Supporting Information

The Excimer formation of Aryl Iodides Chemisorbed on Gold Nanoparticles for Significant Enhancement of the Photoluminescence

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A. Chemicals.

All reagents were commercially available and used without further purification unless otherwise mentioned. Aryl halide derivatives, diiodoethane, tetrabutyl ammonium iodide (TBAI), phenol, aniline and phenyl acetylene were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate tetra hydrate (HAuCl$_4$.4H$_2$O) was purchased from Tanaka Kikinzoku. Sodium tetrahydroborate (NaBH$_4$), sodium sulfite (Na$_2$SO$_3$), potassium carbonate (K$_2$CO$_3$) and poly (N-vinylpyrrolidone) (PVP) (K30, 40 kDa) were obtained from Wako Pure Chemical Industries. Spectroscopic grade methanol was used for all experiments. Milli-Q grade water was used in the present study wherever necessary.

B. Instrumental Techniques

UV-visible absorption spectroscopy (UV-vis)
The Solution phase UV-vis spectra were measured by a JASCO V-670 spectrophotometer at room temperature (298 K) using a quartz cell with optical path length of 1cm.

Photoluminescence spectroscopy (PL)

The luminescence spectra were measured by using a JASCO FP 6500 fluorophotometer at room temperature (298 K) using a quartz cell with optical path length of 1 cm. The solvent was de-aerated by purging with argon gas before photoluminescence measurement. 3D Photoluminescence spectra were measured by allowing the instrument to record the emission profiles of the sample with excitation wavelength range 200 to 600 nm and corresponding emission wavelength range 210 to 850 nm. The study allows us to know exact excitation and emission wavelength of an unknown sample.

Phosphorescence measurement.

Phosphorescence spectrum was recorded on a Parkin Elmer (LS-55) spectrofluorophotometer. Measurement of phosphorescence was performed in 2-methyl THF solution under the freeze condition. For example, 4-iodophenol (**1**) of phosphorescence was shown in Figure S7. The phosphorescence peak of **1** was observed at 430 nm, so the enhanced photoluminescence (at 357 nm) was not corresponding to the phosphorescence of **1**.

PL lifetime measurement

Photoluminescence lifetimes were measured by a HORIBA Scientific time-correlated single-photon counting system (FluoroCube) with the laser light (DeltaDiode, laser diode head, 271 nm) as an excitation source In life time, the decays were fitted with a one-exponential and two-exponential function.

$$F(t) = \sum_{i=1}^{2} a_i \exp\left(-\frac{t}{\tau_i}\right)$$

where F(t) denotes normalized PL decay and a_1 and a_2, are the normalized amplitudes of decay components τ_1 and τ_2, respectively. The average lifetime was obtained from the equation

$$<\tau> = \sum_{i=1}^{2} a_i \tau_i$$

Transmission Electron Microscopy (TEM)

The TEM images of PVP stabilized gold nanoparticles were recorded using a JEOL TEM-3100FE instrument with an accelerating voltage of 200 kV. A water dispersion of gold nanoparticle was drop-casted onto hydrophilic carbon-coated copper grid followed by drying in open air for 2 h.

Optical Image

Optical pictures were captured using a Canon PowerShot SX50 camera.

C. Synthesis of Au:PVP nanoparticles.

Details of the procedure is given in References 1 and 2 (page S12). In brief, an aqueous solution of $HAuCl_4$ (1 mM, 30 mL) was mixed with PVP (K30, 0.6 mmol in monomer unit) and the mixture was stirred for 15 min at 273 K. Next, Au:PVP (1.4 nm) nanoparticles were obtained by mixing aqueous solutions of $HAuCl_4$/PVP and $NaBH_4$ (0.1 M, 3mL) at 273 K under vigorous stirring condition for 30 minutes. Then the as formed aqueous Au:PVP nanoparticle dispersion was purified by ultrafiltration with membrane filter (10kDa Molecular Wt. cut of limit) for a prolonged time at 280 K. The final purified solid Au:PVP (1.4 nm) nanoparticle powder was obtained by lyophilizing the deionized dispersion of the as-prepared Au:PVP nanoparticles obtained through ultrafiltration technique by using fridge dryer.

