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Self-assembly of heteroleptic [2 × 2] and [2 × 3] nanogrids†

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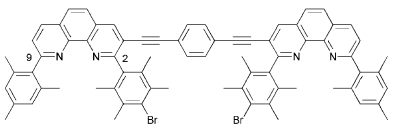
Using the HETPHEN concept a general and quantitative approach to the formation of heteroleptic nanogrids is illustrated.

The design and engineering of nanoscale supramolecular devices possessing unique functionalities has become an active field of research:[1] cylinders,[2] squares, polyhedra[1,3] and grids[4] are among the most targeted assemblies.

Seminal work by Lehn *et al.* has shown how to engineer homoleptic and even multimetallic metallosupramolecular grid architectures.[4] Due to the desire to explore highly functionalised assemblies, however, a strategy to prepare heteroleptic nanogrids would be quite welcome in order to combine different sets of functionalities. While a first example of a heteroleptic grid[5] was explored by Lehn *et al.* the chosen approach proved not to be general.

In recent years we have developed the HETPHEN concept‡[6] and demonstrated its potential for the quantitative formation of nanoscale heteroleptic assemblies, *e.g.* the formation of nanoboxes[7] and ring-in-ring[8] structures. Herein, we describe the synthesis of four truly nanoscale metallosupramolecular grids along this concept and their characterisation.

The rigid bis- and trisphenanthroline ligands **1–5** were synthesised utilising sequential Sonogashira coupling protocols that will be published elsewhere. Ligands **1,5** were encoded with the required control features to furnish exclusively heteroleptic assemblies, *i.e.* the 2,9 positions of each phenanthroline unit in **1,5** are shielded with bulky methylaryl groups thus preventing any association to homoleptic complexes. The appropriate combination of this ligand with metal ions such as Cu(I) is expected to yield heteroleptic grids over homoleptic ones.



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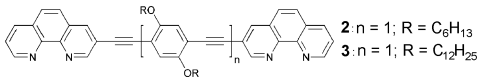
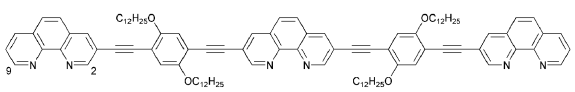


2: n = 1; R = C_6H_{13}
3: n = 1; R = $C_{12}H_{25}$



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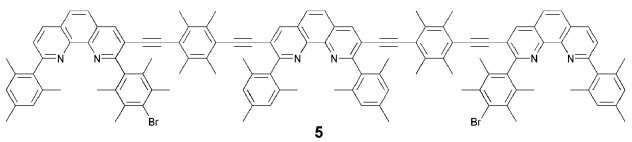

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As a test case for the necessity to apply the HETPHEN concept we first monitored the self-assembly behaviour of **2** and **3** in the presence of $[Cu(MeCN)_4]PF_6$ by ESI. A mixture of the homoleptic [2 × 2] grids $[Cu_4(\mathbf{2})_4]^{4+}$ and $[Cu_4(\mathbf{3})_4]^{4+}$ was formed as well as about an equal amount of the heteroleptic grid $[Cu_4(\mathbf{2})_2(\mathbf{3})_2]^{4+}$. Interestingly, 3 : 1 combinations, such as $[Cu_4(\mathbf{2})_3(\mathbf{3})]^{4+}$ or $[Cu_4(\mathbf{2})(\mathbf{3})_3]^{4+}$, were not detected. The need for additional control becomes even more evident when ligands **2** and **4** were treated in presence of the Cu(I) salt to explore the formation of the [2 × 3] grid. By ESI no [2 × 3] or [3 × 3] grids were observed. As the major product the homoleptic [2 × 2] grid $[Cu_4(\mathbf{2})_4]^{4+}$ was afforded along with small mononuclear complexes. Apparently, entropic reasons favor formation of the [2 × 2] grid over any [2 × 3] and [3 × 3] grids. From the above results it is clear that it is not possible to build heteroleptic nanoscale grids just relying on maximum site occupancy and cooperativity motifs.

