Supporting data

Self-Assembly of Heteroleptic [2x2] and [2x3] Nanogrids

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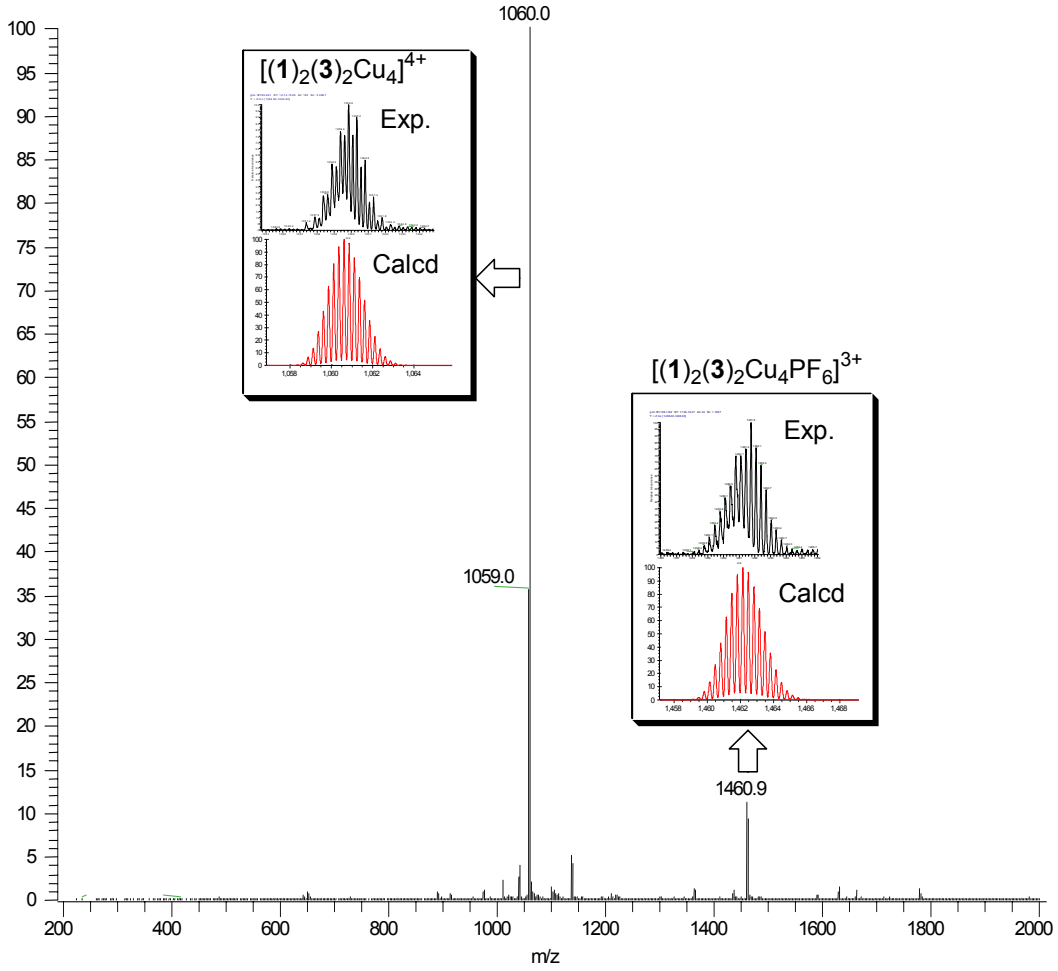
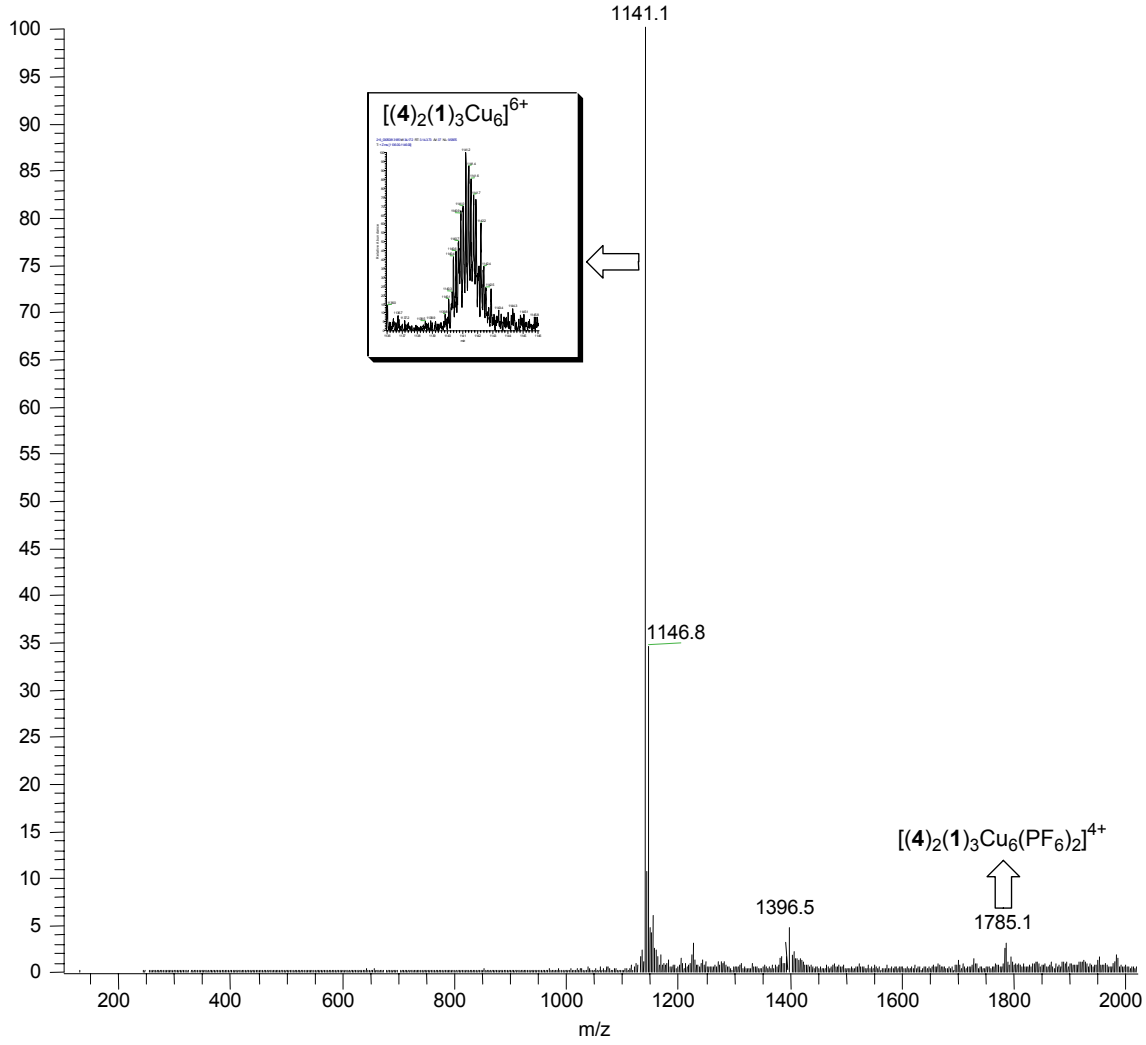
General procedure for preparing copper nanogrids