The larger Au:PVP nanoparticles were prepared by seed mediated growth method using a mild reducing agent (reference 2). Two larger Au:PVP nanoparticles were prepared by reduction of $HAuCl_4$ by Na_2SO_3 in the presence of the previously synthesized 1.4 nm sized Au:PVP nanoparticles as seed. The mixture of deaerated aqueous solutions of $HAuCl_4$ (30 mM) and Na_2SO_3 (90 mM) were quickly added to that of Au:PVP (1.4 nm) (0.5 mM). The Au atomic ratio of $HAuCl_4$ to Au:PVP (1.4 nm) was kept at 3:1 and 10:1 for Au:PVP (3.2 nm) and Au:PVP (7.2 nm) respectively whereas the amount of Na_2SO_3 was 3 times with respect to the amount of $HAuCl_4$ in both cases. The final solutions were purified by ultrafiltration using membrane filter-based centrifuge tube (10kDa Molecular Wt. cut of limit followed by drying under vacuum using fridge dryer.

D. Preparation of organic ligand-Au:PVP nanoparticle adduct in solution.

Spectroscopic grade methanol was used for preparation of these solutions. The solvent was deaerated by prolonged purging with argon for 30 minutes prior to their use as solvent. First, 10 mL stock solution of each ligand {Aryl iodides, other aryl compounds, Diiodoethane and Tetrabutyl ammonium iodide (TBAI)} with 1.5 mmolar concentration was prepared in methanol. Then, 50 mL stock solution of Au:PVP cluster with 1.5 mmolar (with respect to gold) concentration was prepared in in methanol. These two stock solutions were mixed in different ratio along with added fresh methanol in a series of glass vials to have desired concentration ratios of ligand and Au:PVP cluster.

One example is shown here: For 4-iodophenol (**1**) + Au:PVP (1.4 nm) sample preparation, nine glass vials of 20 mL volume were taken and was properly cleaned and dried before use.

Vial no.	Volume of added stock **1** solution	Volume of added Au:PVP stock solution	Volume of Added fresh MeOH	Total Volume	Final concentration of **1**	Final concentration of Au:PVP
1	333.3 μL	0 mL	9.667 mL	10 mL	50 μM	0
2	0 mL	333.3 μL	9.667 mL	10 mL	0	50 μM
3	333.3 μL	33.3 μL	9.634 mL	10 mL	50 μM	5 μM
4	333.3 μL	66.6 μL	9.6 mL	10 mL	50 μM	10 μM
5	333.3 μL	133.2 μL	9.533 mL	10 mL	50 μM	20 μM
6	333.3 μL	199.8 μL	9.466 mL	10 mL	50 μM	30 μM
7	333.3 μL	266.4 μL	9.4 mL	10 mL	50 μM	40 μM
8	333.3 μL	333.3 μL	9.33 mL	10 mL	50 μM	50 μM
9	333.3 μL	399.6 μL	9.26 mL	10 mL	50 μM	60 μM

These solutions were kept in dark at room temperature for 24 hours and afterwards their photoluminescence measurements were performed.

All other ligands (other aryl iodides, alkyl iodide, ionic iodide, aryl amine, aryl thiol, halobenzene (X = Br, Cl), phenol, phenyl acetylene) (40 μM) were also mixed under identical conditions with 1.4 nm sized Au:PVP nanoparticles (40 μM) and PL measurement were taken.

E. Calculation of normalized surface area of three different sized Au:PVP nanoparticles.

First, we assume that all Au:PVP clusters are spherical in shape and all have same density (d).

For a sphere, total surface area = $4\pi r^2$

So, for three different sized Au cluster, their respective surface area (for a single particle) is: $4\pi (r_1)^2$, $4\pi (r_2)^2$ and $4\pi (r_3)^2$. (r_1, r_2 and r_3 are their radius respectively).

The volume for a single particle is: $4/3\pi (r_1)^3$, $4/3\pi (r_2)^3$ and $4/3\pi (r_3)^3$

Now for a unit weight of gold, the total volume is: $1/d$

So, number of particles for a cluster is: total volume/volume of a single particle

$= 1/d / 4/3\pi r^3$

So, Total surface are for this unit weight of gold cluster is: no. of particles × surface area of a single particle.

