

From large 3D assembly to highly dispersed spherical assembly: weak and strong coordination mediated self-aggregation of Au colloids

Xuanjun Zhang, Dan Li* and Xiao-Ping Zhou

Received (in Durham, UK) 1st November 2005, Accepted 8th February 2006

First published as an Advance Article on the web 7th March 2006

DOI: 10.1039/b515501k

Distinctly different 3D assemblies of ~ 1.6 nm Au nanoparticles are constructed based on weak and strong coordination strategies. Reduction of KAuCl_4 with NaBH_4 in the presence of newly-synthesized 4-(4-phenylmethanethiol)-2,2':6',2''-terpyridine (**1**) yields functionalized Au nanoparticles which assemble *in situ* into large 3D aggregates *via* weak coordination between alkali metal ions and terpyridine attached to separated particles. These assemblies are disassembled into individual nanoparticles *via* addition of DMF solvent and further reassembled into highly dispersed 3D spherical nanostructures *via* addition of Co^{2+} (strong coordination with **1**). Wide and small angle XRD measurements show that the assemblies are formed from small Au nanoparticles, consistent with TEM results. It is significant that the large aggregates formed *in situ* can be directly transformed into nearly monodispersed 3D spherical assemblies *via* strong coordination (with Co^{2+}), presenting the first example of a direct transformation of one 3D nanonetwork into another distinctly different 3D nanonetwork. The controlled assembly and disassembly processes are accompanied by distinct shifts in the surface plasmon resonance.

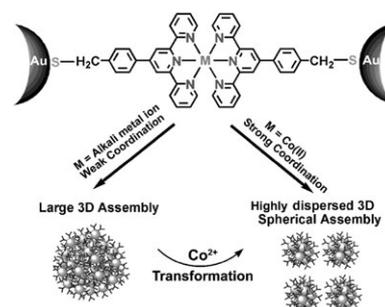
Introduction

The multi-scale organization of metal nanoparticles is a key step in their application as macroscopic nanodevices. Fine control of the spatial arrangement of these building blocks is also fundamentally important because well organized nanostructures often display valuable chemical, optical, or electronic properties that are distinctly different from those of their component parts or those of larger mass.^{1,2} However, the ability to organize nanoparticles into predefined and sophisticated nanostructures in a controllable way is still a significant challenge because of their inability to self assemble without the aid of organic molecules. Existing approaches to overcome these difficulties mainly focus on the exploitation of organic molecules or biological macromolecules to create metal assemblies. Among them, significant success has been achieved based on strategies such as alkanedithiols³ or DNA linking,⁴ polymer-based molecular recognition,⁵ mediator–template assembly,⁶ hydrogen bonding and electrostatic self-organization,⁷ a covalent bonding strategy,⁸ and so on. Despite much progress having been achieved, the ability to reversibly create assemblies of controllable shape in solution remains far from routine. A particular problem of aggregated nanoparticles is their tendency to collapse into larger, insoluble materials which cannot be easily manipulated and further processed.

Metal coordination-induced aggregation⁹ expands the structural diversity while different binding abilities or coordination modes of a ligand with different metal ions can lead to versatile supramolecular structures.¹⁰ In addition, compared with pure organic compounds, the metal–ligand complex

provides rich redox, optical and/or electronic properties,¹¹ which enable it to be a good candidate for constructing functional hybrids. Herein, we report a general and effective approach for constructing distinctly different 3D nanostructures using the same building block based on weak and strong coordination strategies (Scheme 1). The Au nanoparticles aggregated *in situ* through weak coordination can be disassembled *via* the addition of DMF solvent, leading to individual particles that can further reassemble into 3D spherical nanostructures *via* strong coordination. It is significant that the aggregates formed *in situ* can be transformed into these highly dispersed spherical assemblies without collapse to larger, insoluble materials, presenting the first example of a direct transformation from one 3D assembly into another quite different one. This general and effective approach opens up new possibilities for the fabrication of optical and electronic nanodevices.

In our strategy, we used a newly-synthesized thiol-terminated terpyridine, **1**, as a capping ligand and metal ions as “molecular glue” for assembling Au nanoparticles (Scheme 1).



Scheme 1 Distinctly different 3D assemblies fabricated *via* weak and strong coordination.

Department of Chemistry & Institute of Advanced Materials, Shantou University, Shantou 515063, China. E-mail: dli@stu.edu.cn; Fax: (+86) 754-290-2767

The ability of phenanthroline derivatives (with two chelating N atoms) to bind to Li^+ by forming a 2 : 1 ligand–metal complex is known in the detection of Li^+ .^{9a,12} Thus, using a larger ligand with three chelating N atoms is expected to facilitate binding with larger alkali metal ions such as Na^+ or K^+ . Reduction of KAuCl_4 by NaBH_4 in the presence of ligand **1** produces **1**-capped Au nanoparticles, which are expected to aggregate *in situ* by forming terpyridine–metal complexes.

