

# Aryl Iodides as Strong Inhibitor in Gold and Gold-Based Bimetallic quasi-Homogeneous Catalysis

*Raghu Nath Dhital, Choavarit Kamonsatikul, Ekasith Somsook, Yoshinori Sato,  
and Hidehiro Sakurai\**

E-mail: [hsakurai@ims.ac.jp](mailto:hsakurai@ims.ac.jp)

## Contents

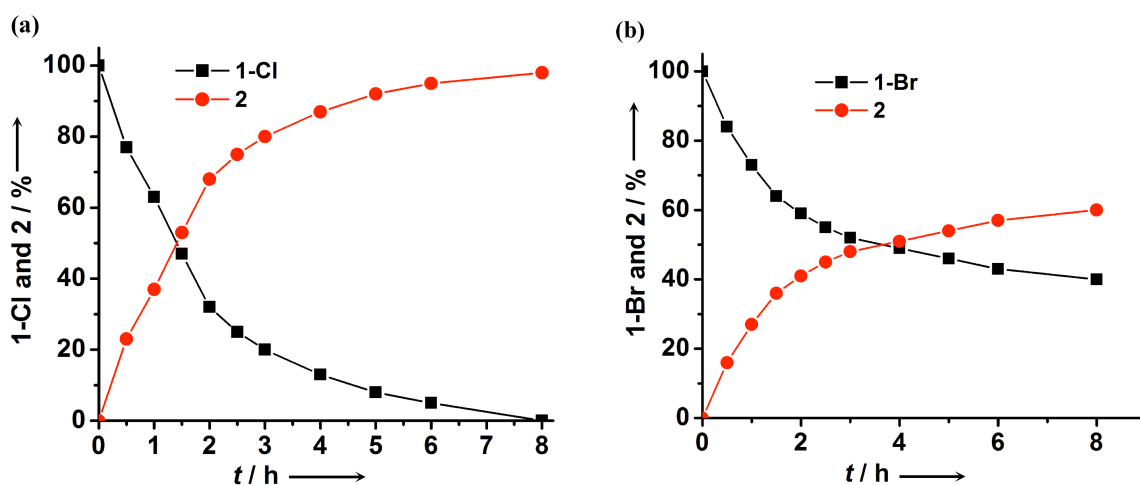
<b>1. General</b>	S2
<b>2. Kinetics of 4-chlorotoluene (1-Cl), 4-bromotoluene (1-Br), and 4-iodotoluene (1-I) catalyzed by Au<sub>0.5</sub>Pd<sub>0.5</sub>:PVP</b>	S3-S4
<b>3. General protocol for Ullmann coupling of 1-Cl catalyzed by bimetallic Au<sub>0.5</sub>Pd<sub>0.5</sub>:PVP</b>	S4
<b>4. General procedure for aerobic homocoupling of arylboronic acids (4) catalyzed by Au:PVP</b>	S4
<b>5. General procedure for aerobic homocoupling of arylboronic acids (4) catalyzed by Au:chit</b>	S5
<b>6. General procedure for aerobic oxidation of 1-indanol catalyzed by Au:PVP</b>	S6
<b>7. Preparation of C-I modified Au NCs and catalytic activities for coupling reaction</b>	S7-S8
<b>8. UV-visible analysis</b>	S9-S12
<b>9. PL analysis</b>	S13
<b>10. Powder X-ray diffraction spectroscopy (XRD)</b>	S14
<b>11. Transmission electron microscope (TEM)</b>	S15
<b>12. SEM-EDS analysis</b>	S16

## Experimental Details

**1. General:** UV-vis spectra were measured by JASCO V-670 spectrophotometer at 24 °C. X-ray diffraction pattern of Au nanoclusters as in thin film mode was recorded using Rigaku Ultimat III, RINT-2000/PC (Cu K $\alpha$  radiation under operation at 40 kV and 40 mA). The high-resolution TEM images of PVP stabilized gold nanoclusters were recorded with a JEOL JEM-3100FE and JEM-2100F at an accelerating voltage of 200 kV respectively. The composition of individual elements in Au:PVP mixed **3-I** and **4-I** was evaluated using EDS (energy-dispersive spectrometry) in Hitachi H-4200 (scanning electron microscope; field emission electron gun, accelerating voltage 25 kV, current emission 10  $\mu$ A, measurement range 0 to 20 keV and measurement magnification 100). The emission spectra were measured by JASCO FP 6500 spectrofluorometer at room temperature. Horiba pH/DO meter, D-55 was used to measure the pH of the solutions. <sup>1</sup>H-NMR spectra were measured using a JEOL JMN LAMBDA 400 spectrometer at 23 °C at 400 MHz. CDCl<sub>3</sub> or acetone-d<sub>6</sub> was used as a solvent and the residual solvent peak was used as an internal standard (7.26 ppm for CDCl<sub>3</sub> and 2.09 ppm for acetone-d<sub>6</sub>). TLC analysis was performed using Merck Silica gel 60 F<sub>254</sub> and preparative TLC were conducted using Wakogel B-5F. GC 2010 (Shimadzu) with Rtx-5MS column (length 30 m, inner diameter 0.25 mm and film thickness 0.25  $\mu$ m) was used for monitoring the kinetics of reactions.

