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Quantitative formation and clean metal exchange processes of large void (>5000 Å^3) nanobox structures†‡

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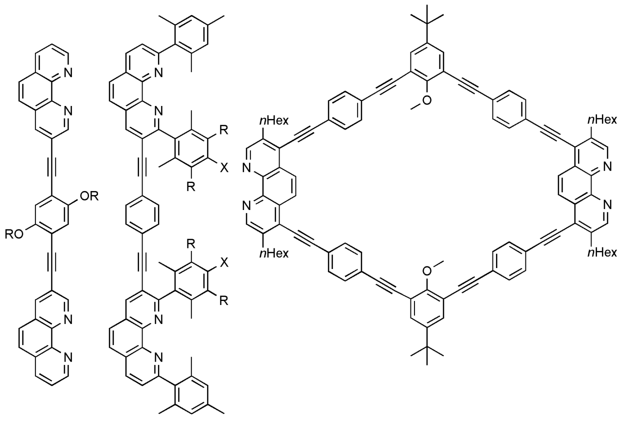
The metallosupramolecular assembly of linear and macrocyclic bisphenanthrolines in the presence of Cu$^+$ provides nanobox structures with internal volumes of > 5000 Å^3 when the ligands are designed along the HETPHEN approach.

The preparation of defined molecular architectures still represents a considerable synthetic challenge, although seminal contributions in the last decade have established highly efficient self-assembly processes,[1] increasingly based on metal–ligand coordination, to provide sparkling supramolecular structures, *e.g.* racks, ladders, grids, cages *etc.*[2] Our interest is to build large porous nano scaffolds in solution with a large internal void (free volume of > 5000 Å^3) the inside of which can be modelled at will.

To prepare a sufficiently large and stable nano scaffold by self-assembly we decided to rely on the thermodynamically stable and kinetically labile[3] copper(I) bisphenanthroline complex as a key unit for the corners of the box. In addition, these complexes are also geometrically well-defined as demonstrated by Sauvage[4] in many examples. However, when following the principle of maximum site occupancy and cooperativity, as successfully employed by Lehn[5] for a related cylindrical architecture, the self-assembly process of **1** and **3**[6a] (Scheme 1) in the presence of copper(I) ions afforded a variety of structures depicted schematically in Fig. 1.

ESI-MS revealed that the desired box $[\mathrm{Cu}_4(\mathbf{1})_2(\mathbf{3})_2]^{4+}$ (**A**) was only formed as a minor constituent beside the homoleptic oligomer $[\mathrm{Cu}_n(\mathbf{1})_n]^{n+}$ (n = 3,4; **B**) and some trace amounts of the mixed triangular structure $[\mathrm{Cu}_3(\mathbf{1})_2(\mathbf{3})]^{3+}$ (**C**). Hence, it is clear that a clean approach to nanobox **B** in solution cannot rely solely on cooperativity and maximum site occupancy effects.



1 (R= $C_{12}H_{25}$) **2a** (R=H, X=CH_3), **2b** (R=CH_3, X=Br) **3**

Scheme 1

We argued that it would be helpful (i) to prevent formation of any *homoleptic* bisphenanthroline complex in order to diminish the number of possible options in the self-assembly process and (ii) to impose even more driving force than in the parent copper(I) bisphenanthroline complex. Hence, we made use of the HETPHEN approach (a quantitative approach to heteroleptic bisphenanthroline metal complexes[7]) to build defined heteroleptic copper(I) complexes. This approach utilizes steric and electronic effects originating from bulky aryl substituents at the bisimine coordination sites (as seen in **2a**,**b**) to control the coordination equilibrium both kinetically and thermodynamically.[7]

Quantitative self-assembly of the deep red supramolecular complexes **4a**,**b**$^{4+}$ (Scheme 2) indeed could be effected when the linear ligand **2a** or **2b**,[6b] the macrocyclic bisphenanthroline **3** and $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}$ (stoichiometric ratio 2:2:4) were simply dissolved in dichloromethane at ambient temperature for a couple of seconds. Both, the ESI-MS and ^{1}H NMR spectra indicated the presence of just one single species. For example, in the electrospray (ESI) mass spectra of complex $[\mathbf{4a}](\mathrm{PF_6})_4$ only one set of signals was observed in the mass range up to

