Construction of conjugated molecular structures on gold nanoparticles *via* the Sonogashira coupling reactions†

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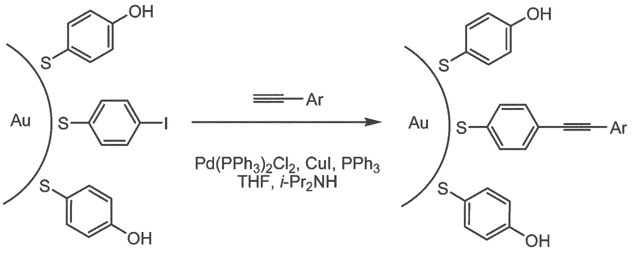
Functional, conjugated molecular structures have been fabricated on Au nanoparticles *via* the Sonogashira coupling reactions.

Monolayer protected metal nanoparticles (NPs)[1] have been an active research subject[2] in nanoscience and nanotechnology since a seminal report from Brust[3] *et al* on the preparation of the first alkanethiol-protected Au NP system. The attachment of different monolayers by using the strong affinity of thiols to metal NPs provides not only the solubility of these nanoentities in various solvents, but also the desired functionality on their surfaces. Additionally, chemical coupling of a functional species to the end group of monolayers on particle surfaces offers an alternative route to further tailor the functionality of NPs.[4] Here, we report a new approach to functionalize monolayer protected Au NPs with conjugated molecules by using the Sonogashira coupling reaction.[5] We expect that this method provides a facile way to modify NPs with fully conjugated molecular species, yielding a new type of hybrid nanomaterials for potential applications in opto-, electronic and sensing devices.

Ligand place-exchange[6] of 4-mercaptophenol on Au NPs[7] with 4-iodobenzenethiol (supporting information†) in methanol resulted in Au NPs protected by a mixed monolayer of 4-mercaptophenol and 4-iodobenzenethiol (denoted as mAuNPs). The mAuNPs were very stable in polar organic solvents, such as methanol and tetrahydrofuran (THF) as verified by a photon correlation spectroscopic (PCS) study.[8]† The elemental analysis showed that one out of every four surface-anchored molecules is 4-iodobenzenethiol. A model of mAuNP is shown in Scheme 1. Three model compounds (Chart 1) were selected to test the feasibility of the Sonogashira coupling reaction on mAuNP surfaces.

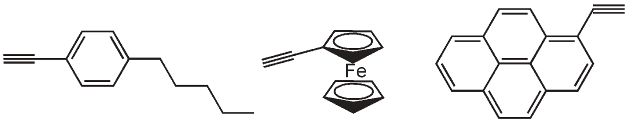


Scheme 1 Sonogashira coupling reactions at mAuNP surfaces.

In a typical preparation (Scheme 1, supporting information †), 500 mg of mAuNPs reacted with one of the terminal alkynes (excess in molar ratio as compared with available iodo reacting sites on particle surfaces) in THF under a N_2 atomsphere. Pd(PPh$_3$)$_2$Cl$_2$ and CuI were used as the catalyst and co-catalyst respectively. PPh$_3$ was selected as the stabilizing ligand for the catalyst and *i*-Pr$_2$NH was used as the base. The reaction mixture was stirred at room temperature for 24 h. The solvent was then removed and the solid residue was redissolved in CH_2Cl_2, washed with saturated NH_4Cl and NaCl aqueous solutions. The final product was purified by slow precipetation from a CH_2Cl_2–hexane mixed solvent several times and dried under vacuum. The removal of uncoupled organic species was verified by thin layer chromatography (TLC).[9] The final product obtained was a deep brown powder.

A noticeable change in these particles after the coupling reaction was that they became more soluble in non-polar solvents, such as CH_2Cl_2 and $CHCl_3$. This can be attributed to the modification of particle surfaces with non-polar groups through the coupling reaction. The ^{1}H NMR of **1**-modified mAuNPs (denoted **1**-mAuNPs) in $CDCl_3$ is shown in Fig. 1B. The disappearance of a proton signal at 3.01 ppm, which originates from the proton of triple bond in free **1** (Fig. 1A), confirms that purified **1**-mAuNPs does not contain free **1**. This result is consistent with the TLC result. Meanwhile, a set of broadened signals around the 1 ppm in this spectrum clearly indicates the presence of methylene chain of **1** on the particle surface.[4] It was observed that the average particle size of Au NPs (TEM) remained the same† after the Sonogashira reaction. The energy dispersive spectroscopic (EDS)[9] analysis (supporting information†) revealed that the Pd catalyst was completely removed. The possible unreacted iodine on the particle surface was not detected by EDS. The above study showed that the Sonogashira reaction was successfully applied to couple the molecule with a terminal alkyne on the aromatic ring on mAuNPs.

