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# Synthesis of DMF-protected Au NPs with different size distributions and their catalytic performance in the Ullmann homocoupling of aryl iodides†

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DMF-stabilized Au nanoparticles (NPs) with three different particle sizes were prepared by controlling the reaction temperatures and times. In the absence of any additional ligands, these Au NPs showed high catalytic activity in the Ullmann homocoupling of aryl iodides in DMF. The effects of Au particle size on the coupling reaction were investigated by the use of three Au catalysts with mean particle sizes of *ca.* 1.0 nm, 2.5 nm, and 5.5 nm, respectively. The catalytic activity of the Au NPs was found to be in the order of Au (2.5 nm) > Au (<1.0 nm) > Au (5.5 nm), indicating that surface Au atoms do not have the same catalytic activity toward such a homocoupling reaction.

## Introduction

Biaryl compounds play a major role in industrial production and pharmaceutical synthesis.[1] To date, transition metal-catalyzed coupling reaction of aryl halides is one of the most efficient and powerful methods for the synthesis of biaryls.[2] The copper-mediated Ullmann homocoupling reactions of aryl halides have some potential limitations because these reactions need high temperatures (over 200 °C) and the consumption of a stoichiometric amount of copper salt.[3] In the past decades, palladium,[4] nickel[5] and other metal catalysts[6] bearing various N-, O- or P-donor ligands could catalyze Ullmann homocoupling reactions of aryl halides under mild conditions. But these coupling reactions need additional reducing agents such as poly(ethylene glycol) (PEG),[4h] tetrakis(dimethylamino)ethylene (TDAE),[4i] glucose[4j] or a fluoride reagent.[4k] In recent years, metal nanoparticles (NPs) in the presence of auxiliary stabilizers such as surfactants,[7] functionalized polymers,[8] inorganic solids[9] or organic ligands[10] have been proven to be effective catalysts for organic transformations such as the Ullmann coupling reaction,[11] Heck reaction,[12] Suzuki–Miyaura reaction,[8c,13] and Sonogashira reaction.[14] These auxiliary stabilizers play an important role in preventing aggregation of the metal NPs and controlling the concentration of active catalytic species, but increase the complexity of the reaction system and the cost.[15] To this end, the development of a simple and environmentally benign metal NP catalyst without any additional coating agents for such C–C bond formations would be necessary. *N*,*N*-Dimethylformamide (DMF) is well known as a solvent with polarity and a wide solubility range for both organic and inorganic compounds. In addition, DMF also acts as a reducing agent[16] in wet chemical synthesis of metal NPs. In recent years, initiated by Marzán, DMF has been used to reduce $Ag^+$,[17] $Ni^{2+}$, $Co^{2+}$,[18] $Cu^{2+}$,[19] $Pd^{2+}$,[20] $Pt^{2+}$,[21] and $Au^{3+}$ [22] ions into the corresponding metal NPs at the appropriate temperatures. Moreover, Cu and Pd NPs stabilized by DMF showed high catalytic activities in the coupling reactions.[19,20] Gold NPs stabilized by thiolate ligands[23] and phosphine ligands[24] have also displayed high catalytic activity towards various organic reactions. However, to our knowledge, the catalytic activity of DMF-protected Au NPs in the coupling reactions has not yet been explored.

Furthermore, the particle size of metal NPs plays an important role in determining their catalytic activity.[25] For example, El-Sayed *et al.* investigated the effects of particle size on the catalytic Suzuki–Miyaura reaction over PVP-Pd (PVP = polyvinylpyrrolidone) nanocatalysts[25e] and found that the catalytic activity of the Pd NPs towards this reaction followed the order of Pd (3.9 nm) > Pd (3.0 nm) ≈ Pd (5.2 nm) > Pd (6.6 nm). Thus, the synthesis of gold NPs with various precise particle sizes is of major importance. Up to now, the size of reported DMF-stabilized Au NPs is less than 1 nm.[22a] In this article, we report the synthesis of DMF-stabilized Au NPs with three par-

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ticle sizes (<1 nm, 2.5 nm, and 5.5 nm diameter), which showed high catalytic activity in the Ullmann homocoupling of aryl iodides. The Au NPs of 2.5 nm diameter exhibit an excellent catalytic performance for such a coupling reaction.