Experimental section

All the chemicals were purchased from Sigma–Aldrich. Ligand **1** was synthesized by following the reaction scheme shown in Fig. 1. 4'-*para*-Tolyl-2,2':6',2''-terpyridine was synthesized by following the method of Cave *et al.* and Yang *et al.*,^{13a,b} with some modifications. 4'-(*para*-Bromomethylphenyl)-2,2':6',2''-terpyridine was synthesized by following the method of Spahni and Calzaferri.^{13c}

Synthesis of 4'-*para*-tolyl-2,2':6',2''-terpyridine

A mixture of *para*-tolylaldehyde (3.6 g, 30 mmol), 2-acetylpyridine (7.26 g, 60 mmol) and solid NaOH (s, 96%) (2.58 g, 62 mmol) was prepared using a mortar and pestle, the yellow medium aggregated until a yellow powder was formed (*ca.* 10 min) and then further ground for 30 min. The powder was transferred to a suspension of ammonium acetate (20 g, excess) in glacial acetic acid (50 mL, *ca.* 100%) and heated to reflux. After reaction for 3 h, a mixture of ethanol (30 mL) and water (40 mL) was added with stirring. Upon cooling, the crystalline product was precipitated from the solution, collected and recrystallized in ethanol to yield white crystals. Yield: 6.98 g (72%, 21.6 mmol). m.p. 172–174 °C. ¹H NMR (CDCl_3): δ = 8.77 (2 H, s), 8.71 (d, ³ $J_{\text{H,H}}$ = 8 Hz, 2 H), 7.92 (d, 2 H), 7.87 (d, ³ $J_{\text{H,H}}$ = 7.9 Hz, 2 H), 7.39 (d, ³ $J_{\text{H,H}}$ = 5 Hz, 2 H), 7.35 (d, ³ $J_{\text{H,H}}$ = 7.9 Hz, 2 H) and 2.46 (s, 3 H, CH_3); m/z 323, in agreement with the literature data.^{13c}

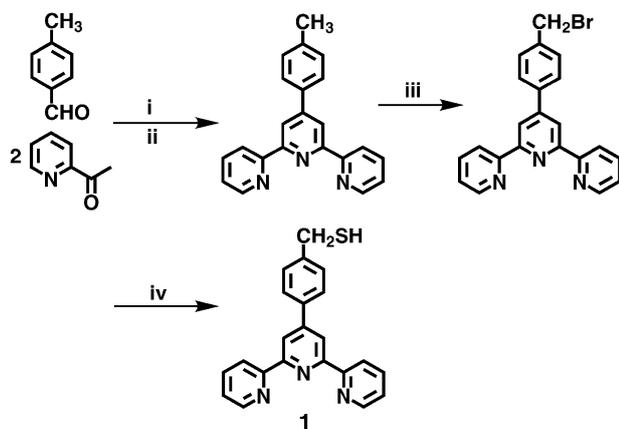


Fig. 1 Reaction scheme for the preparation of ligand **1**. (i) NaOH, solid state reaction; (ii) NH_4OAc , refluxed in HOAc; (iii) NBS, CCl_4 ; (iv) NH_2CSNH_2 , NaOH, HCl.

Synthesis of 4-(4-phenylmethanethiol)-2,2':6',2''-terpyridine (**1**)

4'-(*para*-Bromomethylphenyl)-2,2':6',2''-terpyridine (5 mmol) and thiourea (5 mmol) were mixed in 30 mL of ethanol, refluxed for 3 h and cooled to room temperature. The precipitate was separated and refluxed in 20 mL ethanol. NaOH solution (10%, 40 mL) was added and the mixture refluxed for 10 h. After cooling to room temperature, the mixture was filtered and the filtrate neutralized with dilute HCl (pH = 6). The pale yellow precipitate was collected, washed with water and dried in a desiccator. Yield: 0.94 g (53%). Anal. calc. for $\text{C}_{22}\text{H}_{17}\text{SN}_3$: C, 74.37; H, 4.79; N, 11.83. Found: C, 74.26; H, 4.82; N, 11.75%. δ (CDCl_3) 8.76 (2 H, s), 8.74–8.66 (4 H, m), 7.94–7.85 (4 H, m), 7.58 (2 H, d), 7.38 (2 H, d), 3.32 (2 H, s) and 1.46 (1 H, t); m/z 355.

In situ-formed assembly of 1.6 ± 0.2 nm Au

KAuCl_4 (19 mg, 0.05 mmol) dissolved in 3 mL ethanol was mixed with an acetone solution of **1** (0.05 mmol in 30 mL). The mixture was stirred for 5 min and filtered. With vigorous stirring, 1 mL NaBH_4 solution (0.2 M) was quickly injected into the filtrate. The colour of the solution turned from yellow to orange-brown.

Controlled disassembly of the 3D assembly

The collected Au–**1** powder (by centrifugation) was dispersed into 30 mL acetone. To 1 mL of this colloid (*ca.* 0.3 mg Au–**1**) was added DMF (either 0.5 mL or 0.8 mL). These solutions were stood for five minutes and used for TEM analysis.

Disassembling the 3D assembly into individual nanoparticles

The collected Au–**1** powder obtained by centrifugation (*ca.* 1 mg) was dissolved in 2 mL of DMF. After standing at room temperature for 10 min, almost all the aggregates disassembled into randomly-dispersed nanoparticles.

3D spherical assembly

To the above disassembled Au colloids (1 mg Au–**1** in 2 mL DMF) was added a solution of $\text{Co}(\text{NO}_3)_2$ in DMF (1×10^{-3} M, 1 mL) with stirring. The assemblies were formed after standing at room temperature for five minutes.