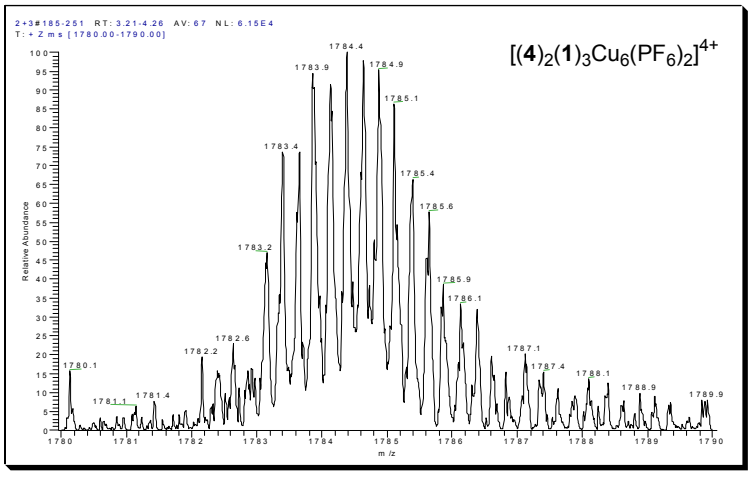
[2x2] nanogrids were prepared by mixing **1** and **2** (or **3**) with $[Cu(MeCN)_4]PF_6$ (1:1:2 equiv. respectively) in methylene chloride. The resulting dark red solution was analysed by ESI MS, ^{1}H NMR, COSY, elemental analysis and UV/vis spectroscopy. [2x3] grids were prepared in a similar way by mixing **4** (or **5**) and **1** (or **2**) with Cu(I) salt in 1: 1.5: 3 equiv. respectively.