# Results and discussion

## Synthesis and characterization of DMF-protected Au NPs

The DMF-protected Au NPs of less than 1 nm in diameter were prepared according to the literature method.[22a] A solution of 0.1 M aqueous $HAuCl_4$ (150 μL) was added to preheated DMF (5 mL, 140 °C). The mixture was refluxed for 6 h at 140 °C with vigorous stirring. The resulting yellow solution contained photoluminescent Au NPs **1**. The DMF background was eliminated before each fluorescence measurement. The DMF solution of $HAuCl_4$ did not show any luminescence upon excitation at 200–400 nm. Upon excitation at 380 nm, Au NPs **1** exhibited strong photoluminescence with emission maxima at around 465 nm (Fig. 1a), which was very similar to that of the reported Au nanoclusters (smaller than 1 nm).[22a] We attempted to obtain an image of Au NPs **1** through high-resolution transmission electron microscopy (HRTEM). Unfortunately, no ideal result was obtained, which may be due to the fact that **1** was too small to be detected. The UV-vis spectrum (Fig. 2a) showed no surface plasmon resonance (SPR) band in the range of 500–550 nm,[26] suggesting that the size of the resulting gold nanoparticles (Au NPs **1**) was below 1 nm, which is similar to that of the reported ones.[22]

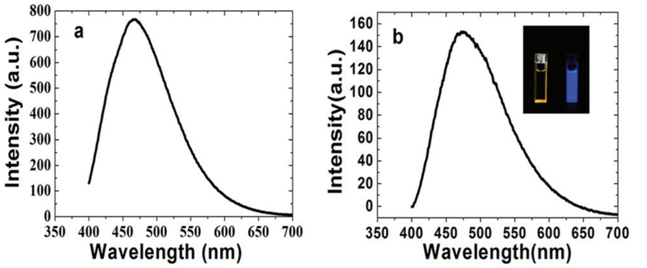


**Fig. 1** Normalized fluorescence spectra of as-prepared Au NPs **1** (a) and Au NPs **2** (b). Inset to (b): photograph of the fluorescence of the Au NPs **2** under ambient light (left) and UV light of 365 nm (right).

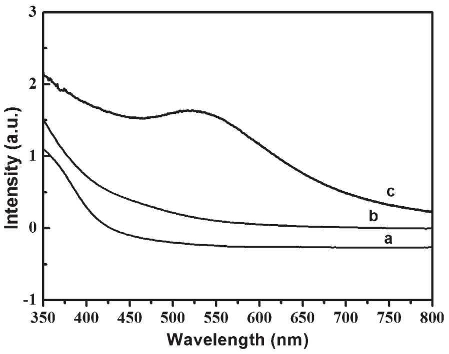


**Fig. 2** The UV-vis absorption spectra of solutions containing Au NPs **1** (a), Au NPs **2** (b) and Au NPs **3** (c).

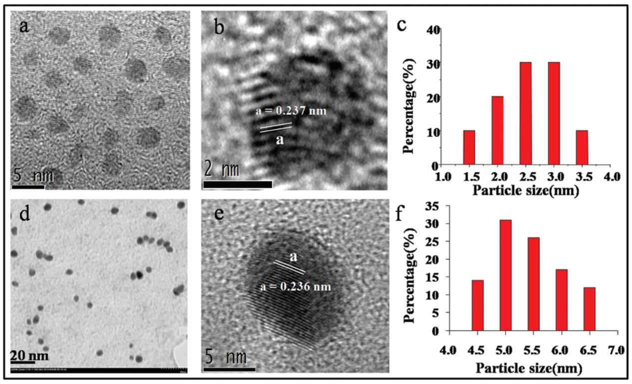


**Fig. 3** TEM images and the corresponding particle size distribution histograms of Au NPs **2** (a, c) and Au NPs **3** (d, f). HRTEM images of a single Au NP **2** (b) and Au NP **3** (e).

