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Copper(II) coordination compounds as building blocks for the formation of gold nanoparticle dimers

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A new way for gold nanoparticle dimer formation based on the coordination interaction of a benzimidazole copper(II) complex with gold nanoparticles has been proposed.

Individual colloidal nanoparticles (NPs) possess a spectrum of useful functional properties (optical, catalytic and magnetic).[1–5] Practical exploitation of these properties requires a reliable methodology for assembly of NPs into mesoscopic structures, so that they can be integrated in electronic devices, fuel cells, solar cells, *etc*. Current methods for NP assembly include the following approaches: DNA base pairing,[6] electrostatic interactions,[7] hydrogen bonding[8] and covalent bonding.[9] However, most of the above methods result in the formation of NP assembles with low yields and lead to the formation of irreversible links between the NPs.

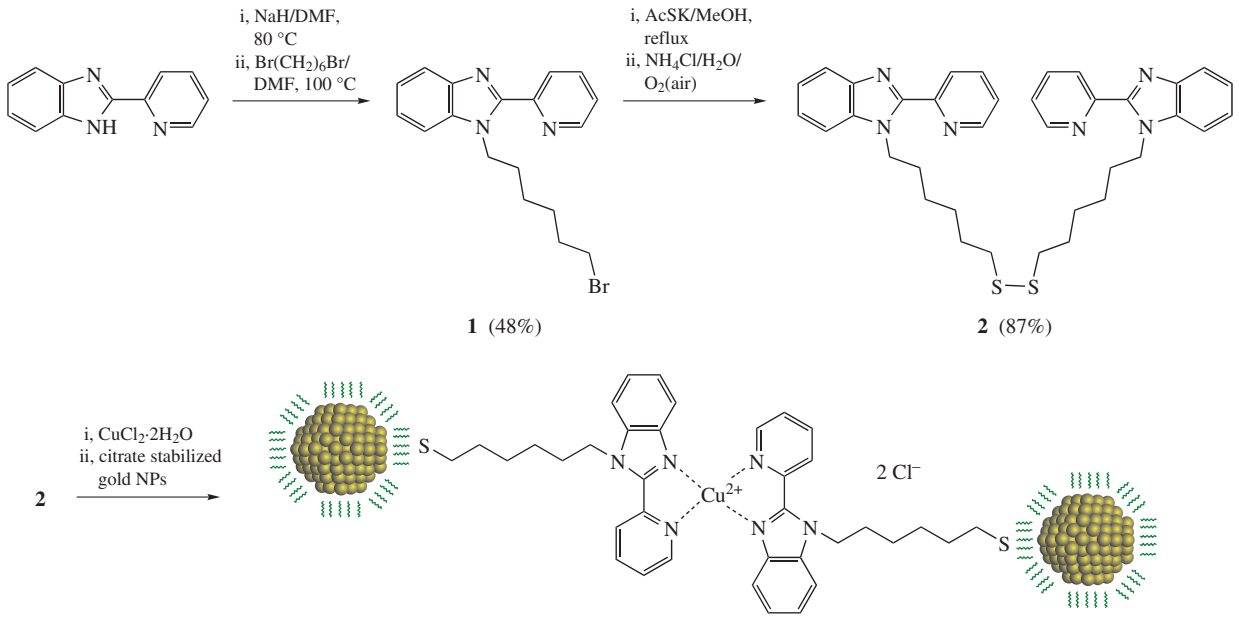
The aim of this work was to develop a new methodology for the controlled assembly of colloidal NPs using the coordination chemistry of transition metals. The advantages of coordination interactions include flexible geometry of transition metals that is switchable by external stimuli (light, electrochemical potential and heat).

We demonstrated that the coordination compounds of transition metals can influence the assembly of gold NPs. We showed that the formation of the dimers of NPs can be initiated by the simple addition of copper(II) cations to a solution of NPs bearing a benzoimidazole chelating group specifically designed for recognizing copper ions.