Coupling of **2** to the surface of mAuNPs rendered Au NPs functionalized with electroactive species (denoted as **2**-mAuNPs).[10] As expected, the particle-bound ferrocene exerted a one redox wave,[11] which was 40 mV less positive than that of its free form



1-ethynyl-4-pentylbenzene, **1** ethynylferrocene, **2** 1-ethynylpyrene, **3**

Chart 1 Molecular structures for surface coupling reactions.

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† Electronic Supplementary Information (ESI) available: detailed preparation and characterization of surface-modified Au NPs and the Sonogashira coupling reactions (PDF). See http://www.rsc.org/suppdata/cc/b4/b415652h/
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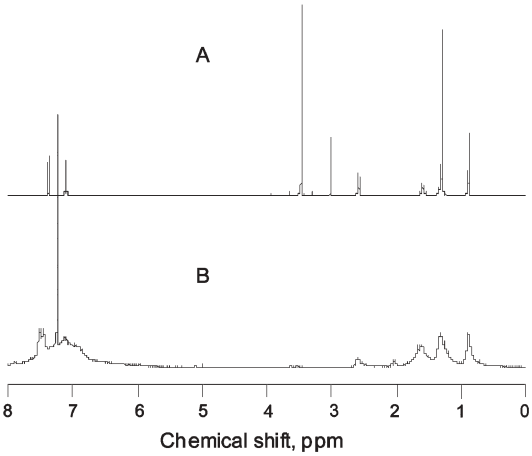

Fig. 1 ^{1}H NMR of (A) free **1** and (B) **1**-mAuNPs in $CDCl_3$.

(Fig. 2). Coupling of **2** to the aromatic ring on the particle surface resulted in a larger conjugated ferrocene system.[12] Thus, the oxidized form of particle-bound ferrocene is thermodynamically more stable, as compared with free **2**.

The attachment of **3** to the surface of mAuNPs resulted in Au NPs modified with a fluorophore-terminated monolayer (denoted **3**-mAuNPs).[13] The steady-state absorption spectrum of **3**-mAuNPs in chloroform is shown in Fig. 3A. The lack of the plasmon band around 520 nm is attributed to the small particle size. Three distinct absorption bands from free **3** (line A in Fig. 3A) merge into a broad peak of particle-bound pyrene which is superimposed on the absorption of Au NPs. This is probably due to the rigidity of particle-bound pyrene after it is coupled to the aromatic ring on Au NPs. Coupling of **3** to 4-iodobenzenethiol on Au NPs leads to a larger conjugated system of pyrene, which in turn, decreases the electronic energy for the absorption. Thus, the particle-bound **3** shows a longer wavelength for its characteristic absorption energy levels. The enlargement of conjugation also results in a red shift for the fluorescence emission of the particle-bound pyrene (line B in Fig. 3B). The prominence of the emission peak of the particle-bound pyrene at 445 nm over other peaks at lower wavelength suggests that the local environment of pyrene is fairly nonpolar. In addition, a broad band at 500 nm extending to longer wavelength was observed. This small degree of excimer emission may result from the interaction of neighboring pyrene moieties,[13a] although on average, only 25% of surface-bound molecules were connected to the pyrene (according to the elemental and EDS analysis)‡

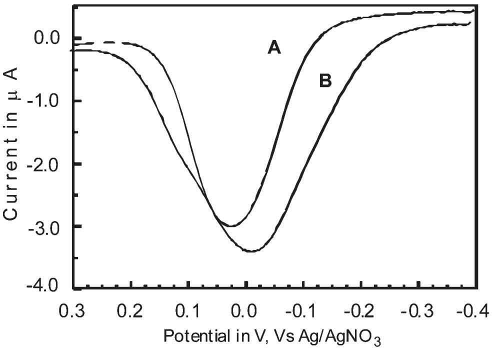

Fig. 2 Square wave voltammgrams (SWVs) of (A) free **2** and (B) **2**-mAuNPs in THF.

