

Supporting data

Quantitative Formation and Clean Metal Exchange Processes of Large Void (> 5000 Å³) Nanobox Structures

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Preparation of copper(I) complexes A-C

A mixture of copper (I) complexes A-C was obtained by reaction of the corresponding linear ligand **1** with macrocycle **3** and [Cu(CH₃CN)₄](PF₆) in dry methylene chloride at room temperature. The formation of the copper complexes was immediately visible by their characteristic dark red colour. The ESI-MS shows formation of (at least!) three different copper(I) phenanthroline aggregates.

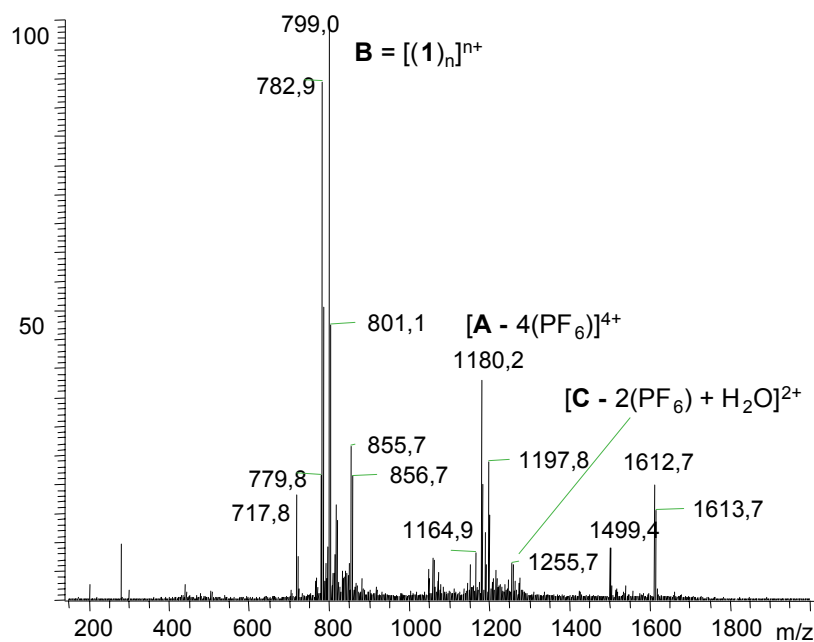


Figure 1. ESI-MS spectrum of the reaction mixture resulting from ligand **1** with macrocycle **3** and [Cu(CH₃CN)₄](PF₆) in dry methylene chloride at room temperature. More details are contained in table 1.

Table 1: ESI-MS data for the reaction mixture containing **A-C** (mass range 300-2000 Dalton).

	Schematic	Ions observed	Calcd. <i>m/z</i>	Exp. <i>m/z</i>	% [%]
[2+2]-box A		[A] ⁺ [A - 2 PF ₆] ²⁺ [A - 3 PF ₆] ³⁺ [A + 4 H ₂ O - 4 PF ₆] ⁴⁺ [A - 4 PF ₆] ⁴⁺ [Cu(3)(H ₂ O) ₂] ⁺	5299.9 2505.0 1621.6 1198.0 1180.0 1613.6	– – – 1197.8 1180.2 1613.7	 24 38 18
triangle C + H ₂ O		[Cu ₃ (1) ₃ (PF ₆)(H ₂ O)] ²⁺	1255.2	1255.7	5
bis-heteroleptic complex		[Cu ₃ (1) ₂ (3)(H ₂ O) ₂] ³⁺	1059.5	1058.9	8
[<i>n</i>]-polymer B		[Cu _{<i>n</i>} (1) _{<i>n</i>} (H ₂ O) _{2<i>n</i>}] ^{<i>n</i>+} [Cu _{<i>n</i>} (1) _{<i>n</i>} (H ₂ O) _{<i>n</i>}] ^{<i>n</i>+} [Cu _{<i>n</i>} (1) _{<i>n</i>}] ^{<i>n</i>+}	818.5 800.3 782.5	818.3 800.1 782.9	15 100 90
Homoleptic complex		[Cu(1) ₂] ⁺	1499.5	1499.4	10
Ligand	1	[1] ⁺	718.9	717.8	18

General procedure for the preparation of the copper(I) nanoboxes [**4**](PF₆)₄:

The copper (I) complexes **4a,b**⁴⁺ were obtained by reaction of the corresponding linear ligands **2a,b** with macrocycle **3** and [Cu(CH₃CN)₄](PF₆) in dry methylene chloride at room temperature. The formation of the copper complexes **4a,b**⁴⁺ was immediately visible by their characteristic dark red colour. After a few minutes the solution was then evaporated to dryness affording a red solid, which was then further characterized.