It has been reported that higher reaction temperatures can enlarge the size of nanoparticles.[27] When the reaction temperature was close to the boiling point of DMF, the DMF molecules were desorbed from the surface of Au NPs, thereby inducing the growth of particles. Thus, a similar reaction was carried out at 150 °C for 2 h to produce Au NPs **2**. No signal of a SPR band at about 520 nm is observed according to the UV-vis spectrum (Fig. 2b). Upon excitation at 380 nm, the DMF solution of Au NPs **2** exhibited strong photoluminescence with an emission maxima at 475 nm (Fig. 1b), which was red-shifted relative to that of the Au NPs **1**. This implied that the size of Au NPs **2** may be larger than that of Au NPs **1**.[28] The HRTEM image of the Au NPs **2** showed gold nanoparticles of approximately 2.5 nm in size (Fig. 3a and 3c). The lattice fringes of the as-prepared Au NPs are consistent with metallic gold having a discerned lattice spacing of 2.37 Å (Fig. 3b), which corresponds to the *d*-spacing of the (111) crystal plane of fcc Au.[29]

To further explore the temperature effects, the reaction was carried out at 160 °C to obtain larger Au NPs. Unfortunately, a large amount of gold metal was precipitated out of the solution (Fig. S1†), which indicates that the formation of gold metal began at 160 °C and the DMF-protected Au NPs were stable up to about 150 °C.[22a] Extending the reaction time was also a useful method to generate large Au NPs. Thus, we prolonged the refluxing time to 8 h at 150 °C. The resulting dark yellow solution of Au NPs **3** exhibited no photoluminescence under the UV light with a wavelength of 365 nm. Its UV-visible spectrum (Fig. 2c) showed the SPR band at 521 nm, which means that the size of the Au NPs **3** was larger than that of the Au NPs **2**. The TEM image (Fig. 3d) showed a homogeneous distribution of Au nanoparticles with an average particle size of 5.5 nm (Fig. 3f). The HRTEM (Fig. 3e) image revealed a typical lattice of gold with a *d*-spacing of 2.36 Å, corresponding to the (111) plane of Au.[29] The XPS Au ($4f_{7/2}$) spectra of the dried Au NPs **1**, **2** and **3** are shown in Fig. 4. Their main peaks, located at 85.0 eV, 84.7 eV and 84.5 eV, respectively, were of

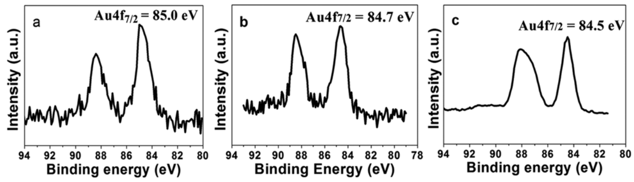
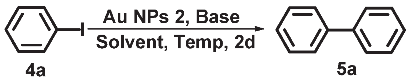


**Fig. 4** XPS Au ($4f_{2/7}$) spectra of Au NPs **1** (a), Au NPs **2** (b) and Au NPs **3** (c).

**Table 1** Optimization of reaction conditions for the Ullmann homocoupling of aryl iodides catalyzed by DMF-protected Au NPs[a]



| Entry | Cat. | Cat. loading (mol%) | Solvent | Base | $T$/°C | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | Au NPs **1** | 3 | DMF | $K_2CO_3$ | 130 | 34 |
| 2 | Au NPs **2** | 3 | DMF | $K_2CO_3$ | 130 | 43 |
| 3 | Au NPs **3** | 3 | DMF | $K_2CO_3$ | 130 | 25 |
| 4 | Au NPs **2** | 3 | DMF | $Na_2CO_3$ | 130 | 28 |
| 5 | Au NPs **2** | 3 | DMF | $Na_3PO_4$ | 130 | 39 |
| 6 | Au NPs **2** | 3 | DMF | $Cs_2CO_3$ | 130 | 30 |
| 7 | Au NPs **2** | 3 | DMF | $Li_2CO_3$ | 130 | n.r. |
| 8 | Au NPs **2** | 3 | DMF | $K_3PO_4·3H_2O$ | 130 | 46 |
| 9 | Au NPs **2** | 3 | DMF | $K_3PO_4$ | 130 | 57 |
| 10 | Au NPs **2** | 5 | DMF | $K_3PO_4$ | 130 | 90 |
| 11 | Au NPs **2** | 10 | DMF | $K_3PO_4$ | 130 | 89 |
| 12 | Au NPs **2** | 5 | DMF | $K_3PO_4$ | 120 | 80 |
| 13 | Au NPs **2** | 5 | DMF | $K_3PO_4$ | 110 | 46 |
| 14 | Au NPs **2** | 5 | DMF | $K_3PO_4$ | 140 | 91 |
| 15 | Au NPs **2** | 5 | NMP | $K_3PO_4$ | 130 | 73 |
| 16 | Au NPs **2** | 5 | Toluene | $K_3PO_4$ | 130 | 12 |
| 17 | Au NPs **2** | 5 | THF | $K_3PO_4$ | 130 | n.r. |