$= 1/d / 4/3\pi r^3 \times 4\pi r^2 = 3/d.r$

So for these three Au:PVP clusters, the ratio of their total surface area is:

$3/d.r_1$: $3/d.r_2$: $3/d.r_3$

$= 1/r_1$: $1/r_2$: $1/r_3$

$= 1/0.7$: $1/1.6$: $1/3.6$ (radius of three Au:PVP clusters are 0.7, 1.6, and 3.6 nm respectively)

$= 1.42$: 0.625 : 0.277

$= \mathbf{5.12}$: $\mathbf{2.55}$: $\mathbf{1}$

The calculation shows that taking same amount (i.e., 40 μM) of Au (gold) from three different sized Au:PVP nanoparticles will have different surface area in the solution. The process discussed in this work is an interface phenomenon between Au nanoparticle surface on which aryl iodides get chemisorbed, thus we must consider the actual surface area of an Au nanoparticle, not the amount of Au present in the nanoparticle. So, comparison of fluorescence intensity (peak area) of 4-iodophenol (**1**) chemisorbed on three different size Au:PVP nanoparticles requires relative of peak areas with respect to normalized surface area of Au particles.
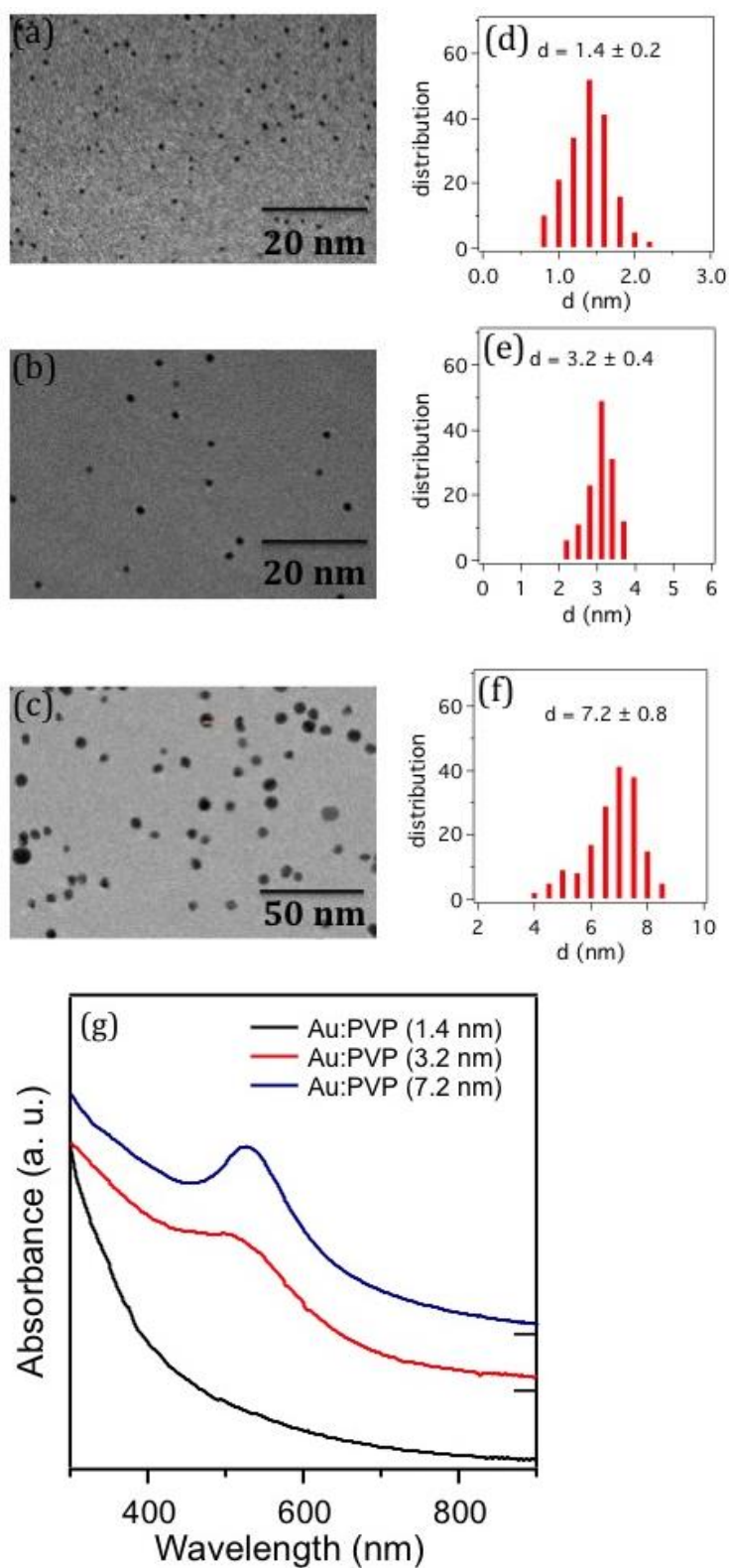
Fig S1. TEM images (a-c) and particle size distributions (d-f) of three different sized Au:PVP nanoparticles, (g) Solution phase UV-vis absorption spectra of three different sized Au:PVP nanoparticles in water at 298 K.
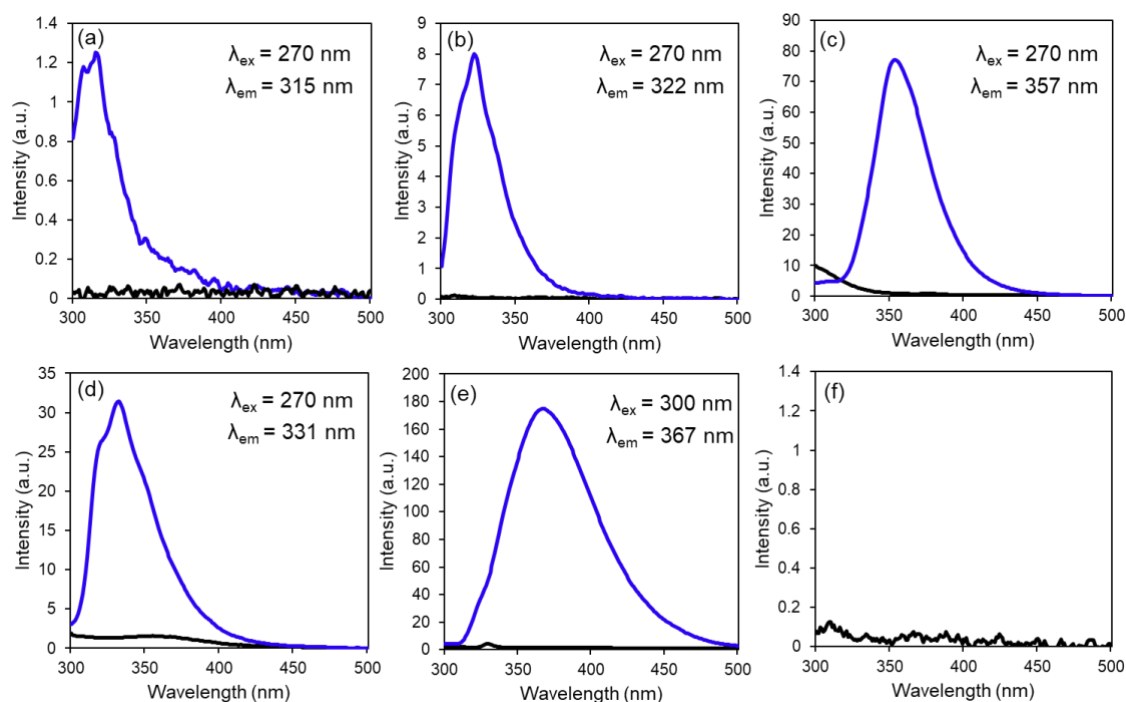
Fig S2. Steady state solution phase emission (fluorescence) spectra of aryl iodides (black lines) and aryl iodides chemisorbed on 1.4 nm sized Au:PVP nanoparticles (blue lines), along with their excitation wavelengths (λ_{ex}) and emission wavelengths (λ_{em}) measured at 298 K. (a) iodobenzene, (b) 1-iodo-4-methylbenzene, (c) 4-iodophenol, (d) 4-iodobenzoic acid, (e) (4-iodophenyl) boronic acid, (f) only Au:PVP (1.4 ± 0.2 nm)
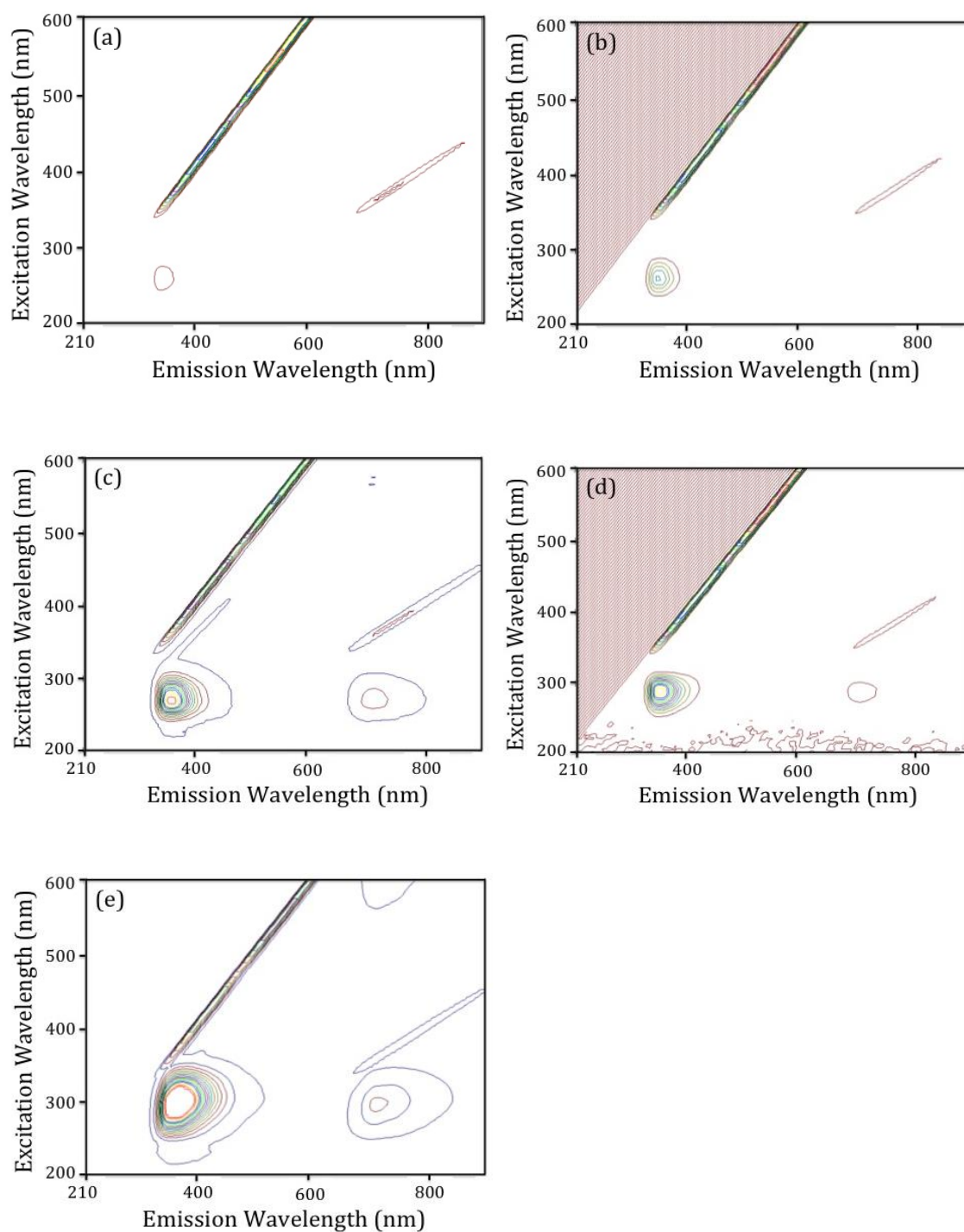
Fig S3. Solution phase 3D fluorescence spectra of different aryl iodide-Au:PVP adduct in methanol at 298 K, to know their respective excitation and emission wavelengths: (a) iodobenzene + Au:PVP, (λ_{ex} = 256 nm , λ_{em} = 350 nm); (b) 4-iodotoluene + Au:PVP, (λ_{ex} = 262 nm, λ_{em} = 352 nm); (c) 4-iodophenol (**1**) + Au:PVP, (λ_{ex} = 270 nm , λ_{em} = 357 nm); (d) 4-iodobenzoic acid + Au:PVP, (λ_{ex} = 288 nm, λ_{em} = 355 nm); (e) 4-iodo phenylboronic acid + Au:PVP, (λ_{ex} = 300 nm, λ_{em} = 375 nm). The X-axis shows emission wavelength, Y-axis