General procedure for the preparation of the silver(I) nanoboxes [**5**](PF₆)₄:

The silver (I) complexes **5a,b**⁴⁺ were obtained by treatment of the corresponding linear ligands **2a,b** with macrocycle **3** and AgBF₄ in dry methylene chloride at room temperature. The formation of silver complexes **5a,b**⁴⁺ was immediately recognized by their characteristic yellow colour. The solution was then evaporated to dryness furnishing a yellow solid, which was then further characterized.

Characterization of **[4a](PF₆)₄**:

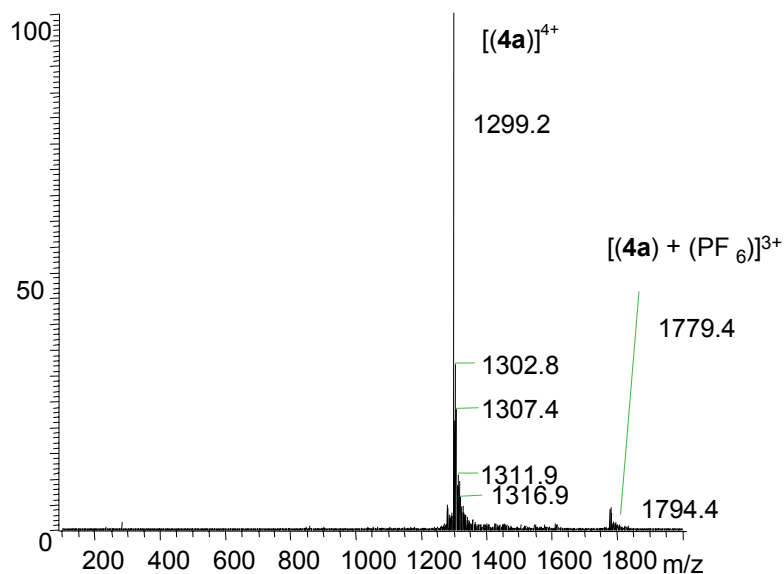


Figure 2. ESI-MS of **4a**⁴⁺ in acetone at room temperature (150 – 2000 Dalton).