All chemicals and solvents were used as received without further purification unless otherwise noticed. Hydrogen tetrachloroaurate tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O Tanaka Kikinzoku), palladium chloride (PdCl<sub>2</sub>, Wako) and sodium tetraborohydride (NaBH<sub>4</sub>, Wako) and poly(N-vinylpyrrolidone) (Kishida chemicals) were used as precursors for the preparation of bimetallic nanoclusters and their monometallic counterparts. 4-chlorotoluene (**1-Cl**), 4-bromotoluene (**1-Br**), 4-iodotoluene (**1-I**), were obtained from Wako. Phenylboronic acid (**4-H**), (4-fluorophenyl)boronic acid (**4-F**), (4-chlorophenyl)boronic acid (**4-Cl**), (4-bromophenyl)boronic acid (**4-Br**), (4-iodophenyl)boronic acid (**4-I**) were purchased from Sigma Aldrich and purified by recrystallization from H<sub>2</sub>O before use. 4-chlorobenzoic acid (**3-Cl**), 4-iodobenzoic acid (**3-I**), 4-bromobenzoic acids (**3-Br**) were obtained from Sigma Aldrich. Ethyl acetate and hexane were purchased from Wako. 1-indanol was purchased from Alfa Aesar. Potassium hydroxide and DMF was obtained from Wako. Milli-Q grade water was used in all experiments. Chitosan [*poly (D-glucosamine)*] with a medium molecular weight of 75-85 % de-acetylated was purchased from Sigma Aldrich. Monometallic Au:PVP, Au:chit and bimetallic Au<sub>0.5</sub>Pd<sub>0.5</sub>:PVP were prepared according to our previous reports.<sup>1, 2, 3</sup>

**2. Kinetics of 4-chlorotoluene (1-Cl), 4-bromotoluene (1-Br), and 4-iodotoluene (1-I) catalyzed by Au<sub>0.5</sub>Pd<sub>0.5</sub>:PVP:** Ullmann coupling of **1-Cl** or **1-Br** was carried out using an organic synthesizer (EYELA, PPS-2510). 0.25 mmol of **1-Cl** or **1-Br** or **1-I** and 150 mol% of KOH (0.375 mmol, 21.0 mg) were placed in a test tube ( $\phi=30$  mm). A hydrosol of Au<sub>0.5</sub>Pd<sub>0.5</sub>:PVP (5 mM, 1 mL, 2 atom%) was added to the mixture, 3.75 mL of DMF and 2.75 mL of Milli-Q water (DMF/H<sub>2</sub>O, 1:1 ratio, 7.5 mL final volume) was added and argon was supplied from balloon without degassed of solution. The reaction was stirred vigorously (1300 rpm) at 35 °C and 0.2 mL of reaction mixture was sampled to monitor the decay of substrate in each time intervals. The reaction mixture was quenched by 0.5 M HCl and extract with ethyl acetate (0.5 mL x 3 times). GC determined the yields of product by using hexadecane as internal standard. Fig. S1 (a) and (b) show the time dependent catalytic reactions of 4-chlorotoluene (**1-Cl**) and 4-bromotoluene (**1-Br**) respectively. Yield of products or decay of substrates as a function to time was evaluated by GC analysis.



**Fig. S1** Plot of yield of the product or decay of reactants versus reaction time intervals. (a) Decay of 4-chlorotoluene (**1-Cl**) and formation of 4,4'-dimethylbiphenyl (**2**). (b) Decay of 4-bromotoluene (**1-Br**) and formation of 4,4'-dimethylbiphenyl (**2**).

Fig. S2 shows the time course of conversion of **1-Cl** or **1-Br**. The rate constant was estimated from the slope of  $-\ln(1-C)$ , where  $C$  is conversion of **1-Cl** or **1-Br**. The observed reaction rates for the decay of **1-Cl** ( $k_{1-Cl}$ ) and of **1-Br** ( $k_{1-Br}$ ) were found to be ( $5.6 \times 10^{-2} \text{ h}^{-1}$ ) and ( $2.0 \times 10^{-2} \text{ h}^{-1}$ ) respectively. Therefore, Ullmann coupling reaction of 4-bromotoluene (**1-Br**) catalyzed by bimetallic Au/Pd alloy nanoclusters (NCs) stabilized by poly(*N*-vinylpyrrolidone) (Au<sub>0.5</sub>Pd<sub>0.5</sub>:PVP, 1:1 ratio of Au and Pd) is nearly three times slower than that of 4-chlorotoluene (**1-Cl**). In each case the rate constant was calculated from initial rate (reaction time only 3 h).

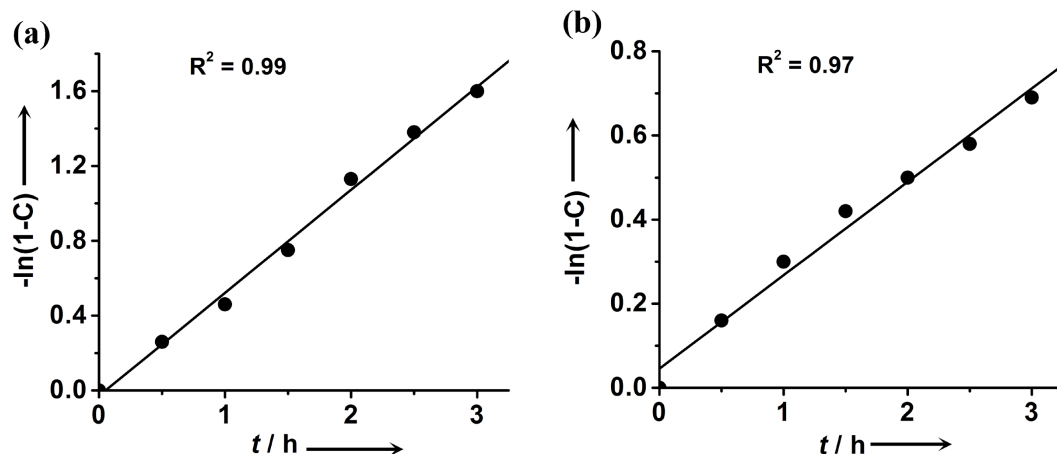


Fig. S2 Plot of  $-\ln(1-C)$  against the time conversion of (a) 1-Cl and (b) 1-Br.