shows excitation wavelength and inner rings show excitation and emission peak position, where red colours indicate highest intensity and blue indicates lowest intensity.

Fig S4. Optical images of a solution of 4-iodophenylboronic acid (40 μM) in methanol (left side with no emission colour) and 4-iodophenylboronic acid (40 mM) + 1.4 nm sized Au:PVP nanoparticle (40 μM) in methanol (right side with strong emission) upon illumination with an UV lamp of 365 nm wavelength.
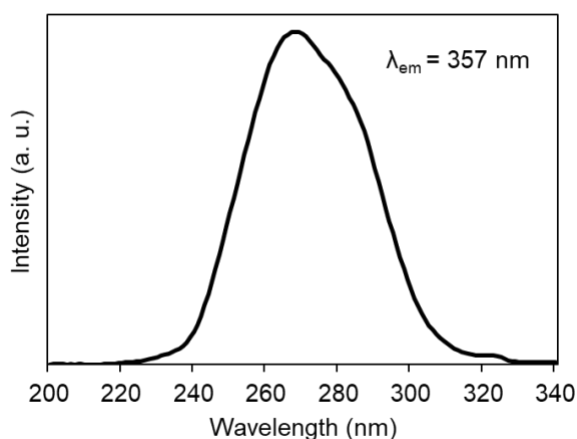

Fig S5. Steady-state excitation spectra of 4-iodophenol (**1**) chemisorbed on 1.4 nm sized Au nanoparticles (**1-Au:PVP**) (40 μM **1**, and 40 μM Au:PVP) in MeOH at 298 K. Emission Wavelength was kept at 357 nm for this measurement.
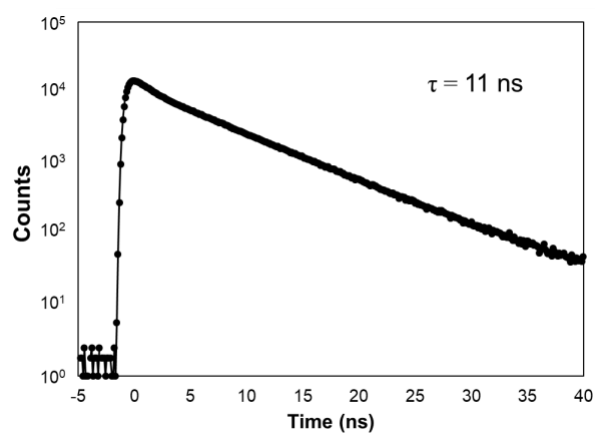
Fig S6. Fluorescence lifetime decay profile of 4-iodophenol (**1**, 20 μM) in methanol with excitation wavelength, 271 nm (black dots) and black solid lines (fitted curve).
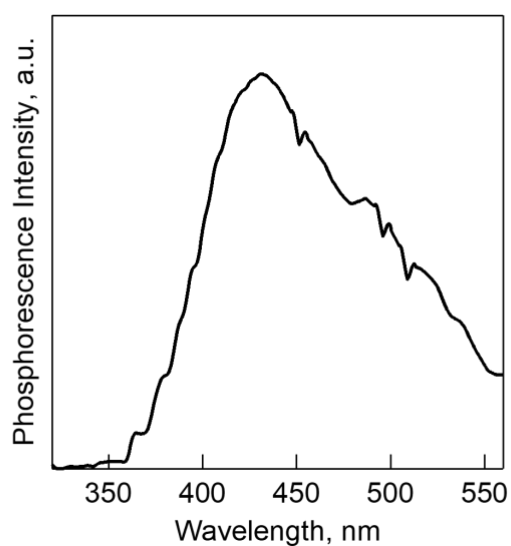

Fig S7. Phosphorescence spectrum of 4-iodophenol (**1**) in 2-methyl THF solution (40 μM) under the freeze condition (77 K).

References:

(1) Tsunoyama, H.; Sakurai, H.; Ichikuni, N.; Negishi, Y.; Tsukuda, T. Colloidal Gold Nanoparticles as Catalyst for Carbon-Carbon Bond Formation: Application to Aerobic Homocoupling of Phenylboronic Acid in Water. *Langmuir* **2004**, *20*, 11293-11296.

(2) Tsunoyama, H.; Sakurai H.; Tsukuda, T. Size Effect on Catalysis of Gold Clusters Dispersed in Water for Aerobic Oxidation of Alcohol. *Chem. Phys. Lett*. **2006**, *429*, 528.