ESI MS of [2x2] Nanogrid



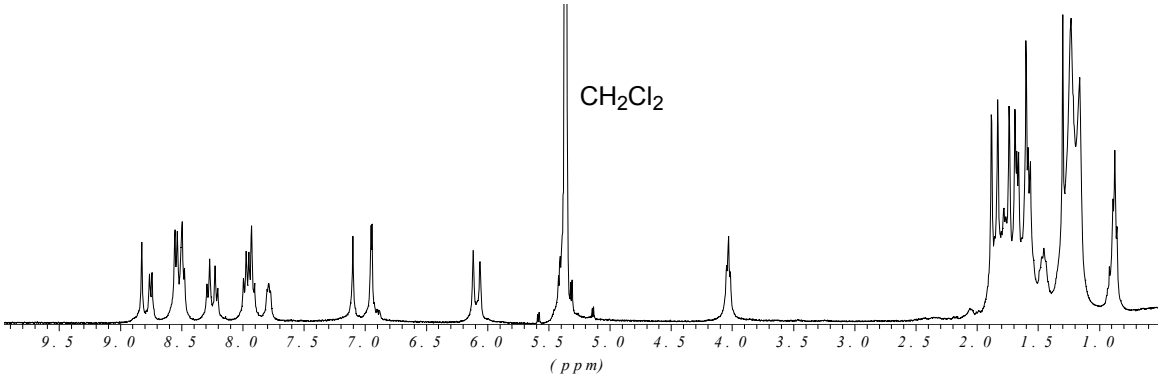
ESI MS of [2x3] Nanogrid



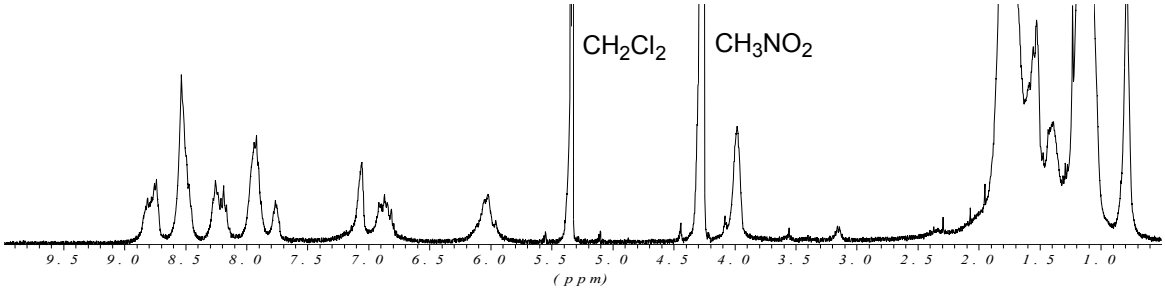


^{1}H NMR of [2x2] and [2x3] grids

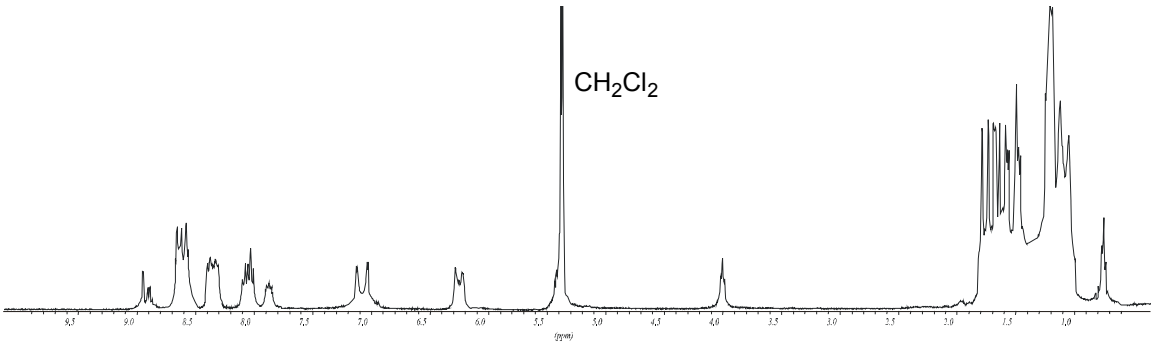
$[(1)_2(3)_2(Cu)_4](PF_6)_4$



$[(1)_3(4)_2Cu_6](PF_6)_6$

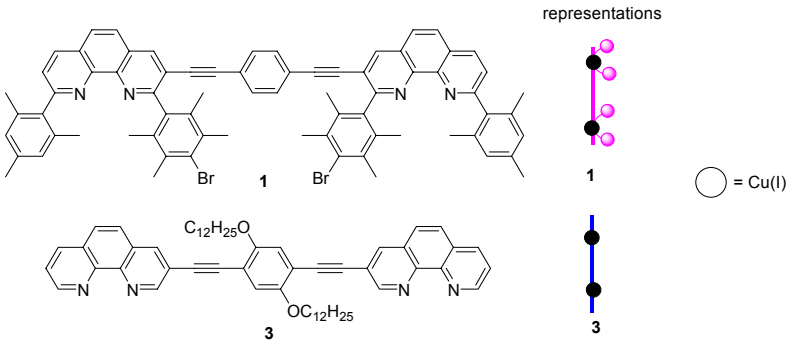


$[(2)_3(5)_2Cu_6](PF_6)_6$



Mechanistic Insight into [2x2] Nanogrid Assembly

ESI MS Titration of $[Cu_4(1)_2(3)_2]^{+4}$



a) ESI-MS titration of 1 and 3 with Cu(I) salt in methylene chloride.

Table 1. ESI MS titration data along with proposed formula of observed species.

Titration Nr.	Stoichiometric ratio of **1**, and **3** Cu(I) resp.	Observed m/z	Formula
1	1: 1: 0.2	1141.6 (100%) 707.7 (50%) 912.8 (40%) 1027.7 (30%) 1082.3 (18%) 1629.7 (35%)	$[(\mathbf{1})(H)]^{+}$ $[(\mathbf{1})(Cu)_2(H_2O)(AN)_3]^{+2}$ $[(\mathbf{3})(Cu)]^{+}$ $[(\mathbf{1})(\mathbf{3})(Cu)(H)]^{+2}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2(AN)PF_6]^{+}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