3D nanonetwork to 3D nanonetwork transformation

The Au–**1** colloid (purified) assembled *in situ* was dispersed in 30 mL acetone. To 1 mL of this colloid was added a solution of $\text{Co}(\text{NO}_3)_2$ (1×10^{-3} M, 0.5 mL) in 1 mL DMF (or acetone). Highly dispersed 3D spherical assemblies with diameters *ca.* 120–130 nm formed 2 min after the addition of the $\text{Co}(\text{NO}_3)_2$ solution.

X-ray power diffraction (XRD) measurements of the as-prepared samples were performed on a Rigaku D/max rA X-ray diffractometer with graphite-monochromatized Cu-K_α radiation ($\lambda = 1.54187 \text{ \AA}$) using a scanning rate of $0.06^\circ \text{ s}^{-1}$. X-ray photoelectron spectroscopy (XPS) was undertaken on an ESCA Lab MkII instrument with Mg- K_α radiation as the excitation source. Transmission electron microscopy (TEM) images were acquired using Philips TECNAI 12 and H600 instruments. UV-visible spectra were collected on a Philips PU-8620 UV-vis spectrophotometer. Elemental analysis

(CHN) was performed with a Perkin-Elmer 240 instrument. The photoluminescence measurements were carried out with a Perkin-Elmer LS 55B spectrofluorimeter.

Results and discussion

The formation of the Au-1 assembled *in situ* was rapid (in seconds) and reproducible. We found that the sizes of the particles in the aggregates could be tuned by changing the 1 : KAuCl₄ ratio. Assemblies of 1.6 ± 0.2 nm and *ca.* 3 nm Au were synthesized with ratios of 1 : 1 and 2 : 5, respectively. To demonstrate the feasibility of our approach, we selected the colloid of 1.6 ± 0.2 nm Au as an example of all of the following processes. The Au particles formed *in situ* were collected by centrifugation and redispersed in acetone and subsequently water. This purification procedure was repeated several times to remove the excess ligands and by-products. The as-prepared sample was characterized using X-ray diffraction (XRD), revealing it to be well-crystallized cubic Au (JCPDS 4-784) (Fig. 2). From the half-width of the XRD peaks, the average nano building unit size is estimated as 1.56 nm, based on the Scherrer equation. Thermal analysis indicated that the well-purified Au colloids contained $\sim 19.88\%$, by weight, of ligand.

The product purity and elemental composition were determined by XPS. The peaks for O can be attributed to O₂, CO₂, or solvent (H₂O or acetone) adsorbed on the surface of the sample, whereas the C peak and weak S and N peaks can be attributed to the capping ligand 1. The K peak can be attributed to K⁺ binding with 1 (Fig. 3). XPS peaks were observed at binding energy values of 83.8 and 87.8 eV for Au4f, 294 eV for K2p and 163 eV for S2p, respectively. Such binding energy values are similar to those reported in the literature.¹⁴

The assemblies formed *in situ* can be seen from any of the TEM images, a representative set of which is shown in Fig. 4a, revealing that the assembly is composed of numerous small nanoparticles with diameters of *ca.* 1.6 ± 0.2 nm. The particle sizes agree well with the XRD analysis. It is noted that no individual particles were observed from the TEM analysis.

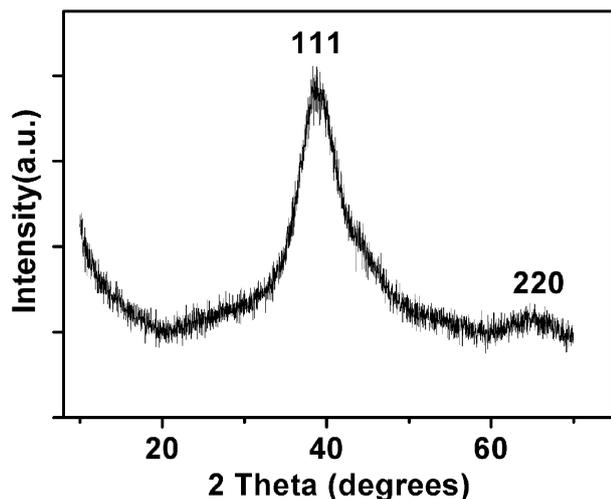


Fig. 2 XRD pattern of the Au sample formed *in situ*.