**3. General protocol for Ullmann coupling of 1-Cl catalyzed by bimetallic  $\text{Au}_{0.5}\text{Pd}_{0.5}$ :PVP:** The reaction was carried out using an organic synthesizer (EYELA, PPS-2510) under argon atmosphere. 0.25 mmol of 1-Cl and 150 mol% of KOH (0.375 mmol, 21.0 mg), and additives specified in Scheme 1, were placed in a test tube ( $\phi = 30$  mm). A hydrosol of  $\text{Au}_{0.5}\text{Pd}_{0.5}$ :PVP (5 mM, 1 mL, 2 atom%) was added to the mixture then 3.75 mL of DMF and 2.75 mL of Milli-Q water (DMF/ $\text{H}_2\text{O}$ , 1:1 ratio, 7.5 mL final volume) was added. The reaction was stirred vigorously (1300 rpm) at 35 °C for the time specified. The reaction mixture was quenched by 0.5 M HCl and was extracted with ethyl acetate (4 x 15 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  then evaporated in vacuo. The crude product was purified by PTLC to afford the pure biaryls 2. The results of coupling reactions were shown in Scheme 1 in manuscript.

**4. General procedure for aerobic homocoupling of arylboronic acids (4) catalyzed by Au:PVP:** Aerobic oxidative homocoupling of phenylboronic and substituted phenylboronic acids (4) were carried out using an organic synthesizer (EYELA, PPS-2510). 0.25 mmol of substrate 4, 5 mL Milli-Q water, 300 mol% of  $\text{K}_2\text{CO}_3$  (0.75 mmol, 104 mg) and additives specified in Table 1 or Table S1, were placed in a test tube ( $\phi = 30$  mm). A hydrosol of Au:PVP (0.5 mM, 10 mL, 2 atom%) was added and the mixture was stirred vigorously (1300 rpm) at 27 °C for 24 h. 0.5 M HCl was used to quench the reaction, and the products were extracted with ethyl acetate (4 x 15 mL). The extracted organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated in vacuo. The products were isolated by PTLC. All products are known compounds and their  $^1\text{H-NMR}$  spectra are in good accordance with those of authentic samples. The results are shown in Table 1 in manuscript and Table S1.

## 5. General procedure for aerobic homocoupling of arylboronic acids (**4**) catalyzed by Au:chit:

Aerobic oxidative homocoupling of **4** was carried out using an organic synthesizer (EYELA, PPS-2510). 0.25 mmol of substrate **4**, acetate buffer (pH 4.57, 5 mL), and additives specified in Table 1 or Table S1 were placed in a test tube ( $\phi = 30$  mm). A hydrosol of Au:chit (0.5 mM, 10 mL, 2 atom%) was added and the mixture was stirred vigorously (1300 rpm) at 30 °C for the required time. The reaction was then quenched with ethyl acetate and the products were extracted with ethyl acetate (4 x 15 mL). The extracted organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo. The products were isolated by preparative thin-layer chromatography (ethyl acetate and hexane). The results are shown in Table 1 in manuscript and Table S1.

**Table S1** Aerobic oxidative homocoupling of phenylboronic acid and its derivatives catalysed by Au:PVP or Au:chit.

$$\text{R-C}_6\text{H}_4\text{-B(OH)}_2 \xrightarrow[\text{2 mol\% additives}]{\text{2 atom\% cat[Au], Conditions A or B}} \text{R-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-R} + \text{R-C}_6\text{H}_4\text{-OH}$$

**4**
**5**
**6**

Entry	R	Catalyst	Additives	Conditions <sup>a</sup>	T (°C)	Yields (%) <b>5<sup>b</sup></b>	<b>6<sup>c</sup></b>
1	Cl	Au:PVP	-	A	27	74	26
2	Br	Au:PVP	-	A	27	65	25
3	<b>I</b>	Au:PVP	-	A	27	0	0
4	H	Au:PVP	<b>3-I or 4-I</b>	A	27	0	0
5	H	Au:PVP	<b>3-Br</b>	A	27	74	26
6	H	Au:PVP	<b>3-Cl</b>	A	27	74	26
7	F	Au:chit	-	B	30	94	6
8	Cl	Au:chit	-	B	30	93	6
9	Br	Au:chit	-	B	30	93	5
10	<b>I</b>	Au:chit	-	B	30	0	0
11 <sup>d</sup>	H	Au:chit	-	B	30	93	7
12	H	Au:chit	<b>3-I or 4-I</b>	B	30	0	0

<sup>a</sup>Reaction conditions: A: **4** (0.25 mmol), H<sub>2</sub>O (5 mL), K<sub>2</sub>CO<sub>3</sub> (300 mol%), 27 °C, 24 h, air; B: **4** (0.25 mmol), acetate buffer (pH 4.57; 5 mL), 30 °C, 24 h, air. <sup>b</sup> Yield of isolated product. <sup>c</sup> Yield by NMR. <sup>d</sup> Reaction was performed up to 9 h.