2	1: 1: 0.4	707.7 (20%) 912.8 (25%) 1060.9(45%) 1082.3 (68%) 1629.7 (100%)	$[(\mathbf{1})(Cu)_2(H_2O)(AN)_3]^{+2}$ $[(\mathbf{1})(Cu)]^{+}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2(AN)PF_6]^{+}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
3	1: 1: 0.6	707.7 (10%) 912.8 (5%) 1060.9(65%) 1082.3 (68%) 1629.7 (100%)	$[(\mathbf{1})(Cu)_2(H_2O)(AN)_3]^{+2}$ $[(\mathbf{1})(Cu)]^{+}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2(AN)PF_6]^{+}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
4	1: 1: 0.8	707.7 (5%) 1060.9(100%) 1629.7 (60%)	$[(\mathbf{1})(Cu)_2(H_2O)(AN)_3]^{+2}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
5	1: 1: 1.0	1060.9(100%) 1461.4 (20%) 1629.7 (60%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
6	1: 1: 1.2	1060.9(100%) 1461.4 (20%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$
7	1: 1: 1.4	1060.9(100%) 1461.4 (20%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$
8	1: 1: 2.0	1060.9(100%) 1461.4 (20%)	$[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$
9	1: 1: 4.0	1060.9(100%) 1461.4 (20%)	$[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$