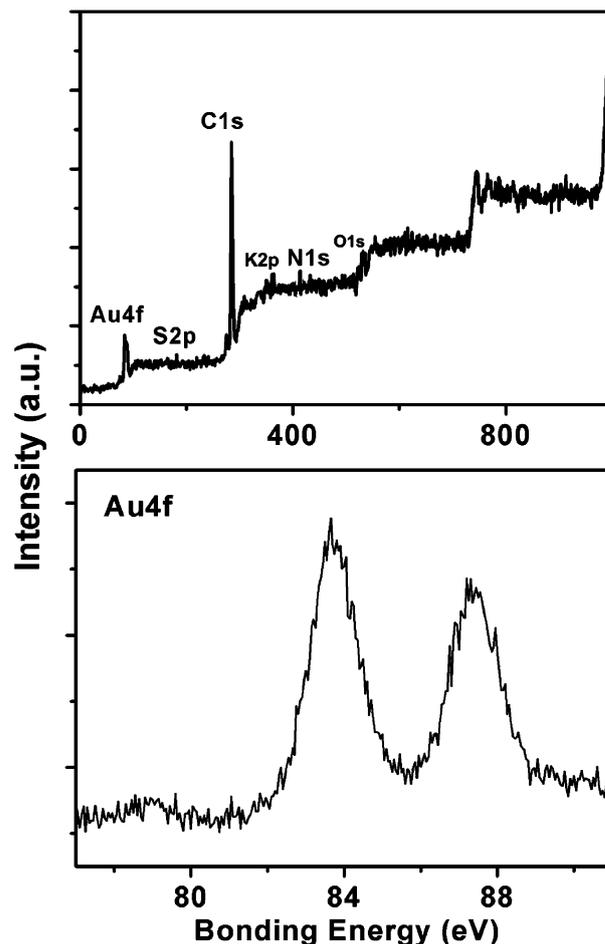


Fig. 3 XPS spectra of Au sample aggregated *in situ* (after purification). Top: survey spectrum. Bottom: bonding energy of Au4f.

These assemblies formed *in situ* were stable in acetone and ethanol systems, and could withstand ultrasound, but could also be disassembled by the addition of DMF solvent in a controllable way. TEM micrographs (Fig. 4b, c) from samples in mixed solution (DMF/acetone) were taken to illustrate the presence of individual nanoparticles along with the non-disassembled aggregates. We found that by increasing the DMF/acetone ratio (v/v), the quantity of individual nanoparticles increased with the consumption of larger aggregates. The brown-black powder obtained by centrifugation could be readily dissolved in DMF (1 mg Au-1 in 2 mL DMF). TEM analysis revealed that almost all the aggregates disassembled into individual nanoparticles (Fig. 4d). This significant finding suggests that the nanoparticles aggregated *in situ* were held together by relatively weak interactions.

While different binding abilities or coordination modes of a ligand with different metal ions can lead to versatile supra-molecular structures, we raise the question whether different assemblies can be achieved using 1-capped nano building blocks by the changing of metal ions. It is well known that 2,2':6',2''-terpyridine can chelate Co²⁺ effectively by forming 2 : 1 complexes.^{15,16} This strong binding would enable the particles to be held together tightly and lead to complex 3D nanostructures.

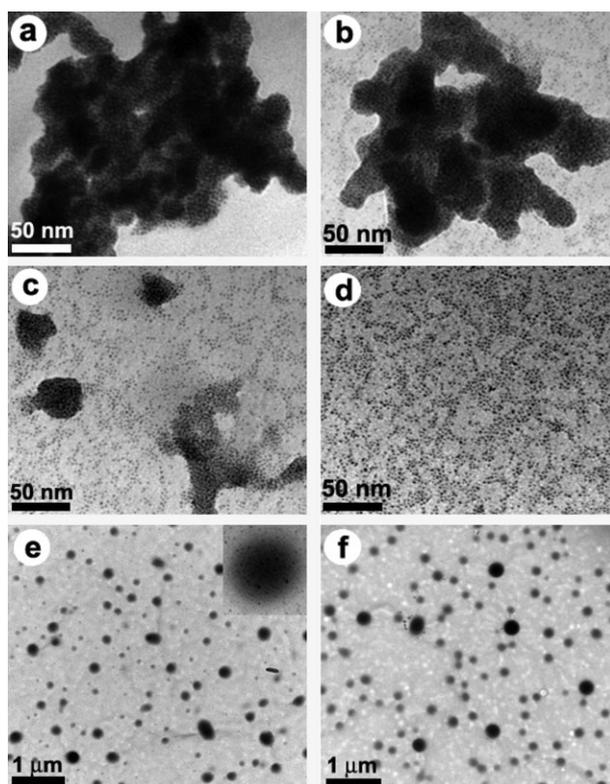


Fig. 4 TEM images of as-prepared Au colloids: (a) large aggregates formed *in situ*; (b) 0.3 mg Au-1 in acetone/DMF (1 mL/0.5 mL); (c) 0.3 mg Au-1 in acetone/DMF (1 mL/0.8 mL); (d) Au powder dissolved in DMF; (e) spherical assemblies formed 2 min after addition of Co^{2+} ; (f) 20 h after addition of Co^{2+} .

As expected, a new kind of 3D assembly formed within minutes of adding a $\text{Co}(\text{NO}_3)_2$ solution into the disassembled Au colloids. TEM analysis revealed that the spherical assemblies were highly dispersed (Fig. 4e), with diameters of *ca.* 100–200 nm. This spherical aggregate was composed of small nanoparticles, with some individual particles at the surface-contact area (Fig. 4e, inset). After standing at room temperature for 20 hours, the assemblies appeared more spherical and compact, and no individual nanoparticles were observed from the TEM analysis (Fig. 4f).

To investigate the influence of Au-1 : Co^{2+} ratio on the aggregation process, two comparison experiments were carried out. When insufficient Co^{2+} was used (1 mg Au-1 in 2 mL DMF mixed with 100 μL $\text{Co}(\text{NO}_3)_2$ solution (1×10^{-3} M)), only a few aggregates, along with a large quantity of individual nanoparticles, were observed according to the TEM analysis (Fig. 5). The result of the other comparison experiment revealed that excess Co^{2+} did not influence the morphology of the aggregates especially, but lead to spheres of relatively smaller sizes (*ca.* 100 nm). It is noted that although the solvents do not change the coordination mode of 1 with Co^{2+} , they indeed affect the dispersivity of the final spherical assembly. We found that the 3D spheres were relatively more monodisperse and uniform when an acetone solution of $\text{Co}(\text{NO}_3)_3$ was used.