In contrast, treatment of HETPHEN ligand **1** with 1–2 equiv. of Cu(I) salt resulted in a yellow solution, the analysis of which by UV–vis, ESI MS and ^{1}H NMR indicated $[(Cu)_2(\mathbf{1})]^{2+}$ as the only species. Obviously, formation of any homoleptic complex of **1** is prevented. Addition of two equiv. of the parent phenanthroline (**6**) led to a red solution which by ESI, ^{1}H-NMR and UV–vis analysis only contained the bisheteroleptic complex $[Cu_2(\mathbf{1})(\mathbf{6})_2]^{2+}$ demonstrating the validity of the HETPHEN concept.[6] The single crystal structure is presented in Fig. 1.§ Accordingly, the molecule has a transoid conformation with C_2 symmetry.

Each copper(I) centre exhibits a pseudotetrahedral coordination geometry (N2–Cu1–N3, 116.1° and N1–Cu–N4, 120.5°) and finds itself encapsulated by two duryl rings of the bisphenanthroline. The duryl groups and the second ligand (phenanthroline **6**) are oriented face-to-face separated by 3.4 Å, suggesting π-stacking. As such, compound $[Cu_2(\mathbf{1})(\mathbf{6})_2]^{2+}$ represents a rigid *anti*-rack complex.

HETPHEN ligand **1** was now reacted separately with ligands **2** or **3** in the presence of $[Cu(MeCN)_4]PF_6$ leading to the instant formation of the corresponding [2 × 2] nanogrids $[Cu_4(\mathbf{1})_2(\mathbf{2})_2]^{4+}$ and $[Cu_4(\mathbf{1})_2(\mathbf{3})_2]^{4+}$ as sole products. Each of them displays a sharp and single set of signals in the ^{1}H NMR, indicating a highly symmetric species. The chemical shifts of the mesityl protons ($\delta \approx$ 7.0 in ligand, $\delta \approx$ 6.0 ppm in complex) are most diagnostic for heteroleptic complex formation as demonstrated earlier.[6] In summary, the observed ^{1}H NMR, COSY, ESI-MS and the elemental analysis data are all consistent with the formation of single, highly symmetric heteroleptic assemblies. Though different configurational isomers should be present in solution, it was not possible to quantify them because of their similar chemical shifts.

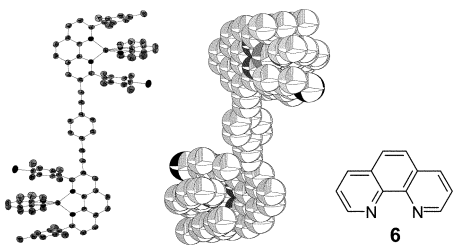

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Fig. 1 Solid state structure of $[Cu_2(\mathbf{1})(\mathbf{6})_2]^{2+}$; ball and stick (left) and space filling (middle) representation.

† Electronic supplementary information (ESI) available: experimental details, including ESI MS and ^{1}H NMR data of grids. See http://www.rsc.org/suppdata/cc/b3/b312807e/

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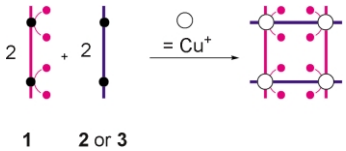
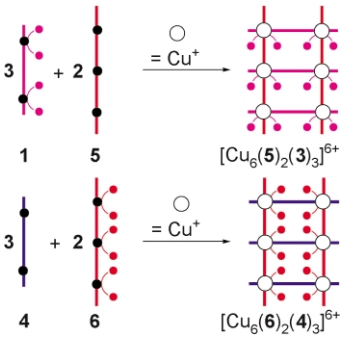


To probe the HETPHEN concept for [2 × 3] grids we reacted **1** with **4** and **3** with **5**. In contrast to the immediate formation of the [2 × 2] grids we noted a sluggish reaction over two days until finally the [2 × 3] grids $[Cu_6(\mathbf{1})_3(\mathbf{4})_2]^{6+}$ and $[Cu_6(\mathbf{3})_3(\mathbf{5})_2]^{6+}$ had formed. Again, as before the spectroscopic data (^{1}H NMR, elemental analysis, ESI-MS), in particular isotopic splitting, indicated clean formation of the desired nanogrids.