It is well known that benzimidazole derivatives containing additional donor atoms are promising ligands for coordination chemistry as they readily form stable complex compounds (ligand : metal ion = 2:1) with transition metal ions due to nitrogen donor atoms even in the presence of other donor atoms (oxygen or sulfur).[10]

The bifunctional organic ligand containing terminal benzimidazole fragment has been synthesized according to Scheme 1. First, the alkylation of 2-(pyrid-2-yl)benzimidazole sodium salt by 1,6-dibromohexane was carried out[†] and then monobromide **1** was converted into disulfide **2** by treatment with potassium thioacetate.[‡]

To obtain gold NP dimers, we investigated the adsorption of ligand **2** on a gold surface. We used two approaches to functionalized gold NPs. The first one was based on the interaction of transition metal ions with gold NPs modified by synthesized organic ligands, which were obtained under interaction of citrate stabilized gold NPs[§] with disulfide **2**. However, in this case, only big aggregate formation was observed by UV-VIS spectroscopy,



Scheme 1 (Lines on gold NP surface represent chemisorbed molecules of ligand **2**.)

DLC and TEM analysis. The addition of disulfide **2** to the solution of citrate stabilized gold NPs leads to a big red shift and intensification of the plasmon resonance band in the absorption spectrum (from 520 to 600 nm). No visible changes in the absorption spectrum were observed upon the addition of $CuCl_2$ to the solution of NP aggregates; this indicates the irreversibility of gold NP association.

The second approach included the interaction of an earlier prepared copper complex compound of benzimidazole-type disulfide **2** with citrate stabilized gold NPs.¶ In this case, we succeeded in obtaining dimer aggregates, which were further proved using different physical and chemical methods. The proposed mechanism for the participation of the ligand in dimerization is given in Scheme 1.

NPs of three different sizes were successfully dimerized using the described process (Table 1). The ratio of NPs to ligand needed is dependent on both the concentration and the size of NPs. Table 1 shows the ratios found to be successful. There is a trend that as the NP diameter decreases then more ligand solution needs to be added to form dimers. It is important to use a correct NP:ligand ratio because dimerization does not occur if a small amount of a ligand solution is added, whereas too much ligand solution will lead to uncontrolled aggregation.

Table 1 NP:ligand ratios for three NP solutions.

Initial NP size (DLS)/nm	NP concentration/cm^{-3}	NP:ligand ratio
35±1	3.3×10^{10}	15:1
19±1	4.2×10^{11}	9:1
13±1	1.4×10^{11}	1:1

The formation of dimers was demonstrated using TEM, which makes it possible to perform the direct visualisation of particles present in the solution. Figure 1(*a*) is a typical image showing the presence of spheres, dimers and trimers. Averaging over a number of different images, we found that 45% of the observed particles were dimers, trimers or tetramers. Figure 1(*b*) exhibits a high resolution image of three dimers. The average distance between two NPs was 2.85 nm.

Dimer structure was predicted by quantum-chemical calculations with the help of density function theory and the non-empirical local Perdew–Burke–Ernzerhof (PBE) functional[11] in a nonrelativistic approach using the Stevens–Basch–Krauss (SBK) pseudopotential[12] in which the outer electron shells are described by the following basis sets: [311/1] for H, [311/311/11] for C, S and N and [51111/51111/5111] for Au atoms. Figure 1(*c*) represents the optimized structure of $(AuSL)_2Cu$ dimer, the calculated distance between two gold particles, which are denoted as atoms, is 2.80 nm; this is consistent with experimental data obtained.

Dimer aggregate formation was also investigated using UV-VIS spectroscopy. As expected, the absorbance spectra exhibited both a transverse and a longitudinal plasmon peak, with the longitudinal peak appearing as a smaller shoulder. Thus, increasing the aspect ratio from 1 to larger values should cause the UV-VIS spectrum of the sample to change from exhibiting one plasmon peak to two plasmon peaks. Figure 2 shows the UV-VIS spectra of the NPs (13 nm) before and after dimerization. In this case, a separate second peak is not observed, but instead a shoulder appears at a longer wavelength. Note that the process of dimerization involves diluting the NPs to varying extents; therefore, the original NP spectra have been normalised, so that both the NP and dimer spectra are the same height at their maxima. The appearance of a shoulder in each case is likely due to the longitudinal plasmon peak occurring close to the transverse peak, causing them to overlap. The absorbance is also likely to have a significant contribution from the single NPs.