The small angle XRD (SAXRD) pattern (Fig. 6a) of Au aggregated *in situ* shows an intense diffraction peak at $2\theta =$

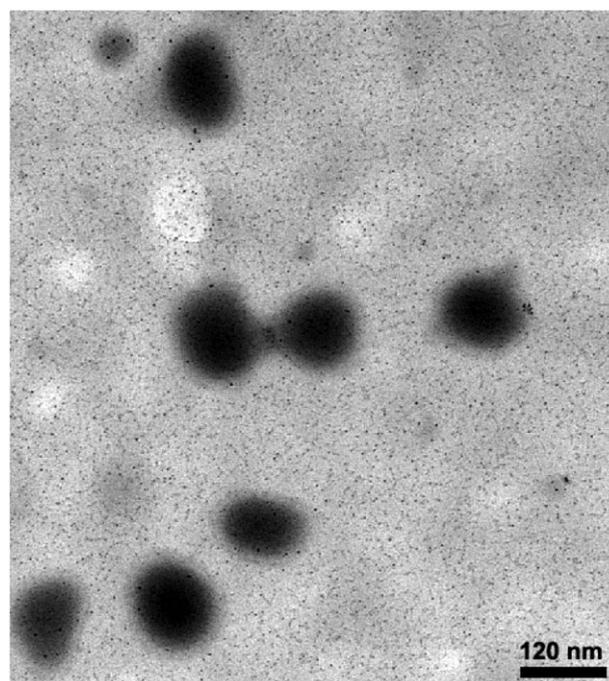


Fig. 5 TEM image of the Au colloids when insufficient Co^{2+} was used.

2.3° , from which we can calculate the center-to-center spacing of approximately 3.84 nm. Fig. 6b shows the pattern of 3D spherical aggregated Au, with a peak at $2\theta = 2.4^\circ$, from which the center-to-center spacing was calculated as approximately 3.68 nm. The slight shortening of the spacing most probably results from the stronger binding of 1 with Co^{2+} compared to alkali metal ions, which hold the particles relatively closer.

Insight into the structures of 1–metal–Au aggregates can be obtained through molecular modelling. Fig. 7 shows a proposed working model for Co^{2+} -induced assembly, from which the interparticle spacing was calculated as 2.26 nm. Taking the particle diameter and two S–Au bonds into account, the center-to-center spacing of the particles in the 1–Co(II)-linked

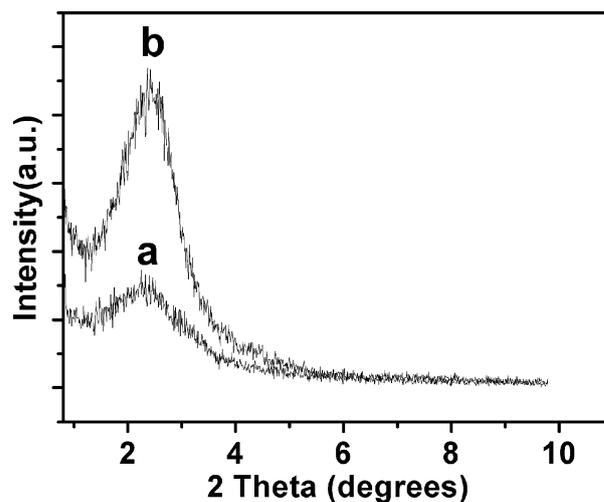


Fig. 6 SAXRD patterns of as-prepared Au samples: (a) aggregates formed *in situ*; (b) 3D spherical aggregates.

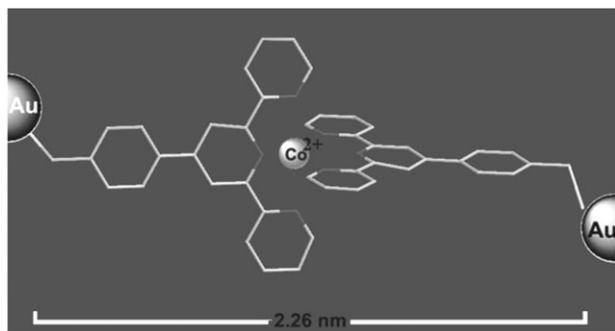


Fig. 7 A proposed working model for Co^{2+} -induced assembly. The molecules were drawn using Chem3D and the length of the coordination moiety was calculated according to the crystal data in ref. 16.

assembly is *ca.* 4.36 nm. This distance is *ca.* 0.6 nm longer than the spacing calculated from SAXRD data and the TEM result. While the exact origin of this difference will be further probed, we believe that the multiple linkages between every two particles *via* metal coordination play a significant role in dictating the overall interparticle spacing. In addition, the ligand **1** is not a rigid molecule due to the existence of the C–S single bond, which enables the spacing to become shorter when the particles are held tightly by the multiple forces derived from numerous **1**–Co(II) linkers.