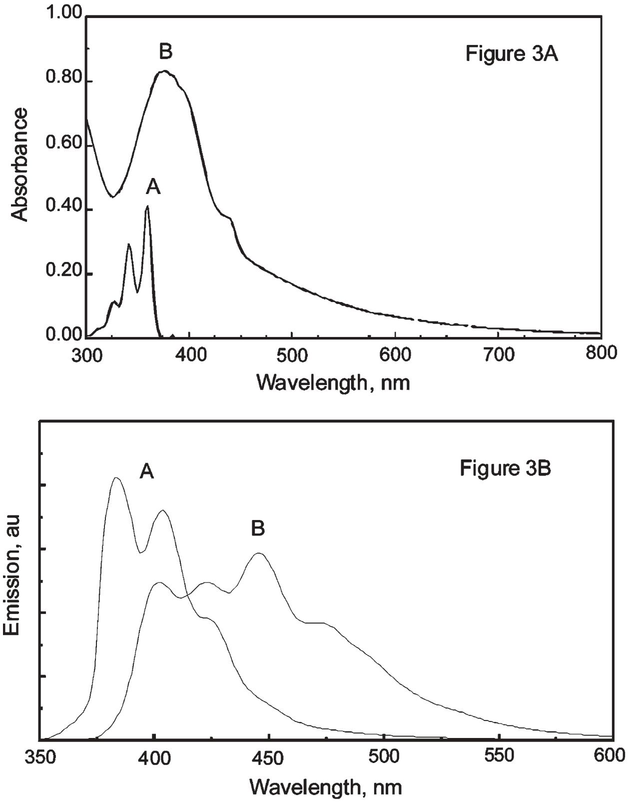

Fig. 3 Electronic absorption of free **3** (line A, Fig. 3A) and **3**-mAuNPs (line B, Fig. 3A) as well as fluorescence (λ_{exc} = 325 nm) of free **3** (line A, Fig. 3B) and **3**-mAuNPs (line B, Fig. 3B).

In summary, we have demonstrated a facile approach to construct fully conjugated molecular structures on Au NPs by the Sonogashira reaction. Coupling of functional groups, such as electroactive or photoactive species, to the surface of NPs tailors not only the functionality of the particle, but also the electronic and optical properties of the organic molecules. These metal NPs may find their applications in the development of new types of opto, electronic and sensing devices.

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Notes and references

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1 A. C. Templeton, W. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27.

2 (*a*) J. J. Storhoff and C. A. Mirkin, *Chem. Rev.*, 1999, **99**, 1849; (*b*) R. Shenhar and V. M. Rotello, *Acc. Chem. Res.*, 2003, **36**, 549; (*c*)

M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; (*d*) M. Sastry, M. Rao and K. N. Ganesh, *Acc. Chem. Res.*, 2002, **35**, 847; (*e*) C. N. R. Rao, G. U. Kulkarni, P. J. Thomas and P. P. Edwards, *Chem. Soc. Rev*, 2000, **29**, 27; (*f*) J. Liu, Metal Nanoparticles Modified by Molecular Receptors, in *Dekker Encyclopedia of Nanoscience and Nanotechnology*, eds. J. A. Schwarz, C. I. Contescu and K. Putyera, Marcel Dekker, New York, 2004, vol. 5, p 1841.

3 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.

4 See, for example, R. S. Ingram, M. J. Hostetler and R. W. Murray, *J. Am. Chem. Soc.*, 1997, **119**, 9175.

5 (*a*) K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467; (*b*) K. Sonogashira, in *Metal-Catalyzed Cross-Coupling Reactions*, F. Diederich and P. J. Stang, Eds., Wiley-VCH, New York, 1998, Chapter 5.

6 M. J. Hostetler, A. C. Templeton and R. W. Murray, *Langmuir*, 1999, **15**, 3782.

7 Preparation of 4-mercaptophenol-modified Au nanoparticle, M. Brust, J. Fink, D. Bethell, D. J. Schiffrin and C. Kiely, *J. Chem. Soc., Chem. Commun.*, 1995, 1655.

8 Example of using PCS for monitoring the stability of nanoparticles in solutions, see J. Liu, J. Alvarez, W. Ong and A. E. Kaifer, *Nano Lett.*, 2001, **1**, 57.

9 J. Liu, S. Mendoza, E. Román, M. J. Lynn, R. Xu and A. E. Kaifer, *J. Am. Chem. Soc.*, 1999, **121**, 4304.

10 For other nanoparticles modified with unconjugated ferrocene species, see (*a*) J. Liu, R. Xu and A. E. Kaifer, *Langmuir*, 1998, **14**, 7337; (*b*) X.-M. Li, M. R. de Jong, K. Inoue, S. Shinkai, J. Huskens and D. N. Reinhoudt, *J. Mater. Chem.*, 2001, **11**, 1919; (*c*) M. J. Hostetler, S. J. Green, J. J. Stokes and R. W. Murray, *J. Am. Chem. Soc.*, 1996, **118**, 4212; (*d*) S. Chen, *Langmuir*, 2001, **17**, 6664; (*e*) A. Labande, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 2002, **124**, 1782.

11 J. Liu, W. Ong, E. Román, M. J. Lynn, R. Xu and A. E. Kaifer, *Langmuir*, 2000, **16**, 3000.

12 J. Liu, R. Castro, K. A. Abboud and A. E. Kaifer, *J. Org. Chem.*, 2000, **65**, 6973.

13 For other nanoparticles modified with pyrene fluorophores, see (*a*) B. I. Ipe, K. G. Thomas, S. Barazzouk, S. Hotchandani and P. V. Kamat, *J. Phys. Chem. B*, 2002, **106**, 18; (*b*) M. M. Y. Chen and A. Katz, *Langmuir*, 2002, **18**, 2413.