All relevant signals appearing during the titration process could be identified and are listed in Table 1. As data in Table 1 indicate, no homoleptic complexes of **1** were formed during the whole titration process, highlighting the **HETPHEN** concept in preparing the heteroleptic assemblies. The data clearly indicate the stepwise assembly of the nanogrid. Excess (4 eq. with respect to ligands) addition of Cu(I) salt did not affect already formed nanogrid.

Fragmentation of the signals further confirmed the assignments. For example, fragmentation of $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$ produced the signal corresponding to $[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and both the species were further confirmed by their isotopic distributions (Figure 2).

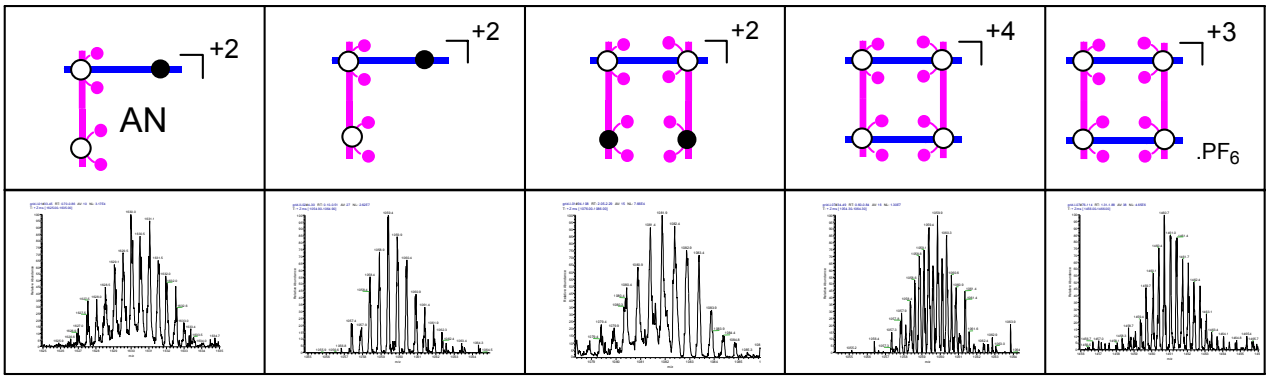


Figure 1.Proposed symbols and their isotopic distributions for the species detected when **1** and **3** were titrated with Cu(I) salt.