The controlled and reversible processes were accompanied by distinct shifts in the UV-vis absorption bands that could be used to diagnose the aggregation state of the Au colloids. The 3D assembly formed *in situ* exhibited a relatively broad absorbance band peaking at *ca.* 615 nm in acetone (Fig. 8a). For the **1**–Au powder dissolved in DMF, a distinct blue shift was observed (Fig. 8b). The absence of sharp absorption peak in the spectrum is due to the small particle size, which agrees well with that reported for highly dispersed Au nanoparticles with sizes less than 3 nm.¹⁷ After the addition of Co^{2+} into the disassembled Au colloids, the absorbance rapidly (within seconds) exhibited a distinct red shift (Fig. 8c), indicating the formation of larger aggregates.

To obtain further evidence for Co^{2+} -induced aggregation, photoluminescence measurements were carried out. The well-

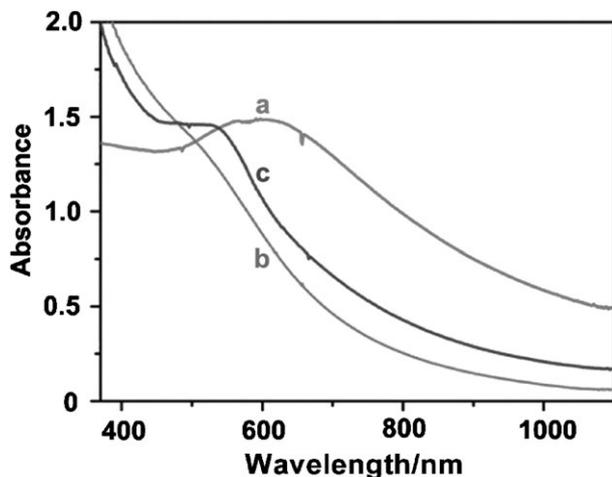


Fig. 8 UV-vis spectra of Au colloids: (a) aggregates formed *in situ*; (b) disassembled Au colloids in DMF; (c) after addition of Co^{2+} .

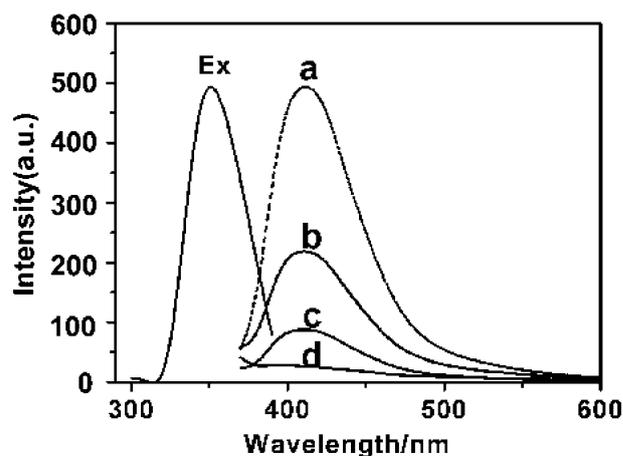


Fig. 9 PL spectra of Au colloids (0.1 mg Au-**1** in 3 mL DMF): (a) without addition of Co^{2+} ; (b) addition of $\text{Co}(\text{NO}_3)_2$ (40 μL , 1×10^{-3} M); (c) addition of $\text{Co}(\text{NO}_3)_2$ (80 μL , 1×10^{-3} M); (d) addition of $\text{Co}(\text{NO}_3)_2$ (150 μL , 1×10^{-3} M).

purified **1**-capped Au colloids emitted at *ca.* 411 nm in DMF (Fig. 9a), with a slight blue shift compared to the free ligand **1**. With the addition of $\text{Co}(\text{NO}_3)_2$ solution drop-wise, the emission weakened gradually and was ultimately quenched, indicating the formation of a non-emissive **1**–Co(II) complex.

It is very interesting that the 3D aggregates formed *in situ* can be transformed directly into 3D spherical assemblies *via* addition of Co^{2+} . The TEM image shown in Fig. 10 reveals that the spherical assemblies were nearly uniform and monodisperse, with diameters of *ca.* 120–130 nm. This effective transformation included two important processes, *i.e.* a coordination exchange reaction and rearrangement of the nanoparticles. To the best of knowledge, this is the first example of

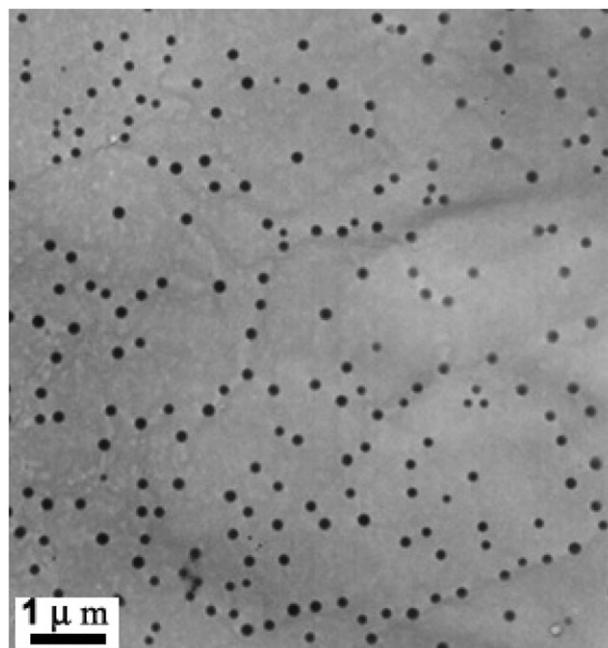


Fig. 10 TEM image of a monodispersed 3D spherical assembly obtained directly from large aggregates formed *in situ* *via* addition of $\text{Co}(\text{NO}_3)_2$ solution.

one 3D assembly being directly transformed into another quite different one without collapse and rapid precipitation. While the coordination complex of Co(II) with two terpyridyl linker molecules having thiol end groups can act as single molecular transistor,¹⁵ the 1–Co complex-linked 3D hybrid network should have potential applications in nanodevice fabrication.