To obtain more insight into the mechanistic scenario leading to these assemblies, formation of $[Cu_4(\mathbf{1})_2(\mathbf{3})_2]^{4+}$ was monitored by both ESI MS (qualitative analysis) and UV–vis (quantitative analysis). Two series of titrations were performed. In the first series **1** and **3** were titrated with Cu(I) salt and in the second series **1** and Cu(I) salt were titrated with aliquot amounts of **3**. Both titrations indicated a three step process on the way to the grid (Fig. 2)

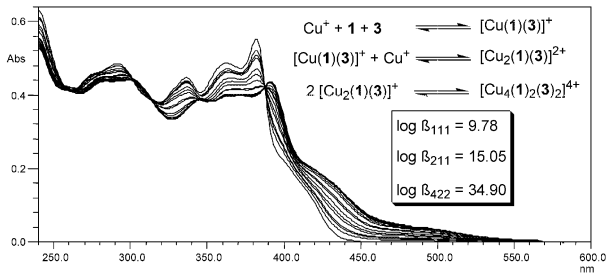


Fig. 2 UV–vis titration of **1** and **3** with Cu^+.

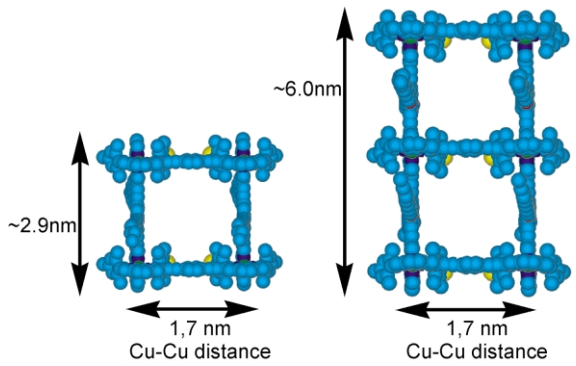


Fig. 3 Hyperchem representations of $[Cu_4(\mathbf{1})_2(\mathbf{3})_2]^{4+}$ (left) and $[Cu_6(\mathbf{1})_3(\mathbf{4})_2]^{6+}$.

providing complexation constants for two intermediate complexes and the final grid.

It has to be mentioned that these truly nanoscopic grids do not readily crystallise due to their large voids. Dimensions of the [2 × 2] grids are 2.9 nm along the edge and 2.5 nm for the Cu–Cu diagonal. The larger [2 × 3] grids exhibit a length of 6.0 nm and a Cu–Cu diagonal of 5.0 nm (Fig. 3).

In conclusion, the formation of four heteroleptic nanogrids using the HETPHEN concept‡ has been unambiguously demonstrated. This concept is very powerful in preparing heteroleptic supramolecular architectures, which have been impossible to prepare using simply maximum site occupancy and cooperativity motifs.

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Notes and references

‡ HETPHEN concept: quantitative approach to heteroleptic bisphenanthroline metal complexes.[6] This approach utilizes steric and electronic effects originating from bulky aryl substituents at the bisimine coordination sites (as seen in **1** and **5**) to control the coordination equilibrium both kinetically and thermodynamically.

§ Crystal data for $[Cu_2(\mathbf{1})(\mathbf{6})_2]^{2+}$. Crystals were obtained by slow diffusion of toluene into methylene chloride solution of the complex. Only poor quality crystals could be obtained so the crystal analysis is poor. Solvent molecules are severely disordered. Formula sum $C_{96}H_{76}Br_2Cu_2F_{12}N_8P_2$, Formula weight 1918.49, Crystal system: triclinic, Space group: $P\bar{1}$, Unit cell dimensions a = 10.4460(21) Å, b = 14.0790(28) Å, c = 16.8010(34) Å, α = 84.70(3) °, β = 80.32(3) °, γ = 88.63(3) °, Cell volume: 2425.23(1407) Å^3, density, calculated: 1.348 g cm^{-3}, Pearson code: aP142, formula type: NOPQ4R58, Wyckoff sequence: i^{71}

CCDC 222763. See http://www.rsc.org/suppdata/cc/b3/b312807e/ for crystallographic data in .cif or other electronic format.

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