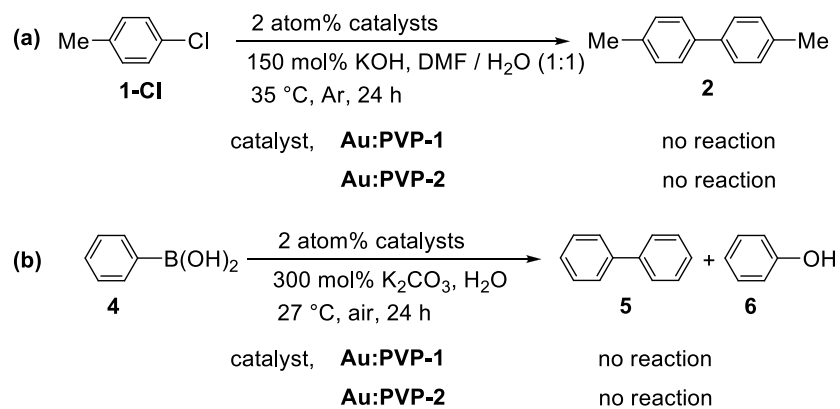
**6. General procedure for aerobic oxidation of 1-indanol catalyzed by Au:PVP:** Aerobic oxidation of 1-indanol (7) was carried out using an organic synthesizer (EYELA, PPS-2510). 1-indanol (0.25 mmol, 33.0 mg), 300 mol%  $K_2CO_3$  (0.75 mmol, 104 mg), 5 mL Milli-Q water, and additives specified in Scheme 2 were placed in a test tube ( $\phi = 30$  mm). A hydrosol of Au:PVP (0.5 mM, 10 mL, 2 atom%) was added and the mixture was stirred vigorously (1300 rpm) at 27 °C for 30 minutes. The reaction was quenched by 0.5 M HCl, and the products were extracted with ethyl acetate (4 x 15 mL). The extracted organic layer was dried ( $Na_2SO_4$ ) and concentrated in vacuo. The products were isolated by preparative thin-layer chromatography (ethyl acetate/hexane). The results of oxidation reaction were shown in Scheme 2 in manuscript.

## 7. Preparation of C-I modified Au NCs and catalytic activities for coupling reaction

Two types of **3-I** modified Au NCs such as **Au:PVP-1** and **Au:PVP-2** were prepared.

*(i) Preparation of Au:PVP-1:* 278 mg (2.50 mmol, monomer unit of polymer) of PVP (K-30) was placed in a hard glass test tube ( $\phi = 42$  mm) and dissolved in 39 mL of Milli-Q water and to the solution was added 1 mL of HAuCl<sub>4</sub> (from 25 mM stock solution) and 5 mL 5 mM solution of *p*-iodobenzoic acid, **3-I** was added and final concentration of Au, **3-I** and monomer unit of polymer was made 1:1:100 ratio. The resulting solution was stirred for 30 min at 27 °C. The solution was maintained 0 °C before reduction in organic synthesizer (EYELA, PPS-2510) and an aqueous solution (5 mL) of NaBH<sub>4</sub> (9.5 mg, 0.25 mmol) was added rapidly under vigorous stirring (1700 rpm). The color of the mixture was turned from pale yellow to brown and solution was monitored by UV-vis spectroscopy in different time interval and result was shown in Fig. S3 (a). The prepared **Au:PVP-1** was subsequently dialyzed through the membrane filter to remove the inorganic impurities such Na<sup>+</sup> and Cl<sup>-</sup>, and non-coordinated **3-I**. The dialyzed hydrosol of **Au:PVP-1** (0.1 mM) was further analyzed by UV-vis and result was shown in Fig. S3 (b). The catalytic activity of thus prepared catalyst was monitored towards the Ullmann coupling of **1-Cl** and oxidative homocoupling of phenylboronic acid as described above and results were shown in Scheme S1.

*(ii) Preparation of Au:PVP-2:* 10 mL of Au:PVP (from 0.5 mM stock) was taken and to the solution 2.04 mL of **3-I** (from 2.5 mM stock) and 2.96 mL of H<sub>2</sub>O was added (final ratio of Au and **3-I** was made 1:1). The solution was kept without stirring for 1 h and monitored by the UV-vis spectroscopy and result was shown in Fig. S4. The observed damping of SPR of Au NCs indicated that the binding of **3-I** on the surface of clusters. The catalytic activity of thus prepared **Au:PVP-2** was monitored towards the Ullmann coupling of **1-Cl** and oxidative homocoupling of phenylboronic acid as described above and results were shown in Scheme S1.

