2$ fragment at *m/z* 1509 which is not structure indicative. However, the subsequent fragmentation at longer irradiation times (Figure S3, bottom spectrum) yields only one 1:1 fragment. A random distribution of metal centres should result in the formation of two different 1:1 fragments. As this is not the case, the mass spectrometric experiments provide evidence for successful self-sorting for **6** as well.
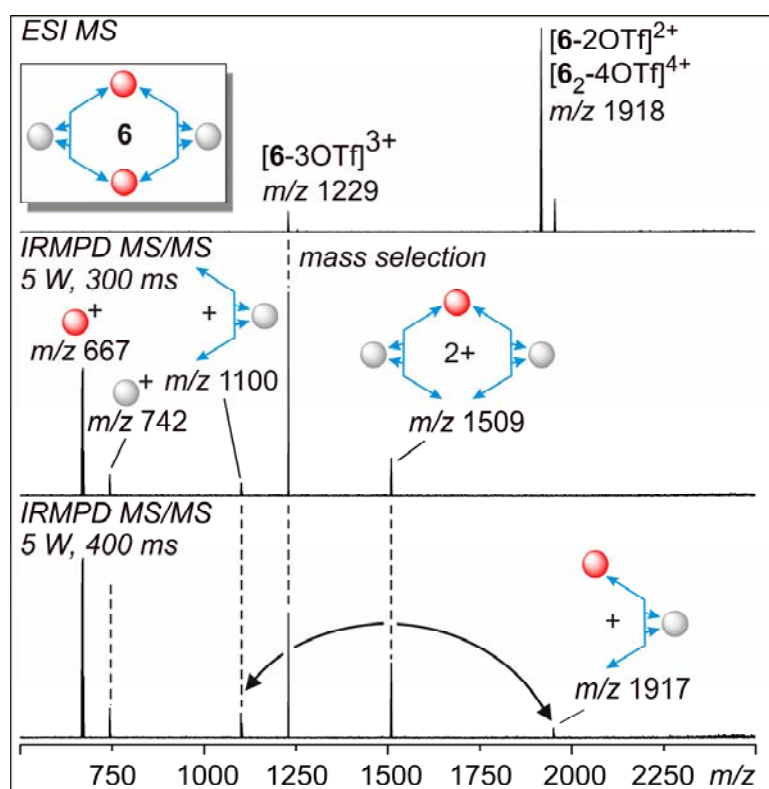
Figure S3. ESI-FTICR mass spectrum (top) and the IRMPD tandem MS experiments at different irradiation times (middle and bottom) of metallo-macrocycle **6**. The M_{bpy}:L = 1:1 fragment ion at m/z = 1100 unambiguously confirms the position of the metal ions and supports the conclusions drawn from the ^{31}P NMR experiments as described in the main text.
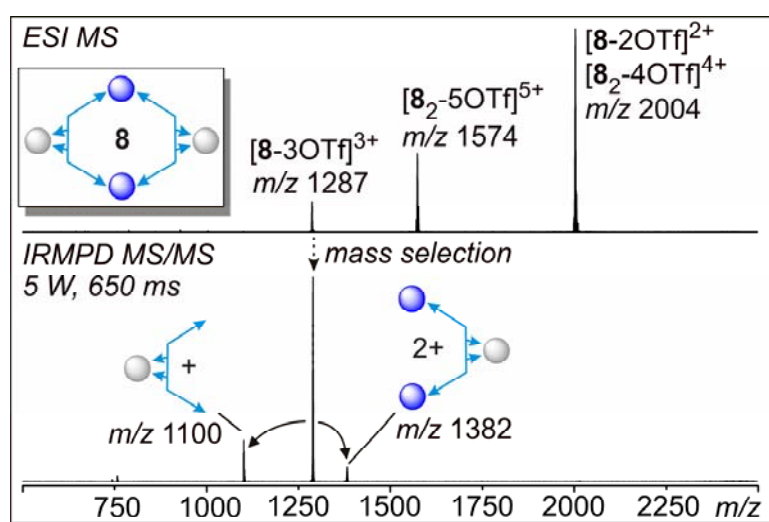
Figure S4. ESI-FTICR mass spectrum (top) and the IRMPD tandem MS experiment (bottom) of metallo-macrocycle **8**. The M_{bpy}:L = 1:1 fragment ion at m/z = 1100 unambiguously confirms the position of the metal ions and supports the conclusions drawn from the ^{31}P NMR experiments as described in the main text.