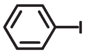
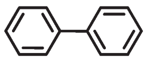
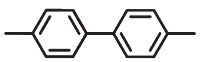
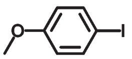
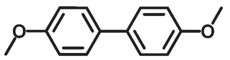
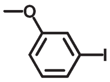
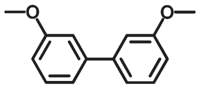
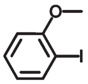
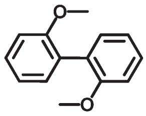
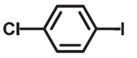
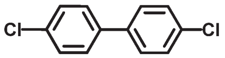
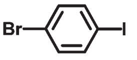
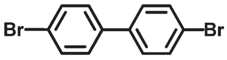
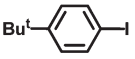
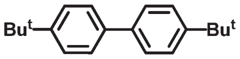
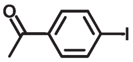
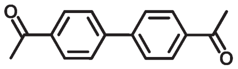
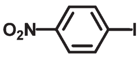
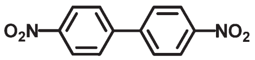
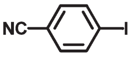
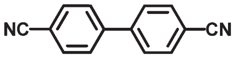
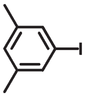
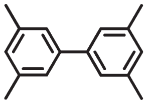
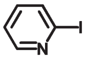
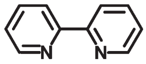
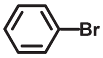
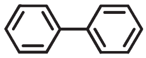
[a] Reaction conditions: iodobenzene (0.2 mmol), base (0.4 mmol), solvent (2 ml) and each catalyst was stirred at reflux temperature (130 °C for DMF) for 48 h. [b] GC yield. n.r. = no reaction.

higher binding energy than that of bulk Au (83.9 eV), and were of lower binding energy than that of $Au^{3+}$ (87.3 eV). The peaks in the XPS spectra seem asymmetric, which may be caused by $Au^0$ NPs coupled with the superficial $Au^+$ ion.[30] Furthermore, it is known that the binding energy of metal nanoparticles increases with the decrease in size,[31] which is in agreement with our results described above (Fig. 4). Au NPs **1–3** are further confirmed by powder X-ray diffraction (PXRD) (Fig. S3†). All of the diffraction peaks could be indexed to Au (JCPDS, 04-0784), which revealed the formation of monodispersed Au NPs. The lattice constants of the three kinds of Au NPs were very similar.[17b]