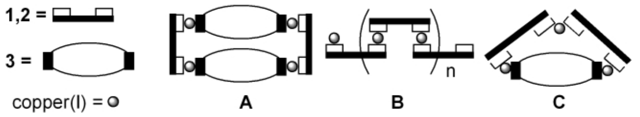
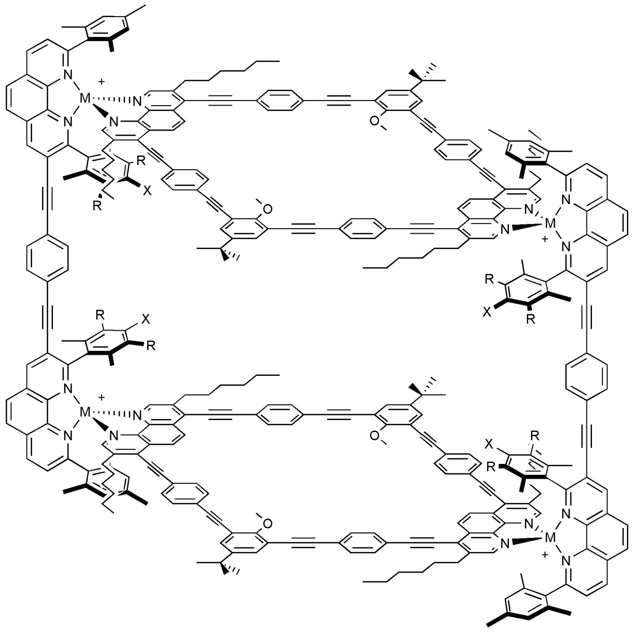


Fig. 1 Schematic representation of complexes **A**–**C** obtained in the reaction of **1** and **3**.



M = Cu {**4a**$^{4+}$ (R=H, X=CH_3) **4b**$^{4+}$ (R=CH_3, X=Br)
M = Ag {**5a**$^{4+}$ (R=H, X=CH_3) **5b**$^{4+}$ (R=CH_3, X=Br)

Scheme 2

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† Electronic supplementary information (ESI) available: experimental procedures, ESI-MS spectral data of the prepared complexes, perspective views and dimensions of nanobox **4a**, UV–Vis spectra of the nanobox conversion. See http://www.rsc.org/suppdata/cc/b2/b207801e/

‡ Dedicated to an enthusiastic chemistry high school teacher, Peter Friedrich, Einstein-Gymnasium Kehl on the occasion of his retirement.

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4000 Dalton: m/z = 2740, 1777 and 1298, corresponding to $[(\mathbf{4a})(PF_6)_2]^{2+}$, $[(\mathbf{4a})(PF_6)]^{3+}$ and $[\mathbf{4a}]^{4+}$ formed by successive loss of counterions. For $\mathbf{4b}^{4+}$ the ESI data were analogous. Moreover, the ^{1}H NMR revealed highly symmetric species $\mathbf{4a}^{4+}$ and $\mathbf{4b}^{4+}$, respectively. The distinct highfield shift of the mesitylene protons (δ = 6.10) in $\mathbf{4a}^{4+}$ (*vs.* in **2a**: δ = 6.93) is clearly indicative of the formation of a heteroleptic complex as demonstrated earlier.[7] Both, $[\mathbf{4a}](PF_6)_4$ and $[\mathbf{4b}](PF_6)_4$ display a single reversible $Cu^+ \rightleftharpoons Cu^{2+}$ redox wave in cyclic voltammetry experiments ($E_{1/2}$ = 1.09 V_{TPP} and 1.12 V_{TPP}, respectively. TPP = triphenylpyrylium), in line with the potentials of mononuclear heteroleptic copper(I) complexes.[7]

All our attempts to receive crystals of **4a**,**b** suitable for X-ray analysis were met with failure. Such problems are well known for other metallosupramolecular structures with a large void;[8] those that can be obtained in a crystalline state usually exhibit voids < 1000 Å^3 and are most often filled with counter ions[9] or are interpenetrating.[10]

Nevertheless, a complete characterisation was possible. As a first indication for the proposed structure we ascertained that the isotopic distribution patterns of $\mathbf{4a},\mathbf{b}^{4+}$ matched the calculated compositions. To further support our assignment and to rigorously exclude alternative catenated, oligomeric or polymeric complexes (*e.g.* $[Cu_6(\mathbf{2a})_3(\mathbf{3})_3]^{6+}$), we investigated the sedimentation coefficient distribution using analytical ultracentrifugation.[11] Sedimentation velocity experiments in acetone at ambient temperature *showed clearly only one single species in solution* (Fig. 2, solid line).