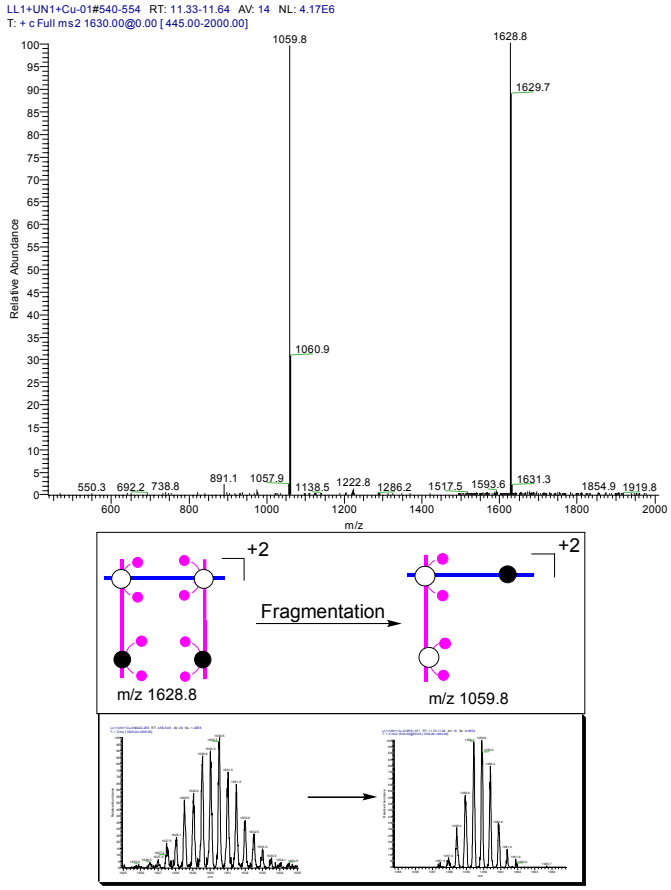


Figure 2. Fragmentation of signal at m/z 1629.

b) ESI-MS titration of 1 and Cu(I) with 3 in methylene chloride.

The second series of experiments was carried out by the titration of **1** and the Cu(I) salt with aliquot amounts of **3** in methylene chloride. As the titration proceeded signals corresponding to the nanobox intensified with the final spectrum only containing signals corresponding to the nanogrid. In contrast to the first titration, excess addition of **3** led to distruction of the nanogrid. Notably, similar intermediates were observed in both the titrations. All the signals are in good agreement with their isotopic splittings.

Table 2. ESI MS titration data along with proposed formula of observed species.

Titration Nr.	Stoichiometric ratio of **1**, Cu(I) and **3** resp.	Observed m/z	Formula
1	1: 1: 0.2	652.4 (40%) 1059.8 (100%) 1220.8 (90%) 1303.0 (55%)	$[(\mathbf{1})(Cu)_2(AN)]^{+2}$ $[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ $[(\mathbf{1})(Cu)(H_2O)]^{+}$ $[(\mathbf{1})(Cu)(AN)_2(H_2O)]^{+}$
2	1: 1: 0.4	1059.8 (100%) 1220.8 (90%) 1303.0 (55%) 1629.8 (8%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ $[(\mathbf{1})(Cu)(H_2O)]^{+}$ $[(\mathbf{1})(Cu)(AN)_2(H_2O)]^{+}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
3	1: 1: 0.6	1059.8 (100%) 1220.8 (10%) 1303.0 (15%) 1629.8 (5%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ $[(\mathbf{1})(Cu)(H_2O)]^{+}$ $[(\mathbf{1})(Cu)(AN)_2(H_2O)]^{+}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
4	1: 1: 0.8	1059.8 (100%) 1220.8 (15%) 1303.0 (10%) 1461.3(10%) 1629.8 (5%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})(Cu)(H_2O)]^{+}$ $[(\mathbf{1})(Cu)(AN)_2(H_2O)]^{+}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
5	1: 1: 1.0	1059.8 (100%) 1220.8 (5%) 1303.0 (5%) 1461.3(5%) 1629.8 (5%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})(Cu)(H_2O)]^{+}$ $[(\mathbf{1})(Cu)(AN)_2(H_2O)]^{+}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
6	1: 1: 1.2	1059.8 (100%) 1220.8 (5%) 1303.0 (5%) 1461.3(5%) 1629.8 (5%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})(Cu)(H_2O)]^{+}$ $[(\mathbf{1})(Cu)(AN)_2(H_2O)]^{+}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$ $[(\mathbf{1})_2(\mathbf{3})(Cu)_2]^{+2}$
7	1: 1: 1.6	1059.8 (100%) 1461.3(15%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$
8	1: 1: 1.8	1059.8 (100%) 1461.3(15%)	$[(\mathbf{1})(\mathbf{3})(Cu)_2]^{+2}$ and $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$
9	1: 1: 2.0	1059.8 (100%) 1461.3(15%)	$[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$
10	1 : 1: 4.0	1059.8 (100%) 1022.5 (100%) 1461.3(10%)	$[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4]^{+4}$ $[(\mathbf{1})(\mathbf{3})_2(Cu)_3(H_2O)_2]^{+3}$ $[(\mathbf{1})_2(\mathbf{3})_2(Cu)_4PF_6]^{+3}$