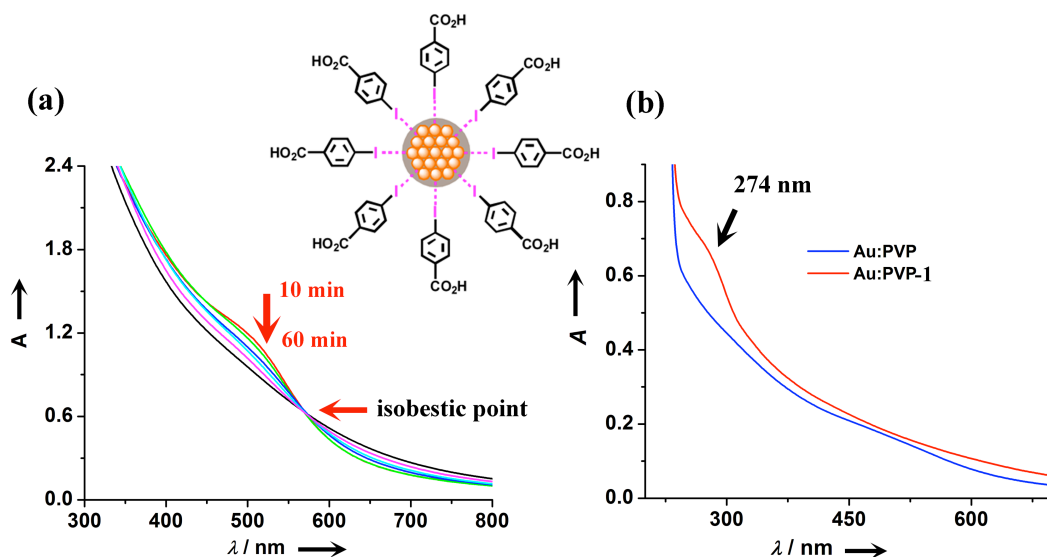


**Scheme S1** (a) Ullmann coupling of **1-Cl** catalyzed by **3-I** modified Au. (b) Oxidative homocoupling of phenylboronic acid catalyzed by **3-I** modified Au.

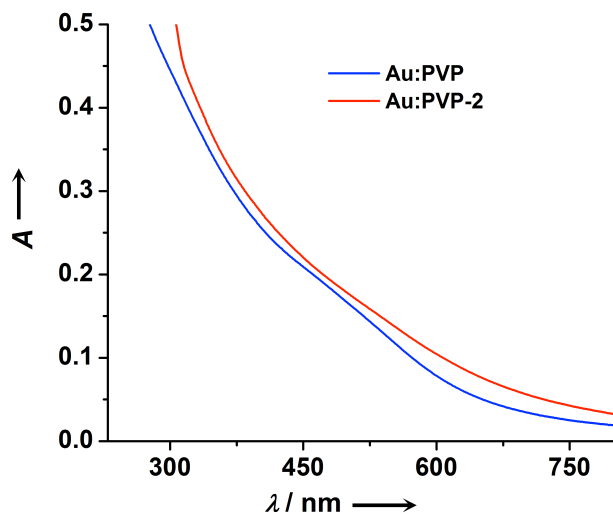


## 8. UV-visible analysis

*i) UV-vis spectra of Au:PVP-1:* The observed UV-vis spectra of **3-I** modified Au clusters was shown in Fig. S3. In the region of the surface plasmon resonance (SPR), damping of SPR was occurred with the time and observed isobestic point at 570 nm is consistent with the binding of **3-I** with Au clusters *via* a complexation equilibrium.



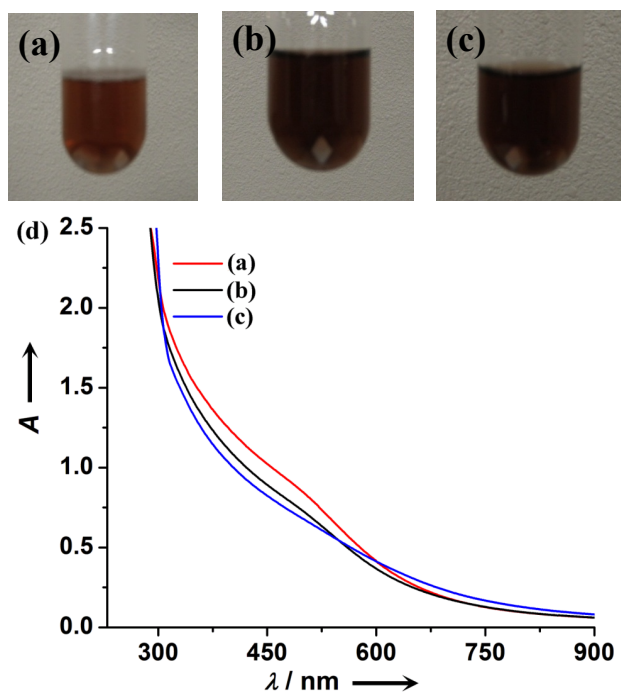
**Fig. S3** (a) Time course change of UV-vis spectra of **Au:PVP-1** (0.5 mM solution of Au) (b) UV-vis spectra of **Au:PVP-1** (0.1 mM solution of Au) after centrifuged at 4000 rpm in reference with **Au:PVP**.



**Fig. S4** UV-vis spectra of **Au:PVP-2** (0.1 mM solution of Au) in reference with **Au:PVP**.

The prepared **Au:PVP-1** was subsequently dialyzed through the membrane filter to remove the inorganic impurities such  $\text{Na}^+$  and  $\text{Cl}^-$ , and non-coordinated **3-I**. The dialyzed hydrosol of **Au:PVP-1** (0.1 mM) further analyzed by UV-vis and result was shown in Fig. S4. The observed new absorption band at 274 nm with damping of SPR of Au clearly indicated that the **3-I** modified Au cluster was formed.

*ii) Stability and recovery of Au:PVP in the presence of iodo arene:* The UV-vis spectra of Au:PVP before reaction without addition of iodo arene such as **3-I**, and after addition **3-I** was monitored. The color of the catalyst and corresponding UV-vis spectra before reaction and after reaction was displayed in the Fig. S5. The result indicated that after 24 h of reaction in the presence of **3-I**, Au:PVP is not agglomerated or precipitate. Instead, we observed the slightly grew of particles from 1.3 nm to 2.7 nm (see in TEM analysis).