**Ullmann homocoupling of aryl iodides catalyzed by DMF-protected Au NPs.** As mentioned above, the (111) planes of Au NPs **2** and **3** were demonstrated to be an active catalytic site for many reactions since the low index plane (111) has low surface energy.[32] To examine the catalytic activity of Au NPs **1–3** towards the Ullmann homocoupling reaction of aryl iodides, each (3 mol%) is mixed with phenyl iodide (0.2 mmol) and $K_2CO_3$ (0.4 mmol) in DMF (2 mL) at 130 °C for 48 h (Table 1, entries 1–3). A standard work-up produced the desired biphenyl product in 34%, 43% and 25% yield, respectively. These preliminary results revealed that the homocoupling reaction of aryl iodides might be efficiently catalyzed by DMF-protected Au NPs and the catalytic activity of the gold nanoparticles decreased in the order of Au NPs **2** (2.5 nm) > Au NPs **1** (<1.0 nm) > Au NPs **3** (5.5 nm). In general, the catalytic activity increases with the decrease of the particle size because the low-coordination number vertex and edge atoms on the particle surface are active sites for coupling reactions.[33] However, it is Au NPs **2** (2.5 nm) not Au NPs **1** (<1.0 nm) which exhibit the highest catalytic activity in our catalytic systems. Compared with the Au NPs **2** (2.5 nm), the smaller metal particles (<1.0 nm) absorbed the reaction intermediates more strongly, which may poison the reaction and reduce the catalytic activity.[25e,34] Therefore, 2.5 nm Au NPs **2** and iodobenzene were chosen as a model system to optimize the reaction conditions such as bases, solvents, catalyst loadings, and temperatures. We employed various bases such as $K_2CO_3$, $Na_2CO_3$, $Na_3PO_4$, $Cs_2CO_3$, $Li_2CO_3$, $K_3PO_4·3H_2O$ and $K_3PO_4$ for this homocoupling reaction. It seemed that $K_3PO_4$ was the best one for this reaction with 3 mol% Au NPs **2** in DMF (Table 1, entry 9). The yield using $K_3PO_4·3H_2O$ (entry 8) as a base was lower than that using $K_3PO_4$ (entry 9). This indicated that the homocoupling reaction was sensitive to $H_2O$.[4c] The catalyst loading may also affect the product yield. The yield of **5a** was increased from 57% to 90% when the catalyst loading was changed from 3 mol% to 5 mol% in DMF at 130 °C (entry 10). However, when the catalyst loading for this reaction was increased from 5 mol% to 10 mol%, the yield of **5a** was not improved (entry 11). The reaction temperature usually exerts a great impact on such a coupling reaction. At lower temperatures (120 °C or 110 °C), the reaction afforded the product **5a** in lower yields (entries 12, 13) while at the higher reaction temperature (140 °C) the yield of **5a** was enhanced. For the solvents used, the Au NPs **2** catalyst worked the best in DMF (Table 1, entry 10), while it gave a relatively bad performance in other solvents such as NMP and toluene and did not work in THF. Thus, the optimized reaction conditions were fixed to be 5 mol% of Au NPs **2**, $K_3PO_4$ as a base at 130 °C in DMF.

With the optimized conditions in hand, we examined the scope of the reaction and found that a variety of functional groups could be tolerated for aryl iodides including methyl, methoxyl, bromide, chloride, carbonyl, cyano and nitryl groups. As shown in Table 2, the coupling reactions were performed well for all the substrates examined, and the desired products were isolated in moderate to excellent yields. It appeared that the steric hindrance of aryl iodides affected the catalytic activity of the homocoupling reaction. The homocoupling reaction of 1-iodo-4-methoxybenzene afforded 4,4′-dimethoxy-1,1′-biphenyl in 85% yield. However, the reaction of 1-iodo-3-methoxybenzene or 1-iodo-2-methoxybenzene produced the corresponding products 3,3′-dimethoxy-1,1′-biphenyl (63% yield; entry 4) and 2,2′-dimethoxy-1,1′-biphenyl (43% yield; entry 5) in lower yields. The electronic nature of substitu-

**Table 2** Ullmann homocoupling of various aryl iodides using the DMF-protected Au NPs **2**[a]

| Entry | Aryl iodide | Product | Yield[b] (%) |
|---|---|---|---|
| 1 |  |  | 91 |
| 2 |  |  | 88 |
| 3 |  |  | 85 |
| 4 |  |  | 63 |
| 5 |  |  | 43 |
| 6 |  |  | 95 |
| 7 |  |  | 93 |
| 8 |  |  | 59 |
| 9 |  |  | 90 |
| 10 |  |  | 94 |
| 11 |  |  | 96 |
| 12 |  |  | 15 |
| 13 |  |  | 50 |
| 14 |  |  | Trace |