Characterization of **[4b](PF₆)₄**

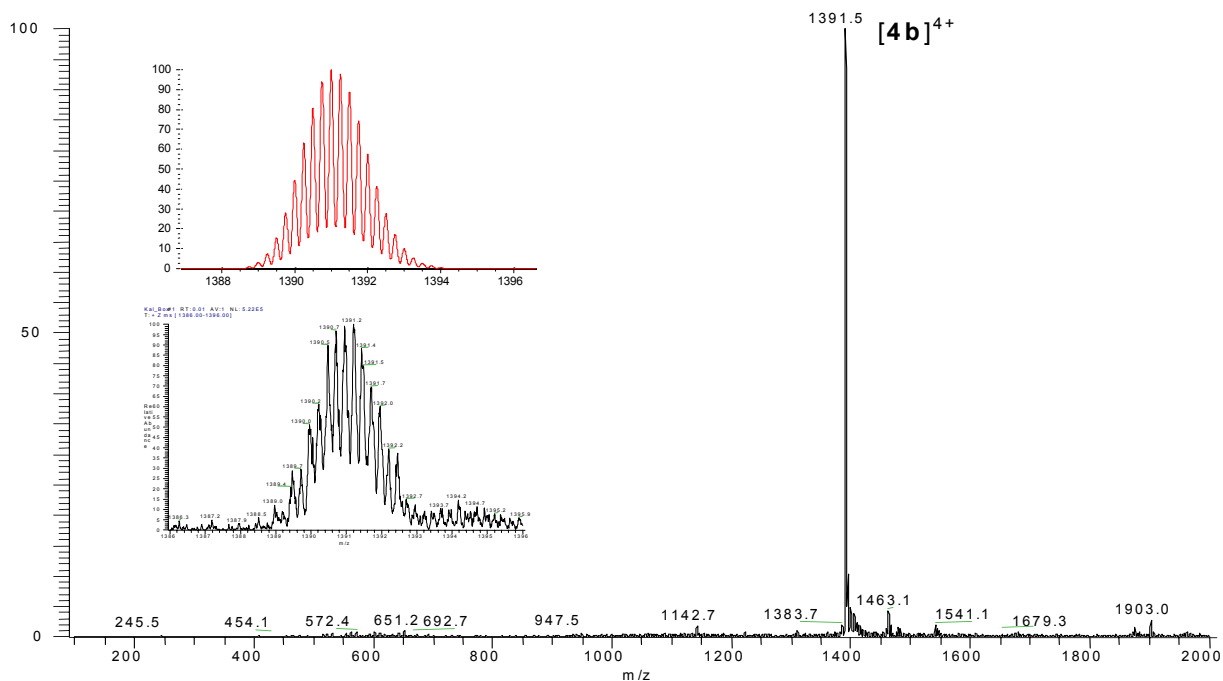


Figure 3. ESI-MS of nanobox **4b**⁴⁺ in acetone at room temperature (100 – 2000 Dalton) including isotopic splitting (insert top: calcd.; insert bottom: exp.).

Characterization of [5a](PF₆)₄.

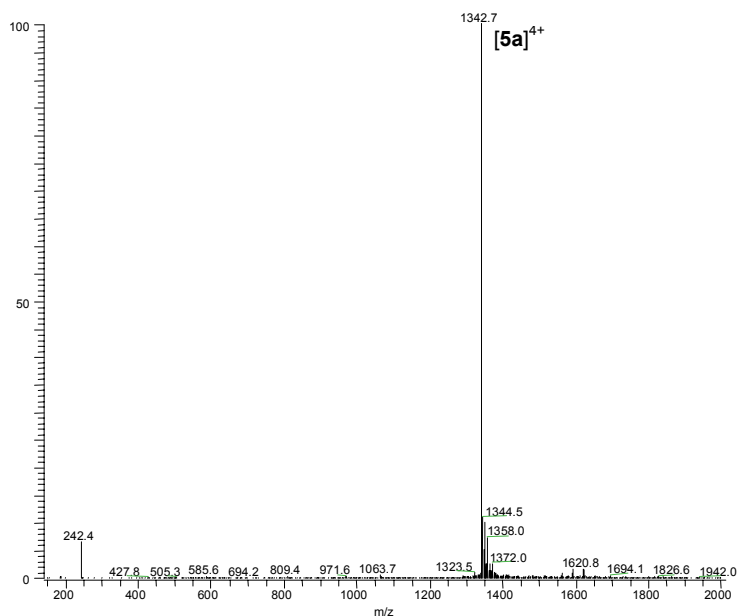


Figure 4. ESI-MS of **5a**⁴⁺ in methylene chloride at room temperature (150 – 2000 Dalton).

Characterization of [5b](PF₆)₄.