In summary, we have demonstrated weak and strong coordination strategies for the controlled assembly of quite different 3D nanostructures. The Au colloids assembled *in situ* through weak coordination could be disassembled into individual particles, which further reassembled into dispersed spherical assemblies *via* strong coordination. It is significant that the large aggregates formed *in situ* can be directly transformed into monodispersed 3D spherical assemblies *via* strong coordination (with Co²⁺), presenting the first example of the direct transformation of one 3D nanonetwork into another quite different one. This effective approach should be general, not limited to Au colloids, and could be extended to the assembly of other important inorganic materials, opening new possibilities for the fabrication of optical and electronic nanodevices.

Acknowledgements

This work was partially supported by the National Natural Science Foundation of China (nos. 20571050 and 20271031), China Postdoctoral Science Foundation and the Natural Science Foundation of Guangdong Province (no. 05300875). We also thank Dr Qingrui Zhao of the University of Science & Technology of China and Dr Mingliang Zhang of City University of Hong Kong for their fruitful discussions.

References

- (a) W. A. Lopes and H. M. Jaeger, *Nature*, 2001, **414**, 735; (b) A. N. Shipway, E. Kata and I. Willner, *ChemPhysChem*, 2000, **1**, 18; (c) F. Remacle and R. D. Levine, *ChemPhysChem*, 2001, **2**, 20; (d) Y. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chem. Rev.*, 1999, **99**, 1823; (e) I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 1692; (f) M. Brust, D. Bethell, D. J. Schiffrin and C. J. Kiely, *Adv. Mater.*, 1995, **7**, 795; (g) S. M. Marinakos, D. A. Schultz and D. L. Feldheim, *Adv. Mater.*, 1999, **11**, 34 and references therein.
- See reviews, for example: (a) M. C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; (b) J. J. Storhoff and C. A. Mirkin, *Chem. Rev.*, 1999, **99**, 1849; (c) A. C. Templeton, W. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27; (d) R. Shenhar and V. M. Rotello, *Acc. Chem. Res.*, 2003, **36**, 549; (e) R. Shenhar, T. B. Norsten and V. M. Rotello, *Adv. Mater.*, 2005, **17**, 657.
- (a) C. R. Mayer, S. Neveu and V. Cabuil, *Adv. Mater.*, 2002, **14**, 595; (b) M. Kimura, S. Kobayashi, T. Kuroda, K. Hanabusa and H. Shirai, *Adv. Mater.*, 2004, **16**, 335; (c) C. Guarise, L. Pasquato and P. Scrimin, *Langmuir*, 2005, **21**, 5537.
- (a) C. A. Mirkin, R. L. Letsinger, R. C. Mucic and J. J. Storhoff, *Nature*, 1996, **382**, 607; (b) A. P. Alivisatos, K. P. Johnson, X. G. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez and P. G. Schultz, *Nature*, 1996, **382**, 609; (c) R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger and C. A. Mirkin, *Science*, 1997, **277**, 1078; (d) H. A. Becerril, R. M. Stoltenberg, D. R. Wheeler, R. C. Davis, J. N. Harb and A. T. Woolley, *J. Am. Chem. Soc.*, 2005, **127**, 2828; (e) C. M. Niemeyer, *Appl. Phys. A: Solid Surf.*, 1999, **68**, 119; (f) N. C. Seeman, *Chem. Biol.*, 2003, **10**, 1151; (g) E. Braun, Y. Eichen, U. Sivan and G. Ben-Yoseph, *Nature*, 1998, **391**, 775; (h) J. Richter, M. Mertig, W. Pompe, I. Mönch and H. K. Schackert, *Appl. Phys. Lett.*, 2001, **78**, 536; (i) C. F. Monson and A. T. Woolley, *Nano Lett.*, 2003, **3**, 359; (j) H. Xin and A. T. Woolley, *J. Am. Chem. Soc.*, 2003, **125**, 8710; (k) K. Keren, R. S. Berman, E. Buchstab, U. Sivan and E. Braun, *Science*, 2003, **302**, 1380; (l) H. A. Becerril, R. M. Stoltenberg, C. F. Monson and A. T. Woolley, *J. Mater. Chem.*, 2004, **14**, 611; (m) K. Keren, M. Krueger, R. Gilad, G. Ben-Yoseph, U. Sivan and E. Braun, *Science*, 2002, **297**, 72; (n) K. Keren, R. S. Berman and E. Braun, *Nano Lett.*, 2004, **4**, 323.