**Fig. S5** Change of color of Au:PVP on mixing with **3-I**. (a) mixture of Au:PVP, 0.25 mmol phenylboronic acid and 300 mol%  $\text{K}_2\text{CO}_3$ . (b) and (c) mixture of Au:PVP, 0.25 mmol phenylboronic acid, 300 mol%  $\text{K}_2\text{CO}_3$  and **3-I** (in 1:1 ratio with Au) before set up of reaction and after 24 h of reaction. (d) Corresponding UV-vis spectra.

**iii)  $Au_{0.5}Pd_{0.5}:PVP$  vs **3-I**:** For all UV-vis observation, 100  $\mu\text{M}$  concentration of  $Au_{0.5}Pd_{0.5}:PVP$  was taken and concentration of **3-I** was varied from 0  $\mu\text{M}$  to 50  $\mu\text{M}$ . The round bottom flasks (10 mL) were cleaned by aqua regia, rinsed with ultrapure water and dried. 2 mL (from 500  $\mu\text{M}$  stock solution) of  $Au_{0.5}Pd_{0.5}:PVP$  was placed in each flasks. Then, 0  $\mu\text{L}$ , 10  $\mu\text{L}$ , 20  $\mu\text{L}$ , 30 .....120  $\mu\text{L}$  of **3-I** (from 2500  $\mu\text{M}$  stock solution prepared in 2500  $\mu\text{M}$  aqueous solution of  $\text{K}_2\text{CO}_3$ , the propose to use the is  $\text{K}_2\text{CO}_3$  to dissolve **3-I**) was added and final volume was maintained by addition of Milli-Q water (final concentration of metal is 100  $\mu\text{M}$ ). The thus prepared solution was kept for 1 day without stirring and recorded the UV-vis spectra at room temperature. The recorded spectra were shown in Fig. 2a in manuscript.

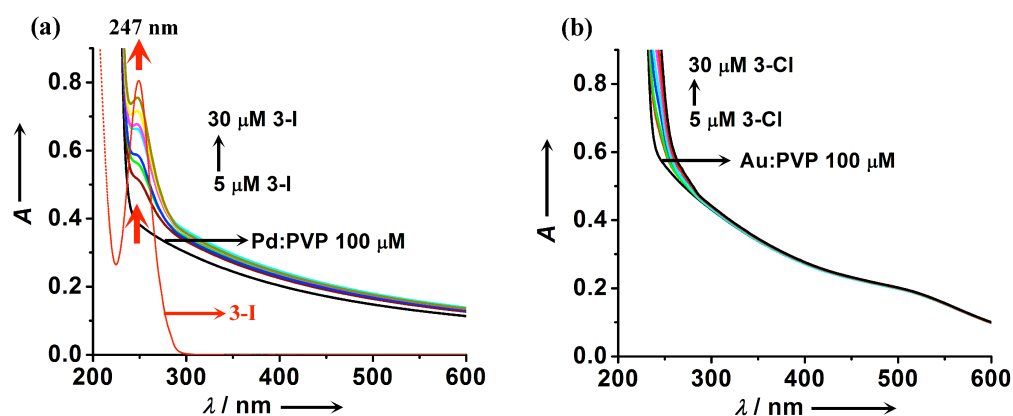
**iv)  $Au:PVP$  vs **3-I**:** The round bottom flasks (10 mL) were cleaned by aqua regia, rinsed with ultrapure water and dried. 2 mL (from 500  $\mu\text{M}$  stock solution) of  $Au:PVP$  was placed in each flasks. Then, 0  $\mu\text{L}$ , 10  $\mu\text{L}$ , 20  $\mu\text{L}$ , 30  $\mu\text{L}$  .....200  $\mu\text{L}$  of **3-I** (from 2500  $\mu\text{L}$  stock solution prepared in 2500  $\mu\text{M}$  aqueous solution of  $\text{K}_2\text{CO}_3$ ) was added and final volume was maintained by addition of Milli-Q water (final concentration of Au is 100  $\mu\text{M}$ ). The thus prepared solution was kept for 1 day without stirring and recorded the UV-vis spectra at room temperature. The recorded spectra were shown in Fig. 2c in manuscript.

**v)  $Au:PVP$  vs **4-I**:** A round bottom flasks (10 mL) was cleaned by aqua regia, rinsed with ultrapure water and dried. 400  $\mu\text{L}$  (from 2500  $\mu\text{M}$  stock solution) of **4-I** was placed and to the solution 2 mL of  $Au:PVP$  (from 500  $\mu\text{M}$  stock solution) was added. The solution was kept for 24 h without stirring and the recorded the UV-vis spectra at room temperature. The recorded spectrum was shown in Fig. 3c in the manuscript.

**vi)  $Pd:PVP$  vs **3-I**:** The round bottom flasks (10 mL) were cleaned by aqua regia, rinsed with ultrapure water and dried. 2 mL (from 500  $\mu\text{M}$  stock solution) of  $Pd:PVP$  was placed in each flasks. Then, 0  $\mu\text{L}$ , 10  $\mu\text{L}$ , 20  $\mu\text{L}$ , 30 .....120  $\mu\text{L}$  of **3-I** (from 2500  $\mu\text{L}$  stock solution, prepared in 2500  $\mu\text{M}$  aqueous solution of  $\text{K}_2\text{CO}_3$ ) was added and final volume was maintained by addition of Milli-Q water (final concentration of Pd is 100  $\mu\text{M}$ ). The thus prepared solution was kept for 1 day without stirring and recorded the UV-vis spectra at room temperature. The recorded spectra were shown in

Fig. S6 (a). Only absorption at 247 nm, characteristic of monomeric absorption of **3-I** was observed with increasing the concentration of **3-I**. There is no absorption band around 274 nm. Therefore, it was assigned that there is no interaction of **3-I** with Pd NCs.