From the density variation in two different solvents (acetone and d_6-acetone) a dry molar mass of 5831 g mol^{-1} was derived. This is in excellent agreement (±1%) with the calculated mass for $[\mathbf{4a}](PF_6)_4$ of 5772 g mol^{-1}. Moreover, the experimental hydrodynamic diameter of 4.2 nm (compare to 5.0 nm for Stangś cuboctahedron[8]) correlates nicely with the calculated size of the box (the diagonal distance between two copper(I) centres amounts to 3.5 nm, the diagonal between two phenanthrolines to 4.7 nm). From sedimentation velocity experiments a molecular mass for the solvated box of 19.8×10^3 g mol^{-1} was obtained (Fig. 2, dotted line), which amounts to a solvation of 2.44 g g^{-1}. This means that the solvation of the box not only involves *240 molecules of acetone* but also accounts for 71% of the overall mass and for 80% of the volume. Knowing these numbers, the low tendency to form X-ray suited crystals is readily understood. The experimental volume of the solvated box **4a** amounts to 38.8×10^3 Å^3 that agrees nicely with the volume from MM+ calculations§ (36.2×10^3 Å^3). MM+ calculations of **4a**,**b** predict an inner volume of 6×10^3 Å^3, indicating that about 50 molecules of acetone fill the inner void.

The tendency to form $\mathbf{4a},\mathbf{b}^{4+}$ from its constituents is remarkable. When $[\mathbf{4a}](PF_6)_4$ was treated with trifluoroacetic acid, both the ESI-MS data and the loss of the red colour evidenced complete disintegration through protonation of the ligands. However, after addition of aqueous potassium hydroxide a red product reappeared, which dissolved in the dichloromethane layer. ESI-MS showed again the signal of $\mathbf{4a}^{4+}$.

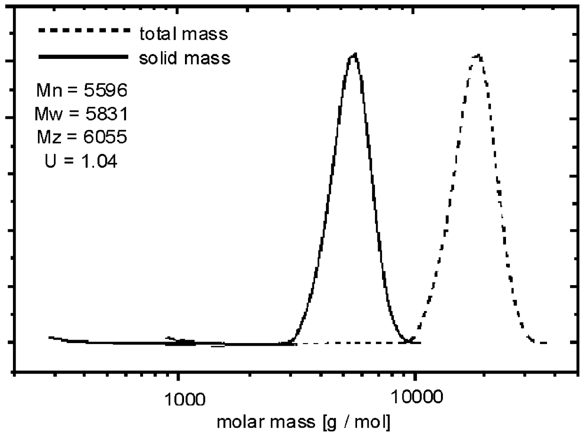

Fig. 2 Determination of the molar mass of $[\mathbf{4a}](PF_6)_4$ in acetone in a sedimentation velocity experiment (solid line: dry weight; dotted line: weight of solvated box).

Using the above procedure, the yellow silver(I) nanoboxes $\mathbf{5a},\mathbf{b}^{4+}$ were also readily formed in quantitative yield from bisphenanthrolines **2a** or **2b**, **3** and $AgPF_6$ (2 : 2 : 4) as witnessed by ESI–MS and ^{1}H NMR data. Because silver(I) phenanthroline complexes are usually less stable than the corresponding copper(I) complexes, we treated $[\mathbf{5b}](PF_6)_4$ (3.5 μmol) with CuI (14.7 μmol) at rt. The transformation $\mathbf{5b}^{4+} \rightarrow \mathbf{4b}^{4+}$ could readily be followed by UV/Vis (disappearance of λ_{max} (sh) = 389 nm) and by ESI–MS, as all intermediate $Ag_mCu_n^{4+}$ complexes ($m + n = 4$) were observed by their characteristic mass signals. From the ESI signals at different times it appears that aggregates with m, n being even numbers are slightly favored thermodynamically, presumably because of cooperativity reasons. For example, after 90 min the various species were: $\mathbf{5b}^{4+}$ (26%), $[Ag_3Cu(\mathbf{2b})_2(\mathbf{3})_2]^{4+}$ (23%), $[Ag_2Cu_2\ (\mathbf{2b})_2(\mathbf{3})_2]^{4+}$ (51%), but no $[AgCu_3\ (\mathbf{2b})_2(\mathbf{3})_2]^{4+}$. After 24 h $\mathbf{4b}^{4+}$ was the only species present in solution. The silver box $\mathbf{5b}^{4+}$ can be regenerated from $\mathbf{4b}^{4+}$ in the presence of cyanide and excess Ag^+.

In conclusion, only a combination of the HETPHEN concept with maximum site occupancy and cooperativity allows to establish a quantitative self-assembly process in solution for copper phenanthroline nanoboxes. The large void aggregates are unambiguously characterized by ESI, NMR and ultracentrifuge/light scattering techniques. From the size of the inner void (6×10^3 Å^3) it is clear that in contrast to smaller analogous systems any templating effects by counter ions can be excluded. The large cavity of these boxes is ideally suited for future internal functionalisations. The unprecedented conversion of the $Ag_4^{4+} \rightarrow Cu_4^{4+}$ nanobox convincingly underlines the reliability, robustness and flexibility of our approach.

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§ Molecular modeling is based on MM$^+$, implemented in Hyperchem®.

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