[a] Reaction conditions: iodobenzene (1 mmol), base (2 mmol), DMF (5 mL) and catalyst (5 mol%) was stirred at reflux temperature (130 °C for DMF) for 48 hours. [b] Isolated yield.

ents on the aryl iodides might also influence the yields of the coupling products. The electron-deficient substituted aryl iodides were found to proceed in higher yields than those with electron-donating substituent groups. For example, higher yields (entries 6 and 7) were obtained for 1-chloro-4-iodobenzene and 1-bromo-4-iodobenzene relative to 1-iodo-4-methylbenzene and 1-iodo-4-methoxybenzene (entries 2 and 3). These results were consistent with those obtained by Au-catalyzed homocoupling reactions reported previously.[4a] The reactions of heterocycle iodide-like 2-iodopyridine gave the corresponding product in a good yield (50% yield; entry 13). Encouraged by the high efficiency for the reactions of aryl iodides described above, we also examined whether the catalyst system worked well with aryl bromides. Surprisingly, reaction of bromobenzene in the presence of 5 mol% catalyst was rather reluctant. Table 3 lists a comparison of the results for the homocoupling reactions using different catalysts. Comparative runs with Cu (82% yield), CuI–$PEt_3$ (66% yield), $Ni(cod)_2$ (71% yield), Ni powder (73% yield), In (78% yield) $CoBr_2$ (67% yield), $Pd(dba)_2$ (86% yield) and Pd/C (85.8% yield) indicated that Au NPs **2** exhibited a better catalytic performance (91% yield). In the presence of reducing agents such as hydroquinone and PEG (Table 3, entries 7 and 8), some Pd catalysts showed higher activity than that of the Au NPs **2**.

**Reusability of catalyst.** The reusability of the Au NP **2** catalyst was examined under the optimized conditions using iodobenzene as the model substrate in the Ullmann homocoupling reaction. As shown in Table 4, the homocoupling reaction of **4a** with 5 mol% catalyst loading formed 1,1′-biphenyl **5a** in 91% yield. After the completion of the first cycle, the organic product and the catalyst were separated. The isolated catalyst Au NPs **2** was used for catalyzing the second cycle by adding **4a** and $K_3PO_4$. This catalyst still exhibited activity in the homocoupling reaction of iodobenzene (Table 4, entry 2). The catalytic activity went down gradually with the increase of reaction cycles (Table 4, entries 3–5), which may be ascribed to the loss of Au NPs, which are being absorbed by the base. After the fifth cycle, the remaining Au NP catalyst was directly employed to prepare the samples for TEM. As shown in Fig. S2,† aggrega-

**Table 3** Catalytic characteristics of conventional catalysts for the Ullmann homocoupling of iodobenzene

| Entry | Cat. | Cat. loading (mol%) | Addition | Solvent | Yield[a] (%) | Ref. |
|---|---|---|---|---|---|---|
| 1 | Cu | >100 | — | — | 82 | 3*c* |
| 2 | CuI–$PEt_3$ | 200 | Lithium naphthalide | DME | 66 | 3*d* |
| 3 | $Ni(cod)_2$ | ≈50 | — | DMF | 71 | 5*d* |
| 4 | Ni powder | 67 | KI | DMF | 73 | 5*e* |
| 5 | $Pd(dba)_2$ | 10 | TBAF | DMF | 86 | 4*k* |
| 6 | Pd/C | 5 | Ethanol | DMSO | 85.8[b] | 4*d* |
| 7 | $Pd(OAc)_2$ | 2–4 | As(*o*-tol)$_3$, hydroquinone | DMA | 96 | 4*a* |
| 8 | $Pd(OAc)_2$ | 2 | $PEG_{4000}$ | — | 95 | 4*h* |
| 9 | $Pd(dppf)Cl_2$ | 10 | — | DMSO | 96.7[b] | 4*g* |
| 10 | Indium metal | 100 | — | — | 78 | 6*a* |
| 11 | $CoBr_2$ | 10 | Mn, $C_3H_5Cl$ | $CH_3CN$ | 67 | 6*d* |
| 12 | Zn | 100 | $HCOONH_4$ | MeOH | 96 | 6*b* |
| 13 | Au NPs **2** | 5 | — | DMF | 91 | This work |

[a] Isolated yield. [b] GC yield.