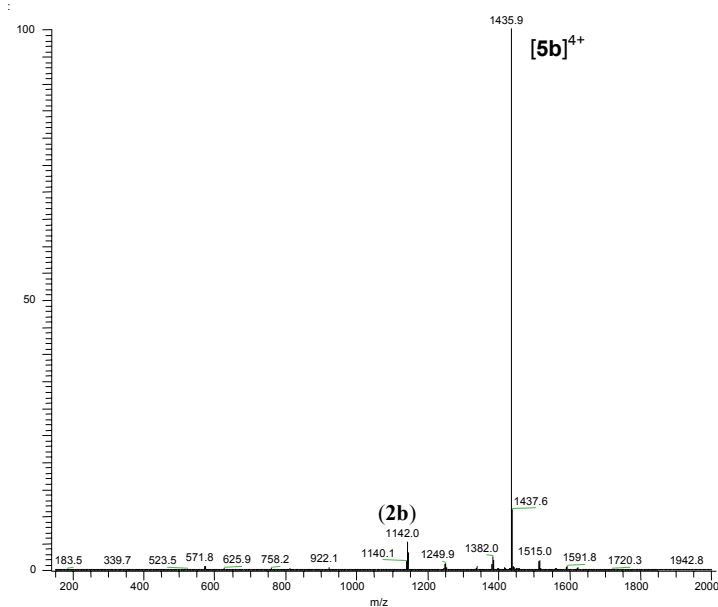


Figure 5. ESI-MS of nanobox **5b**⁴⁺ in methylene chloride at room temperature (150 – 2000 Dalton).

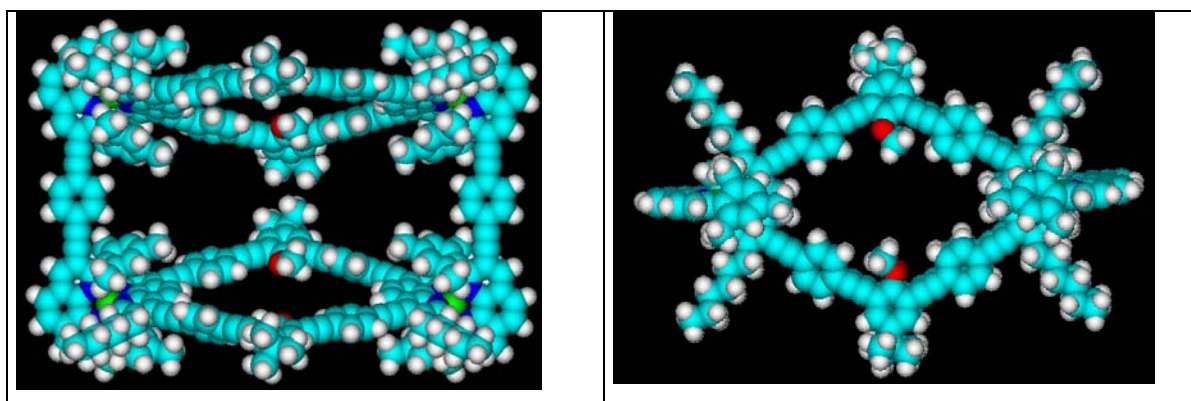


Figure 6. Two perspective views of nanobox **4a** (calculated by Hyperchem[®])