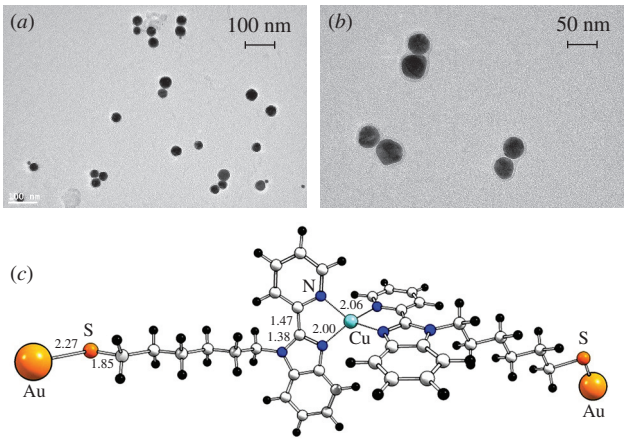


Figure 1 (*a*) Typical TEM image of NPs following dimerization, (*b*) high resolution TEM images of dimers, and (*c*) optimized structure of $(AuSL)_2Cu$ dimer, calculated distances are given in Å.

† *Synthesis of 1-(6-bromohexyl)-2-(pyrid-2-yl)-1*H*-benzimidazole* **1**. 2-(Pyrid-2-yl)benzimidazole (3 g, 16 mmol) was added to a stirred suspension of sodium hydride (60% suspension in mineral oil, 0.8 g, 20 mmol) in dry DMF (50 ml), and the mixture was heated to 80 °C for 2 h under an argon atmosphere. The hot suspension was carried to a dropping funnel under argon stream and added to a hot solution of 1,6-dibromohexane in dry DMF (50 ml). The mixture was heated to 100 °C and stirred at this temperature for 2 h. After cooling to room temperature, the saturated solution of ammonium chloride (100 ml) was added to the mixture and extracted with ethyl acetate (3×50 ml). Combined organic layers were washed with brine (100 ml) and water (100 ml) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was purified by column chromatography (light petroleum–ethyl acetate, 5:1). Yield of product **1**, 2.56 g (48%), yellow oil. ^{1}H NMR, δ: 8.68 (dd, 1H, HC^6-Py, J_1 1.0 Hz, J_2 4.8 Hz), 8.41 (dt, 1H, HC^3-Py, J_1 1.0 Hz, J_2 7.9 Hz), 7.85 (dd, 2H, HC$^{4'}$, HC$^{7'}$ – benzimidazole, J_1 1.2 Hz, J_2 5.5 Hz), 7.81 (dt, 1H, HC^4-Py, J_1 1.5 Hz, J_2 7.6 Hz), 7.43 (dd, 1H, HC^5-Py, J_1 2.6 Hz, J_2 6.5 Hz), 7.30 (m, 2H, HC$^{5'}$, HC$^{6'}$ – benzimidazole), 4.80 (t, 2H, CH_2–N, J 7.7 Hz), 3.33 (t, 2H, CH_2–Br, J 6.8 Hz), 1.89 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 1.40 [m, 4H, $(CH_2)_2$]. ^{13}C NMR, δ: 148.6, 136.9, 123.6, 119.8, 114.9, 110.2, 45.3, 33.5, 29.8, 27.6, 25.0. Found (%): C, 60.01; H, 5.40; N, 11.98. Calc. for $C_{18}H_{20}N_3Br$ (%): C, 60.34; H, 5.58; N, 11.73.