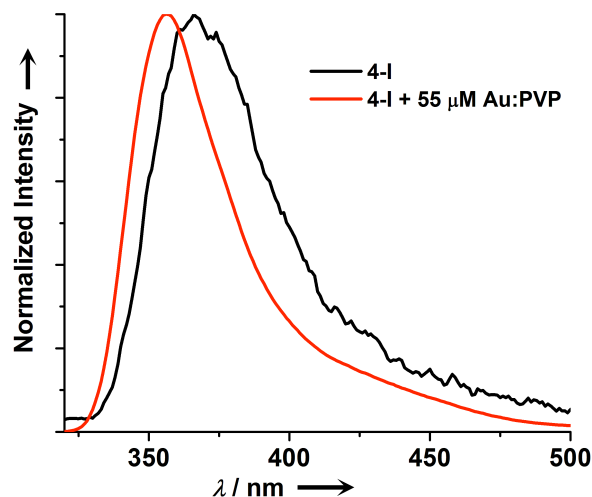
**vii) Au:PVP vs 3-Cl:** The round bottom flasks (10 mL) were cleaned by aqua regia, rinsed with ultrapure water and dried. 2 mL (from 500  $\mu\text{M}$  stock solution) of Au:PVP was placed in each flasks. Then, 0  $\mu\text{L}$ , 10  $\mu\text{L}$ , 20  $\mu\text{L}$ , 30 .....120  $\mu\text{L}$  of **3-Cl** (from 2500  $\mu\text{L}$  stock solution, prepared in 2500  $\mu\text{M}$  aqueous solution of  $\text{K}_2\text{CO}_3$ ) was added and final volume was maintained by addition of Milli-Q water (final concentration of Au is 100  $\mu\text{M}$ ). The thus prepared solution was kept for 1 day without stirring and recorded the UV-vis spectra at room temperature. The recorded spectra were shown in Fig. S6 (b). No absorption band at 274 nm was obtained, therefore, it was assigned that there is no interaction of **3-Cl** with Au NCs.



**Fig. S6** Changes in the UV-vis spectra of (a) 100  $\mu\text{M}$  Pd:PVP on addition of **3-I** (5–30  $\mu\text{M}$ ) and of (b) 100  $\mu\text{M}$  Au:PVP on addition **3-Cl** (5–30  $\mu\text{M}$ ). The red dotted line in (a) represents the absorption spectrum of aqueous **3-I** solution

## 9. PL analysis

(i) *Au:PVP Vs 4-I*: For all fluorescence spectroscopy observation, 100  $\mu\text{M}$  concentration of **4-I** was taken and concentration of Au (Au:PVP) was varied from 25  $\mu\text{L}$  to 1200  $\mu\text{L}$  (1.25  $\mu\text{M}$  to 60  $\mu\text{M}$ ). The round bottom flasks (10 mL) were cleaned by aqua-regia, rinsed with ultrapure water and dried. 400  $\mu\text{L}$  (from 2500  $\mu\text{M}$  stock solution, prepared in Milli-Q water) of **4-I** was placed in each flask. Then, 0  $\mu\text{L}$ , 25  $\mu\text{L}$ , 50  $\mu\text{L}$ , 75  $\mu\text{L}$ , 100  $\mu\text{L}$ , ...1200  $\mu\text{L}$  of Au (Au:PVP) (from 500  $\mu\text{L}$  stock solution) was added and final volume was maintained by addition of Milli-Q water (final concentration of **4-I** is 100  $\mu\text{M}$ ). The thus prepared solution was kept for 1 day without stirring and recorded the Fluorescence spectra at room temperature [ $(\lambda_{ex}) = 280 \text{ nm}$ ,  $(\lambda_{em}) = 356 \text{ nm}$ ]. The recorded spectra were shown in Fig. 3 (a) and (b) in manuscript. The normalized emission spectra of monomeric **4-I** and mixture of **4-I** and Au were shown in Fig. S7.



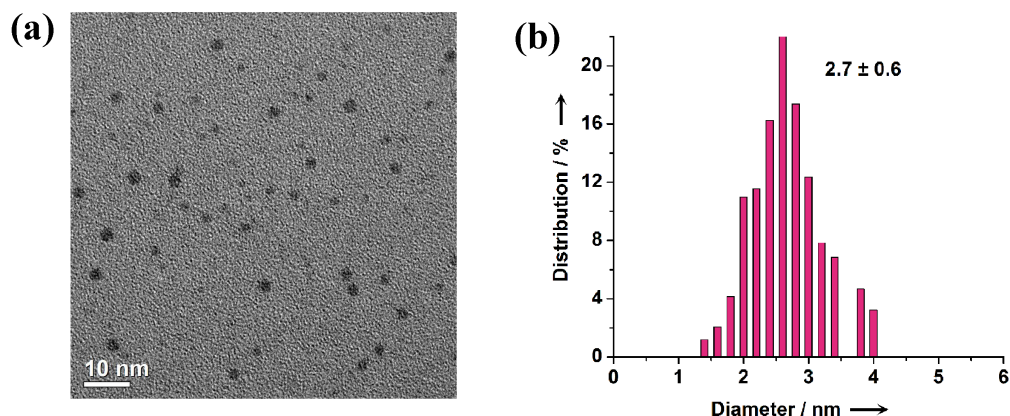
**Fig. S7** Normalized emission spectra of monomeric **4-I** and mixture of Au and **4-I**, ( $\lambda_{ex} = 280 \text{ nm}$ ).

