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Simple and supramolecular copper complexes as precursors in the HRTEM induced formation of crystalline copper nanoparticles

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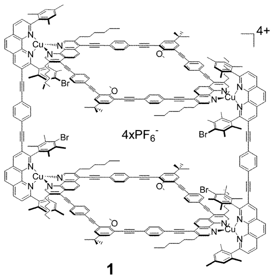
In the HRTEM investigations of copper(I) bisphenanthroline nanoscaffolds and simple precursor complexes, nanoparticles were generated that upon closer inspection turned out to be pure crystalline copper nanoparticles.

The synthesis of discrete supramolecular assemblies in the 3–10 nm regime is a fascinating and rapidly growing area of research. Amazing structures, such as dodecahedra, hexagons and grids, have been reported in seminal contributions by Stang,[1] Newkome,[2] Lehn[3] and others.[4] Due to the large size and huge void of these structures, that mostly contain disordered solvent molecules, X-ray diffraction data are difficult to obtain. Hence, scanning probe microscopy techniques and high resolution TEM (HRTEM)[5] have been serving as important supplementary tools for characterisation.[1,2] Metallosupramolecular aggregates, a nanoscopic dodecahedron and a hexagonal metallocycle, were among the first to be structurally supported by HRTEM.[1,2] In the following, we will describe our experience with HRTEM investigations of copper(I) bisphenanthroline nanoscaffolds, showing that these investigations do not provide pictures of the nanostructures but instead lead to crystalline copper nanoparticles that can easily be confused with the original aggregates.

The formation and investigation of ordered and defined metal nanoparticles have been actively pursued areas of research. In particular, due to an increased surface to volume ratio their properties, *cf.* copper particles in heterogeneous catalysis, are different from those of bulk materials.[6] Metal nanoparticles have been generated by using reducing agents or reverse micelles, *via* photoreduction, and by γ-irradiation, sonochemical and radiolytic methods or thermal decomposition.[7] Mostly their formation was effected in aqueous media. In contrast, the present study suggests a way to prepare copper nanoparticles from coordination precursors in non-aqueous media.



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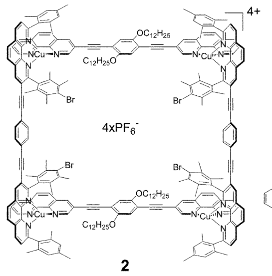

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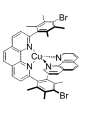

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The compounds of the present study, the copper(I) bisphenanthroline nanoscaffolds (**1** and **2**), have been described earlier,[8] while complex **3** was prepared along the same strategy.†

Nanoscaffold **1** (M = Cu) was prepared for HRTEM‡ and SAED (selected area electron diffraction) investigations by either spreading the solid powder of **1** on Cu- or Al-grids (sample 1, 2) or a solution of **1** in acetone on a Al-grid (sample 3). The use of Al-grids was required for quantitative EDX measurements.

As samples 1 and 2 displayed no differences in the real structure, we will not separate them in the ensuing discussion. The HRTEM micrographs of samples 1 and 2 showed nanoaggregates of 5 nm size, roughly that expected for **1** (d = 4.2 nm). EDX spectra proved an enrichment of copper within the nanoaggregates of the matrix. As a consequence, such pictures may be interpreted as cast iron proof for the formation of the organic nanostructure **1**. However, these nanoaggregates are not present in the initially homogeneous matrix, they are formed after a short time of exposure (*ca.* 1 min). Ongoing exposure increases the crystal quality of the nanoaggregates, finally transforming them to perfect nanocrystals. The distribution and density of the copper nanoparticles within the matrix is random (see Fig. 1).

The exposed area and the region with massive formation of copper nanoparticles are quite apart. In some cases, the nanoparticles form a circle around the exposed area. Hence, the radiation damage of the material can easily be overlooked, as the loci of exposure and nanoparticles formation are different.

A clear determination of the nanoparticle structure is possible by applying SAED and HRTEM combined with image processing. The SAED pattern depicted in Fig. 2 on the left was recorded in a region with many nanoparticles. The diffraction pattern exhibits sharp Bragg intensities as expected for perfect single crystals. The reflections were located on concentric circles due to unsystematic orientations of the nanoparticles. The diameters of the circles correspond to d-values expected for pure copper (d_{Cu}: d_{111} ~ 2.09 Å, d_{200} ~ 1.81 Å, d_{220} ~ 1.28 Å, d_{311} ~ 1.09 Å). The crystalline nature of the nanoparticles was also evidenced by HRTEM, see Fig. 2, right. The HRTEM micrographs display a periodic arrangement of stripes corresponding with net planes of copper, as evidenced by the FFT (fast Fourier transform) of this image. After massive exposure, it is possible to detach the nanoparticles from the surface of the matrix. As evidenced by EDX, these unattached nanoparticles consist of pure copper without oxidic layer. Again, their

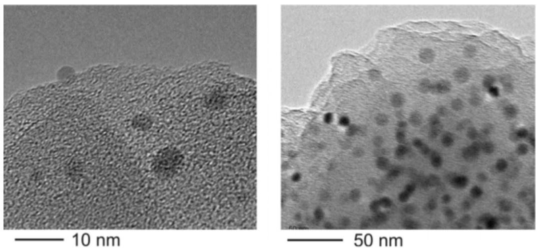

Fig. 1 Bright field images of copper nanoparticles prepared from sample 1, 2.