**Table 4** Recyclability studies on the Ullmann homocoupling of iodobenzene using DMF-protected Au NPs **2**[a]

| Cycle | Yield[b] (%) |
|---|---|
| 1 | 91 |
| 2 | 83 |
| 3 | 75 |
| 4 | 61 |
| 5 | 43 |

[a] Reaction conditions iodobenzene (1 mmol), $K_3PO_4$ (2 mmol), DMF (5 mL) and catalyst (5 mol%) were stirred at reflux temperature (130 °C for DMF) for 72 hours. [b] Isolated yield.

tion of the Au NPs was not observed, which indicated that the DMF-protected Au NPs were stable during the reaction. Catalyst deactivation was witnessed during each run, which was consistent with other metal NP catalysts reported in the literature.[4j,6c,11f] When Pd NPs catalysed the homocoupling reaction of iodobenzene,[6c] the product yields decreased gradually from 94% (initial run) to 21% (the fourth cycle) as the number of cycles increased.

## Conclusions

In summary, we have demonstrated a DMF reduction method for the synthesis of DMF-protected Au NPs. The size of the Au NPs could be controlled through changing the reaction temperatures and reaction times. These Au NPs can be used as an efficient catalyst for the Ullmann homocoupling reaction of aryl iodides without addition of any other organic ligand. Among these Au NPs, the 2.5 nm Au NPs showed the highest catalytic activity. In this catalytic coupling reaction, DMF behaved as an interesting multi-functional molecule and served as a stabilizer, a reductant, and a reaction solvent. This approach could also tolerate a variety of functional groups and the catalytic system could be reused several times. The DMF-stabilized Au NPs may be applied to catalyse other organic reactions like C–H activation. Studies in this area are under way in our laboratory.

## Experimental section

### General procedures

All solvents and $HAuCl_4 \cdot 4H_2O$ (99.9%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other reagents were obtained from TCI and J & K and were used without further purification. The $^1H$ and $^{13}C$ NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. The $^1H$ and $^{13}C$ NMR chemical shifts were referenced to the solvent signal in $CDCl_3$. UV-vis absorption spectra were obtained using HITACHI U-2810 spectrometer with 1 cm optical path length. Fluorescence emission spectra were measured on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a continuous xenon lamp. Transmission electron microscopy (TEM) was performed on a HITACHI HT-7700 electron microscope operating at 120 kV. High-resolution transmission electron microscopy (HRTEM) was performed on a FEI Tecnai G20 (USA) electron microscope operating at 200 kV. X-ray photoelectron spectra (XPS) were recorded with an X-ray photoelectron spectrometer (AXIS Ultra DLD, USA). The binding energies were referenced to C 1s at 284.6 eV from hydrocarbon to compensate for the charging effect. Powder X-ray diffraction (PXRD) patterns were recorded on an X'Pert PRO SUPERrA rotation anode X-ray diffractometer with Ni-filtered Cu-Kα radiation ($\lambda$ = 1.5418 Å).

**Preparation of Au NPs (1) (less than 1 nm).** A solution of 150 μL of 0.1 M aqueous $HAuCl_4$ was added to 5 mL of DMF that was preheated to 140 °C. The resulting DMF solution was refluxed by simply heating with vigorous stirring for 6 h. The as-prepared gold nanoparticles were dispersed in DMF.

**Preparation of Au NPs (2) (2.5 nm).** A solution of 150 μL of 0.1 M $HAuCl_4$ dissolved in DMF was added to 5 mL of DMF that was preheated to 150 °C. The resulting DMF solution was refluxed by simply heating with vigorous stirring for 2 h. The DMF-protected Au NPs were dispersed in DMF.

**Preparation of Au NPs (3) (5.5 nm).** A solution of 150 μL of 0.1 M $HAuCl_4$ dissolved in DMF was added to 5 mL of DMF that was preheated to 150 °C. The resulting DMF solution was refluxed by simply heating with vigorous stirring for 8 h. The DMF-protected Au NPs were dispersed in DMF.