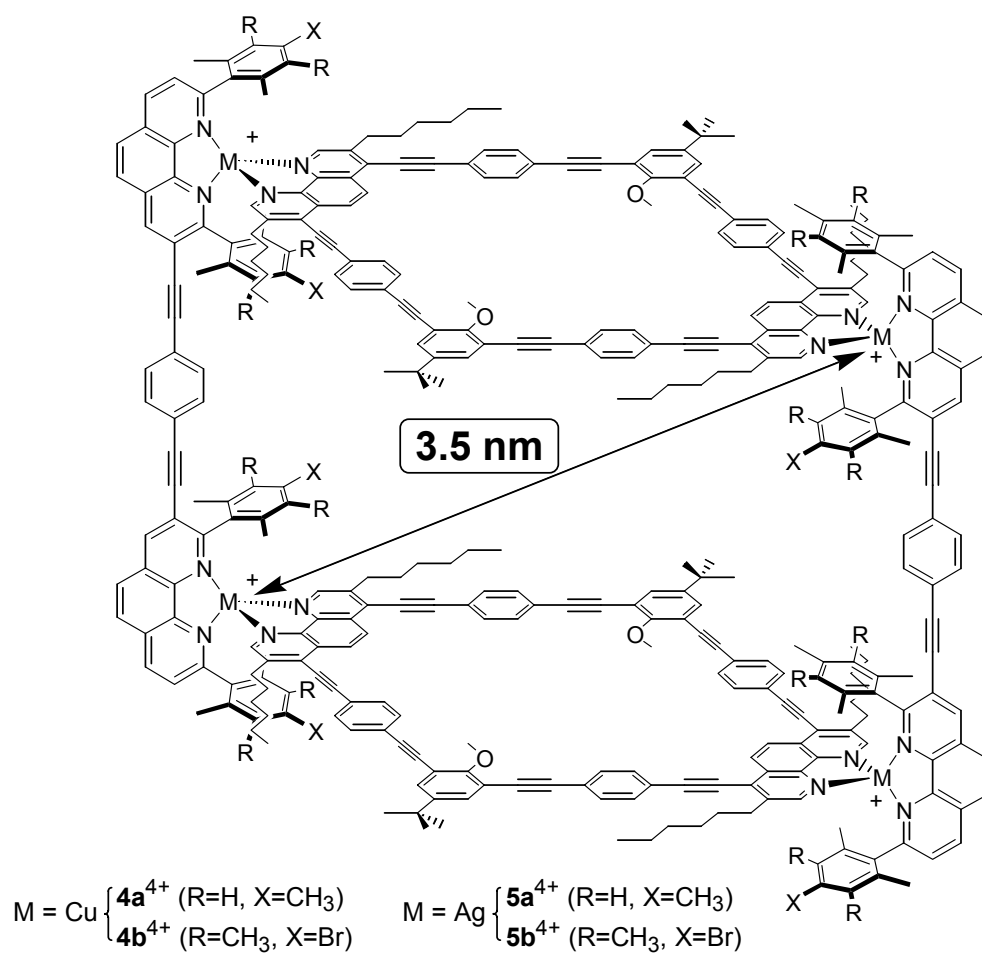
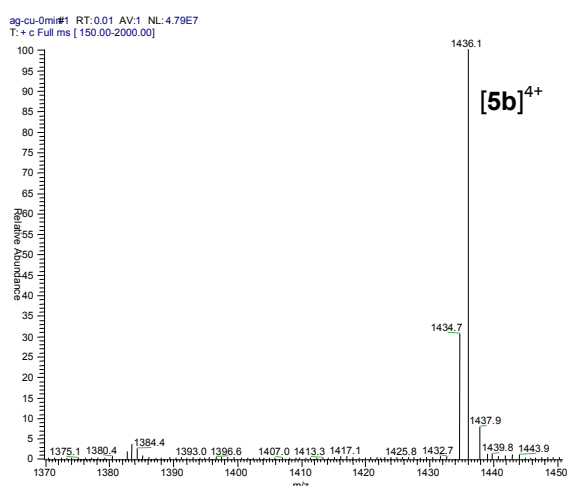


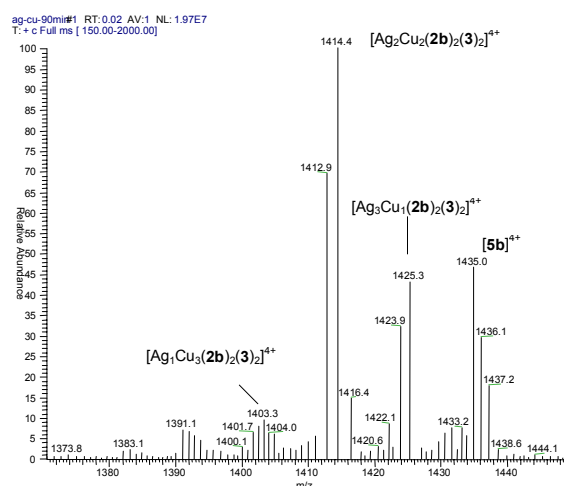
Figure 7. Dimensions of the box.

Conversion of Silver(I) → Copper(I) Nanobox: $5b^{4+} \rightarrow 4b^{4+}$.