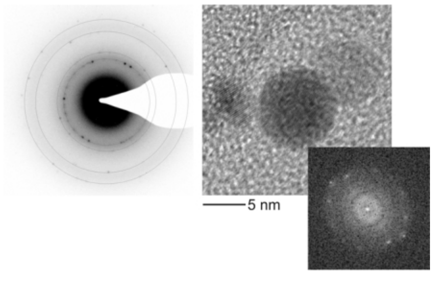

Fig. 2 SAED (left) and HRTEM (right) of copper nanoparticles prepared from sample 3.

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structure can be attributed to the fcc structure of bulk copper by the above mentioned techniques.

Sample 3 was received after evaporating a thin liquid film of red **1** on the Al-grid. Before radiation damage, no Bragg intensities can be observed in electron diffraction patterns of this material—not even within nanosized regions.

The SAED pattern and HRTEM micrograph of Fig. 3 were recorded after radiation damage of the amorphous film. Both are consistent with the formation of copper nanoparticles in sample 3. As described above, the composition of isolated nanoparticles was checked by EDX.

In conclusion, the combination of HRTEM, SAED and EDX confirms nanoparticle formation in samples 1–3 as a result of radiation damage. Definitely, these particles do not show the suprastructure of nanoscaffold **1**.

As a control experiment we have investigated the supramolecular grid assembly **2**. Similar to **1**, assembly **2** proved also sensitive to radiation damage. The obtained results were again in line with formation of crystalline copper nanoparticles during the exposure. Following the procedures described earlier, the formation of copper nanoparticles was checked by SAED patterns recorded on aggregates of nanoparticles (see Fig. 3), EDX (not shown) and Fourier transformation of HRTEM images of individual nanoparticles (not shown).

To elucidate whether there is a unique templating effect of the supramolecular scaffolds **1** and **2**, the much simpler copper complex **3** was investigated by HRTEM and SAED. As shown in Fig. 4, the high resolution image again shows copper nanoparticles with a size of 4–5 nm. These findings led us to conclude that the nanoparticle size is independent of any unique templating effect of suprastructures **1** and **2**.

We have shown that copper nanoparticles form from several copper bisphenanthroline precursors. Surprisingly, the dimensions of the nanoparticles are independent of the size and shape of the precursor structure. The observed results point to radiation damage mediated formation of crystalline copper nanoparticles and rule out any supramolecular template effect. Hence, we assume that a multitude of copper bisphenanthroline or bisbipyridine complexes could equally serve as precursors. These findings also raise serious questions about using TEM as a proof of metallosupramolecular aggregates. Moreover, the formation of ordered nanoparticles in non-aqueous media certainly is an interesting aspect of our approach that does not require special reducing additives (*i.e.* detergents) due to the electron beam. Therefore, Cu(I) bisphenanthroline complexes can now be considered as precursors for crystalline copper nanoparticles.

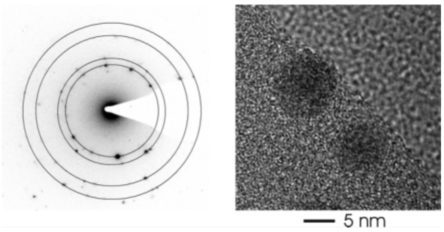

Fig. 3 SAED pattern (left, with circles indicating d_{Cu}) and HRTEM micrograph of copper nanoparticles (right) obtained from grid assembly **2**.

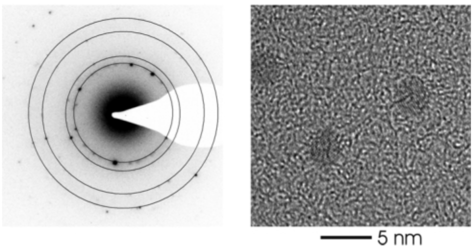

Fig. 4 SAED pattern (left, with circles indicating d_{Cu}) and high resolution image of copper nanoparticles (right) of model complex **3**.

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Notes and references

† Model complex **3** was prepared by mixing [Cu(MeCN)$_4$]PF$_6$, 2,9-bis(4-bromo-2,3,5,6-tetramethylphenyl)-[1,10]phenanthroline,[9] and [1,10]phenanthroline (1 : 1 : 1 equiv.) in dichloromethane. The resulting dark red compound was identified by ^{1}H NMR, ESI MS and elemental analysis.

‡ The electron microscope (Philips CM30ST, LaB$_6$-cathode) was operating at 300 kV (resolution: 1.9 Å). Fourier transforms (FFT) of high resolution micrographs were calculated with the software Digital Micrograph 3.6.1 (Gatan). EDX (Si–Li-Detector, Noran) was performed with a nanoprobe (point analyses) and in the scanning mode (spectral imaging).

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