**Typical procedure for the Ullmann homocoupling reactions (Table 2, entry 1).** A mixture containing iodobenzene (1 mmol), Au NPs (5 mol%), $K_3PO_4$ (2 mmol), and DMF (5 mL) was loaded into a 25 mL round bottomed flask. The mixture was stirred at 130 °C for 48 h in air. Then, it was cooled to ambient temperature, and extracted three times with diethyl ether (3 × 15 mL). The combined organic layer was washed with brine (3 × 15 mL), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether as the eluent.

**Biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.59–7.57 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.44–7.40 (t, 4H, aromatic CH), 7.34–7.31 (t, 2H, aromatic CH). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 141.4, 128.9, 127.4, 127.3.

**4,4′-Dimethyl-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.52–7.50 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.28–7.26 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 2.42 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 138.3, 136.7, 129.4, 126.8, 21.1.

**4,4′-Dimethoxy-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.48–7.46 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 6.96–6.94 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 3.84 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 158.7, 133.5, 127.7, 114.1, 55.3.

**3,3′-Dimethoxy-biphenyl**: pale yellow oil liquid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.39–7.35 (t, 2H, aromatic CH), 7.21–7.19 (d, 2H, $J$ = 8.0 Hz, aromatic CH), 7.15 (s, 2H, aromatic CH), 6.93–6.91 (d, 2H, $J$ = 8.0 Hz, aromatic CH), 3.87 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 159.9, 142.6, 129.7, 119.7, 112.9, 112.8, 55.3.

**2,2′-Dimethoxy-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.38–7.34 (t, 2H, aromatic CH), 7.29–7.27 (d, 2H, $J$ = 8.0 Hz, aromatic CH), 7.06–7.00 (m, 4H, aromatic CH), 3.81 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 157.05, 131.48, 128.6, 127.8, 120.4, 111.1, 55.7.

**4,4′-Dichloro-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.51–7.49 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.44–7.42 (d, 4H, $J$ = 8.0 Hz, aromatic CH). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 138.4, 133.7, 129.1, 128.2.

**4,4′-Dibromo-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.60–7.58 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.45–7.43 (d, 4H, $J$ = 8.0 Hz, aromatic CH). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 138.9. 132.0, 128.5, 122.0.

**1,1′-Biphenyl,4,4′-bis(1,1-dimethylethyl)**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.58–7.56 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.50–7.48 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 1.40 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 149.9. 138.2, 126.7, 125.6. 34.5, 31.4.

**4,4′-Diacetyl-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 8.07–8.05 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.74–7.72 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 2.66 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 170.7. 117.5, 109.7, 102.2, 100.6.

**4,4′-Dinitro-biphenyl**: yellow solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 8.40–8.38 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.82–7.80 (d, 4H, $J$ = 8.0 Hz, aromatic CH). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 148.1. 145.0, 128.3, 124.4.

**4,4′-Dicyano-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.82–7.80 (d, 4H, $J$ = 8.0 Hz, aromatic CH), 7.73–7.71 (d, 4H, $J$ = 8.0 Hz, aromatic CH). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 143.5. 132.9, 127.9, 118.4, 112.5.

**3,3′,5,5′-Tetramethyl-biphenyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 7.23 (s, 4H, aromatic CH), 7.02 (s, 2H, aromatic CH), 2.41 (s, 12H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 141.5, 138.1, 128.7, 125.1, 21.4.

**2,2′-Bipyridyl**: white solid; $^1H$ NMR ($CDCl_3$, ppm, 400 Hz): $\delta$ 8.72–8.70 (d, 2H, $J$ = 8.0 Hz, heterocyclic CH), 8.43–8.41 (d, 2H, $J$ = 8.0 Hz, heterocyclic CH), 7.85–7.84 (m, 2H, heterocyclic CH), 7.35–7.32 (m, 2H, heterocyclic CH). $^{13}C$ NMR ($CDCl_3$, ppm, 100 MHz): 156.1, 149.2, 137.0, 123.8, 121.1.

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