- (a) A. K. Boal, F. Ilhan, J. E. DeRouchey, T. Thurn-Albrecht, T. P. Russell and V. M. Rotello, *Nature*, 2000, **404**, 746; (b) W. A. Lopes and H. M. Jaeger, *Nature*, 2001, **414**, 735; (c) T. Tozawa, *Chem. Commun.*, 2004, 1904; (d) Y. Lin, A. Böker, J. He, K. Sill, H. Xiang, C. Abetz, X. Li, J. Wang, T. Emrick, S. Long, Q. Wang, A. Balazs and T. P. Russell, *Nature*, 2005, **434**, 55.
- (a) M. M. Maye, I. S. Lim, J. Luo, Z. Rab, D. Rabinovich, T. Liu and C.-J. Zhong, *J. Am. Chem. Soc.*, 2005, **127**, 1519; (b) M. M. Maye, S. C. Chun, L. Han, D. Rabinovich and C.-J. Zhong, *J. Am. Chem. Soc.*, 2002, **124**, 4958.
- (a) H. Yao, H. Kojima, S. Sato and K. Kimura, *Langmuir*, 2004, **20**, 10317; (b) A. K. Boal and V. M. Rotello, *Langmuir*, 2000, **16**, 9527; (c) M. Kanehara, Y. Oumi, T. Sano and T. Teranishi, *J. Am. Chem. Soc.*, 2003, **125**, 8708; (d) T. H. Galow, A. K. Boal and V. M. Rotello, *Adv. Mater.*, 2000, **12**, 576; (e) Z. Zhong, A. S. Subramanian, J. Highfield, K. Carpenter and A. Gedaken, *Chem.–Eur. J.*, 2005, **11**, 1473.
- (a) Q. Dai, J. G. Worden, J. Trullinger and Q. Huo, *J. Am. Chem. Soc.*, 2005, **127**, 8008; (b) K.-M. Sung, D. W. Mosley, B. R. Peele, S. Zhang and J. M. Jacobson, *J. Am. Chem. Soc.*, 2004, **126**, 5064.
- (a) S. O. Obare, R. E. Hollowell and C. J. Murphy, *Langmuir*, 2002, **18**, 10407; (b) T. B. Norsten, B. L. Frankamp and V. M. Rotello, *Nano Lett.*, 2002, **2**, 1345; (c) Y. Kim, R. C. Johnson and J. T. Hupp, *Nano Lett.*, 2001, **1**, 165; (d) F. P. Zamborini, J. F. Hicks and R. W. Murray, *J. Am. Chem. Soc.*, 2000, **122**, 4514; (e) R. Shenhar, E. Jeoung, S. Srivastava, T. B. Norsten and V. M. Rotello, *Adv. Mater.*, 2005, **17**, 2206; (f) W. P. Wuelfing, F. P. Zamborini, A. C. Templeton, X. Wen, H. Yoon and R. W. Murray, *Chem. Mater.*, 2001, **13**, 87; (g) J. M. de la Fuente, P. Eaton, A. G. Barrientos, M. Menéndez and S. Penadés, *J. Am. Chem. Soc.*, 2005, **127**, 6192.
- (a) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796; (b) N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794; (c) I. M. Müller and D. Möller, *Angew. Chem., Int. Ed.*, 2005, **44**, 2969; (d) F. Zhang, T. Yajima, Y.-Z. Li, G.-Z. Xu, H.-L. Chen, Q.-T. Liu and O. Yamauchi, *Angew. Chem., Int. Ed.*, 2005, **44**, 3402; (e) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273.
- (a) P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat and L. De Cola, *Angew. Chem., Int. Ed.*, 2005, **44**, 1806; (b) M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003; (c) Z. Peng, *Angew. Chem., Int. Ed.*, 2004, **43**, 930.
- (a) K. Hiratani, M. Nomoto, H. Sugihara and T. Okada, *Analyst*, 1992, **117**, 1491; (b) C. Dietrich-Buchecker, B. Colasson, D. Jouvenot and J.-P. Sauvage, *Chem.–Eur. J.*, 2005, **15**, 4374.
- (a) G. W. V. Cave and C. L. Raston, *J. Chem. Soc., Perkin Trans. J.*, 2001, 3258; (b) J.-X. Yang, X.-T. Tao, C. X. Yuan, Y. X. Yan, L. Wang, Z. Liu, Y. Ren and M. H. Jiang, *J. Am. Chem. Soc.*, 2005, **127**, 3278; (c) W. Spahni and G. Calzaferri, *Helv. Chim. Acta*, 1984, **67**, 450.
- (a) M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. David Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans and R. W. Murray, *Langmuir*, 1998, **14**, 17; (b) P. Bera and M. S. Hegde, *Catal. Lett.*, 2002, **79**, 75; (c) J. Cemek, P. Jiricek, O. Gedeon, B. Lesiak and A. Jozwik, *J. Non-Cryst. Solids*, 2005, **351**, 1665; (d) X. Zhang, Y. Tian, F. Jin, J. Wu, Y. Xie, X. Tao and M. Jiang, *Cryst. Growth Des.*, 2005, **5**, 565.
- J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen and D. C. Ralph, *Nature*, 2002, **417**, 722.
- (a) T. Yutaka, I. Mori, M. Kurihara, N. Tamai and H. Nishihara, *Inorg. Chem.*, 2003, **42**, 6306; (b) N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen and P. Saarenketo, *J. Chem. Soc., Dalton Trans.*, 2000, 1447.
- J. D. Grunwaldt, C. Kiener, C. Wögerbauer and A. Baiker, *J. Catal.*, 1999, **181**, 223.