## 10. Powder X-ray diffraction spectroscopy (XRD)

**(i) Au:PVP vs 4-I:** A glass vial (15 mL) cleaned by aqua-regia, rinsed with ultrapure water and dried. 7.5 mL Au:PVP was placed in glass vial (from stock 1000  $\mu\text{M}$ ). To this solution 3.0 mL **4-I** was added (from stock 2500  $\mu\text{M}$ , prepared in Milli-Q water) and finally Au and **4-I** becomes in 1:1 molar ratio. The color of the solution was changed from light brown to dark brown immediately after mixing with **4-I** (Fig. S5). The solution mixture was centrifuged at 4800 rpm to remove the non-coordinated **4-I**. After centrifuged the catalyst was deposited on the glass slide followed by vacuum air-drying. The process was repeated and made a thin film having smooth surface and measured the XRD. The result of XRD was shown in Fig. 4a in manuscript. From the Scherrer equation the size of the Au core was found to be 3.7 nm while 2.7 nm was estimated from TEM. The observed slightly bigger size of Au in XRD may be attributed from the aggregation of cluster during the preparation of thin film on the glass slide.

## 11. Transmission electron microscope (TEM)

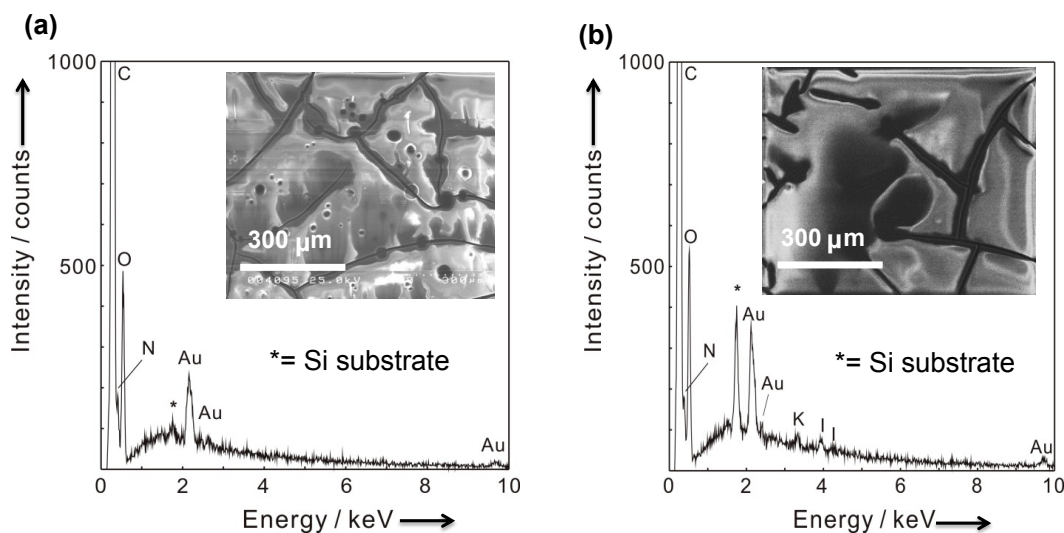
(i) **Au:PVP vs 4-I**: A glass vial (15 mL) cleaned by aqua-regia, rinsed with ultrapure water and dried. 7.5 mL of Au:PVP was placed in glass vial (from stock 1000  $\mu\text{M}$ ). To this solution 3.5 mL of **4-I** was added (from stock 2500  $\mu\text{M}$ ) and finally Au and **4-I** becomes 1:1 molar ratios. The resulting solution mixture was centrifuged at 4800 rpm to remove the non-coordinated **4-I**. After centrifuged a drop of mixture was put in the TEM grid followed by vacuum dried and measured by TEM. By counting more than 300 particles the histogram was plotted which is shown in Fig. S8. It shows the average particle size of Au was increased from 1.3 nm to 2.7 nm after mixing with **4-I** in 1:1 ratio. The observed high resolution TEM images of Au:PVP after mixed with **4-I** was shown in Fig. 4 (e) in manuscript.



**Fig. S8** (a) Transmission electron microscopy image of Au:PVP after mixing with **4-I** in 1:1 ratio and (b) Histogram plot of (a).

## 12. SEM-EDS analysis:

(i) *Au:PVP vs 3-I or 4-I*: The composition of each individual element was analyzed by EDS spectra. The observed SEM/EDS spectra of Au:PVP on mixing with **4-I** was shown in Fig. 4 b in manuscript. The observed spectra of Au:PVP on mixing with **3-I** was shown in Fig. S9.



**Fig. S9** SEM/EDS spectra of Au:PVP (a) before mixing with **3-I** and (b) after mixing with **3-I** in 1:1 ratios (the sample was prepared after removal of non-coordinated **3-I** by centrifuged in 4000 rpm and washed five times by Milli-Q water).

## References

- 1 H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi and T. Tsukuda, *Langmuir*, 2004, **20**, 11293.
- 2 (a) A. Morugadoss and H. Sakurai, *J. Mol. Catal. A; Chem.*, 2011, **341**, 1; (b) R. N. Dhital, A. Murugadoss and H. Sakurai, *Chem. Asian J.*, 2012, **7**, 55.
- 3 (a) S. Yudha S, R. N. Dhital and H. Sakurai, *Tetrahedron Lett.*, 2011, **52**, 2633; (b) R. N. Dhital and H. Sakurai, *Chem. Lett.*, 2012, **41**, 630. (c) R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.*, 2012, **134**, 20250.