‡ *Synthesis of bis{6-[2-(pyrid-2-yl)-1*H*-benzimidazol-1-yl]hexyl}-disulfide* **2**. Potassium thioacetate (2.44 g, 21 mmol) was added to a stirred solution of compound **1** (2.56 g, 7 mmol) in methanol (20 ml). The mixture was stirred under reflux for 24 h. After the reaction was complete, a saturated solution of ammonium chloride (50 ml) was added and the mixture was extracted with dichloromethane (3×30 ml). Combined organic layers were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure. Yield of product **2**, 1.93 g (87%), yellow oil. ^{1}H NMR, δ: 8.68 (ddd, 1H, HC^6-Py, J_1 1.0 Hz, J_2 1.8 Hz, J_3 4.8 Hz), 8.42 (dt, 1H, HC^3-Py, J_1 1.1 Hz, J_2 8.0 Hz), 7.85 (ddd, 2H, HC$^{4'}$, HC$^{7'}$ – benzimidazole, J_1 1.0 Hz, J_2 2.4 Hz, J_3 4.1 Hz), 7.82 (dt, 1H, HC^4-Py, J_1 1.9 Hz, J_1 5.2 Hz), 7.45 (dd, 1H, HC^5-Py, J_1 2.1 Hz, J_2 5.7 Hz), 7.32 (m, 2H, HC$^{5'}$, HC$^{6'}$ – benzimidazole), 4.83 (t, 2H, CH_2–N, J 7.5 Hz), 2.62 (t, 2H, CH_2–S, J 7.2 Hz), 1.90 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 1.39 [m, 4H, $(CH_2)_2$]. IR (KBr, ν/cm^{-1}): 1571 (C=N). MS (ESI), *m*/*z* (%): 621 (100) (MH^+). Found (%): C, 69.90; H, 6.64; N, 13.25; S, 9.90. Calc. for $C_{36}H_{40}N_6S_2$ (%): C, 69.68; H, 6.45; N, 13.55; S, 10.32.

§ *Synthesis of gold NPs.* Gold NPs were synthesized by reduction of hydrogen tetrachloroaurate(III), $HAuCl_4$, with trisodium citrate and tannic acid in aqueous solution according to the reported procedure.[13] Gold NPs stabilized by disulfide **2** were obtained by interaction of citrate stabilized gold NPs with ligand **2**.[14]

¶ *Preparation of NP dimers.* 80 mg of disulfide **2** was dissolved in 1.5 ml of dichloromethane; 18.75 μl of this ligand solution was mixed with one drop of ethanol and 10 ml of water to form solution 1. Solution 2 was made up by dissolving 1 mg of copper(II) chloride dihydrate in 10 ml of water. 3.64 ml of solution 1 was added to 1 ml of solution 2. The resulting solution was then added to an aqueous solution of NPs to cause their assembling into dimers and trimers.

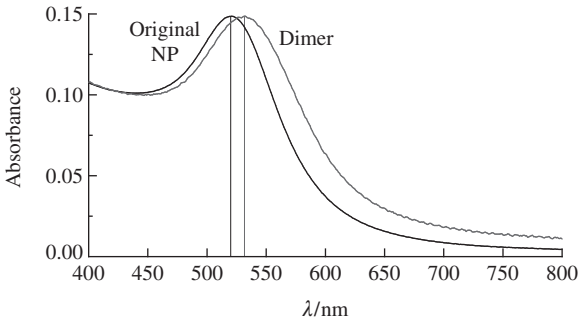


Figure 2 UV-VIS absorption spectra showing the change in absorption upon dimerization for the NPs with the average size of 13 nm; λ_{max} is 520 (original NPs) or 539 nm (dimers).

Thus, UV-VIS spectroscopy is a suitable instrument for confirming when NPs aggregate forms small aspect ratio (<3) clusters, as this manifests itself in the form of a shoulder on the longer wavelengths side of the original NP peak.

Therefore, we report a novel synthetic process for the gold NP dimer formation using copper(II) pyridylbenzimidazole complex as a building block. Formation of dimers was proved by TEM, DLS and UV-VIS spectroscopy. The new approach has advantages in comparison with known techniques such as reversible aggregation.

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