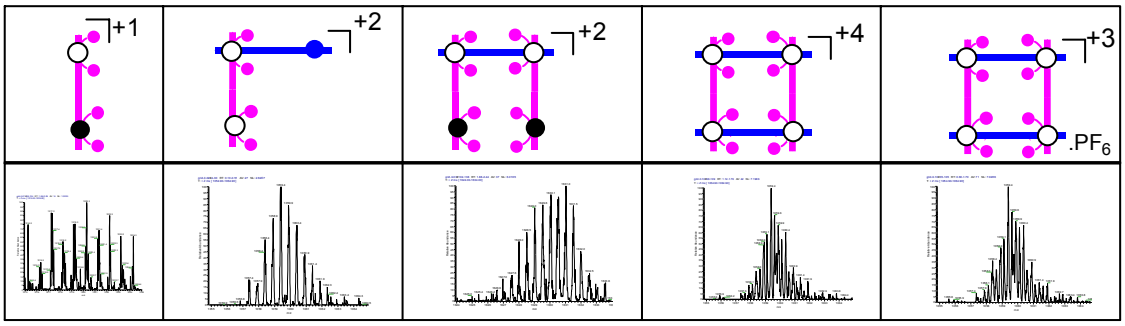
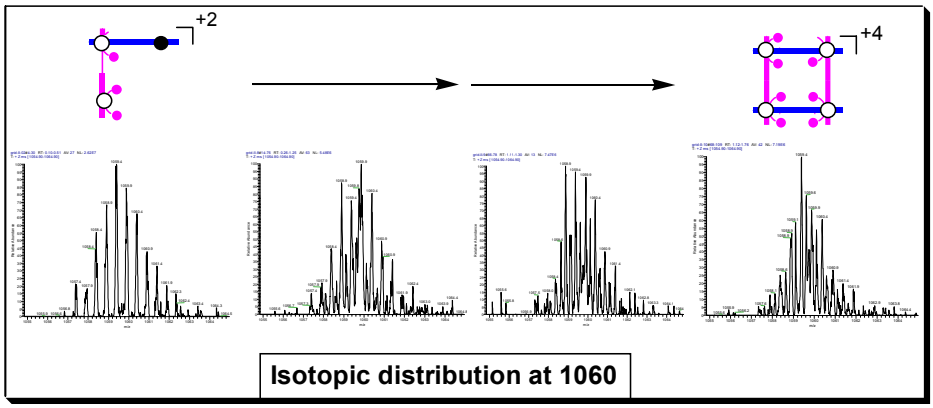


Figure 3. Proposed symbols for the species detected when **1** and Cu(I) salt were titrated with aliquot amounts of **3**.

ESI-MS titrations provide a qualitative picture of possible intermediates on the way to the nanogrid assembly and the observed intermediates are independent of the type of titration. These models (Figure 1 and 3) were then used to calculate the equilibrium constants from analysis of the corresponding spectrophotometric titration curves.

Change of the 2+ charged to 4+ charged species in the titration



Spectrophotometric Titrations and Thermodynamic Parameters

Ligand **1** and **3** were titrated with aliquot amounts of Cu(I) salt in methylene chloride at 25 °C. Upon complexation with Cu(I) ions significant shifts were observed in UV/vis spectra. The characteristic MLCT band appeared at ~ 490 nm that is responsible for the red colour of the complexes.[i] Figure 4 displays the UV/vis changes upon Cu(I) salt titration with the solution containing ligand **1** and **3**. Three isosbestic points can be distinguished at 302, 312, and 387 nm. As the titration proceeds, π to π* bands are shifted bathochromically because of complex formation. Insert in figure 4 indicates that the final complex nanogrid is fully formed at 2 equiv. of Cu(I) salt. Excess addition of the Cu(I) salt did not affect the already formed nanogrid, as demonstrated by ESI MS data. The data obtained from the titration spectra were used to determine the binding constants (Table-3) of the intermediates and the nanogrid using the program SPECFIT[ii].