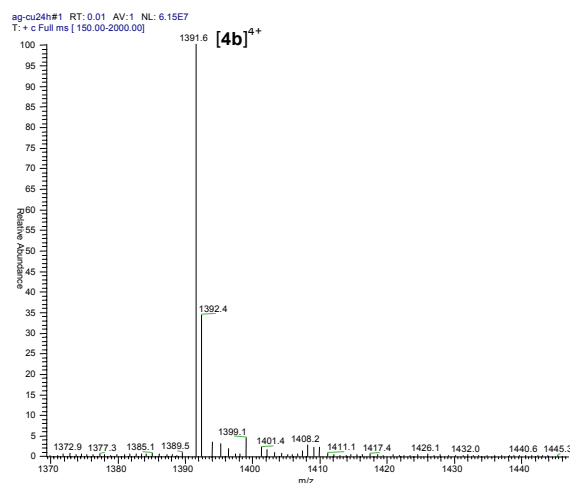
ESI-MS showing the signals corresponding to the intermediate nanobox structures formed through successive exchange of Ag^+ by Cu^+ starting from $[5b](PF_6)_4$ (in methylene chloride, room temperature, ESI-spectra: 1370 – 1450 Dalton). The metal exchange was obtained by treatment of silver box $[5b](PF_6)_4$ (3.5 μ mol) with CuI (14.7 μ mol). After 180 min the formation of $[4b](PF_6)_4$ was almost complete. In the spectrum below the situation is depicted for $t = 24$ h.



a) ESI-MS of the pure nanobox $5b^{4+}$



b) ESI-MS after 90 min.



c) ESI-MS after 24 h, which corresponds to pure $4b^{4+}$.

Figure 8. ESI-MS spectra of the silver(I) → copper(I) nanobox conversion.

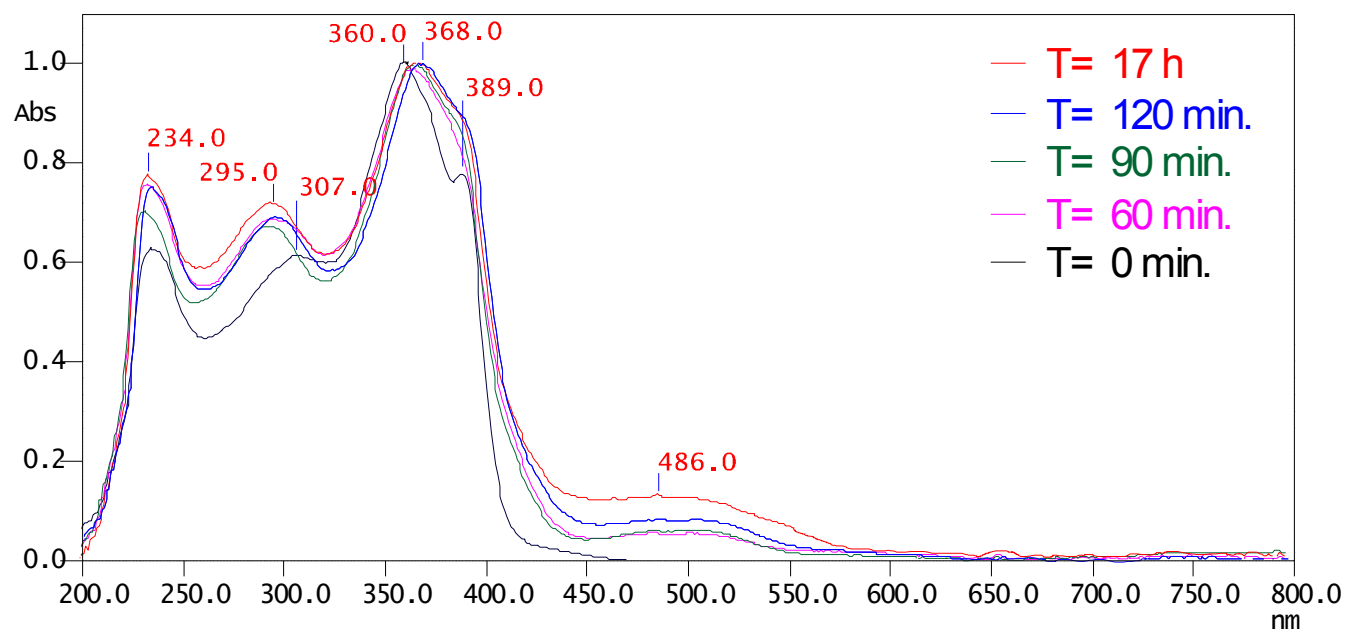


Figure 9. UV-Vis spectra of the silver(I) → copper(I) nanobox conversion.