As evidenced by the ESI MS and spectrophotometric titration, a three step formation process was proposed for the formation of the eight-component nanogrid assembly. Step 1 leads

to the formation of the heteroleptic $[Cu(\mathbf{1})(\mathbf{3})]^{+}$ complex. In the second step, the $[Cu(\mathbf{1})(\mathbf{3})]^{+}$ complex takes up one more Cu(I) salt to furnish the $[Cu_2(\mathbf{1})(\mathbf{3})]^{2+}$ complex, with Cu(I) most likely attached to ligand **1** due to the larger stabilisation of Cu^{+} in between two aromatic rings (cation-π interactions). In the final step, two of the $[Cu_2(\mathbf{1})(\mathbf{3})]^{2+}$ complexes combine together to afford the final nanogrid.

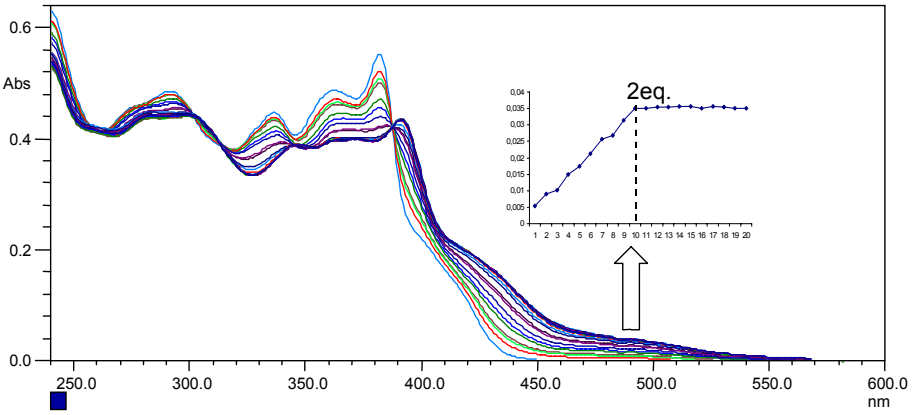


Figure 4. UV/vis spectral changes of **1** and **3** on addition of Cu(I) salt in methylene chloride. The inset shows the plot of absorbances at 497 nm against the molar ratio of Cu(I) salt.

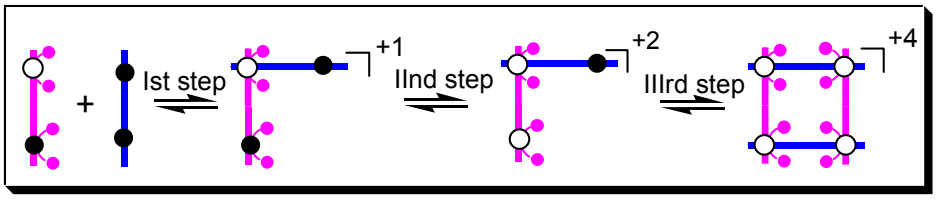
$$Cu^{+} + \mathbf{3} + \mathbf{1} \rightleftharpoons [(Cu)(\mathbf{3})(\mathbf{1})]^{+} \qquad \log ß_{111} = 9.78$$

$$[(Cu)(\mathbf{3})(\mathbf{1})] + Cu^{+} \rightleftharpoons [(Cu)_2(\mathbf{3})(\mathbf{1})]^{+2} \qquad \log ß_{211} = 15.05$$

$$2\,[(Cu)_2(\mathbf{3})(\mathbf{1})]^{+2} \rightleftharpoons [(Cu)_4(\mathbf{3})_2(\mathbf{1})_2]^{+4} \qquad \log ß_{422} = 34.90$$

Table 3. Obtained binding constants for different intermediates.

Proposed mechanistic three-step pathway to $[Cu_4(\mathbf{1})_2(\mathbf{3})_2]^{+4}$assembly;



[i] E. Müller, C. Piguet, G. Bernardinelli, A. F. Williams, *Inorg. Chem*. **1988**, *27*, 849-855.
[ii] M. Maeder, A. D. Zuberbühler. *Anal. Chem.* **1990**, *62*, 2220-2224.