# **Supporting Information**

# Photoluminescence of Doped Superatoms M@Au<sub>12</sub> (M = Ru, Rh, Ir) Homoleptically Capped by (Ph<sub>2</sub>)PCH<sub>2</sub>P(Ph<sub>2</sub>): Efficient Room-Temperature Phosphorescence from Ru@Au<sub>12</sub>

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# **Experimental**

### Chemicals

Solvents except for dichloromethane (DCM), sodium borohydride, and sodium hexafluorophosphate were purchased from Fujifilm Wako Pure Chemical Industries. Dichloromethane (dehydrated) was purchased from Kanto Chemicals. Bis(diphenylphosphino)methane (dppm) and indocyanine green (ICG) were purchased from Tokyo Kasei Industry. The water used was Milli-Q grade (>18 M $\Omega$ ). All commercially available reagents were used as received. (AuCl)<sub>2</sub>dppm, [RuCl<sub>2</sub>(dmod)]<sub>2</sub> (dmod = 2,7-dimethyl-2,6-octadienylene), [Rh(cod)Cl]<sub>2</sub>, and [Ir(cod)Cl]<sub>2</sub> (cod = 1,5-cyclooctadinene) were synthesized according to the reported procedures.<sup>1-4</sup>

#### General

Positive- and negative-mode ESI-MS spectra were recorded on a Jeol JMS-T100LC time-offlight mass spectrometer. The DCM solution of a sample was directly infused at a flow rate of 3.0 mL/h via a syringe pump. The measurement parameters were as follows (for positive and negative in that order): spray voltage 2.5 or -2.5 kV; ring electrode: 20 or -60 V; orifice 1 voltage: 5 or -30 V; orifice 2 voltage: 0 or -5 V; desolvation temperature: 120 °C; and cone temperature: 80 °C. The spectra were calibrated using  $[Cs(CsI)_n]^+$  or  $[I(CsI)_n]^-$  clusters as an external reference, generated from a 99% aqueous MeOH solution of CsI (0.5 mg/mL) under the same parameters. The isotope patterns were calculated using mMass software.<sup>5</sup>

UV-Visible spectra were measured using a Jasco V-670 spectrophotometer with a 1 cm quartz cuvette. Photoluminescence (PL) spectra of **1** at room temperature was recorded using a Jasco FP-6600 spectrofluorometer. The detector sensitivity was corrected using a semicalibrated tungsten lamp unit and a concentrated solution of rhodamine 6G in ethylene glycol. A DCM solution of a sample was placed in a 1 cm quartz cuvette with five transparent windows and a septum. PL spectra in the NIR region were recorded using a Horiba Fluorolog NIR spectrofluorometer equipped with a liquid-N<sub>2</sub>-cooled InGaAs detector with corrected sensitivity.

The solutions were sparged by high-purity Ar (>99.9999 vol%) for 10 min at room temperature for successive measurement. For the different atmosphere, the corresponding gases were sparged to the solution. The absorbance of the solutions at the excitation wavelength was less than 0.1. The following conditions were used for the measurement of the PL spectra shown in Figure 2: excitation at 440 nm and emission at 720 nm for  $1 \cdot (B_5)_2$ ; excitation at 690 nm and emission at 910 nm for  $2 \cdot (PF_6^-)_3$ ; and excitation at 440 nm and emission at 735 nm for  $3 \cdot (PF_6^-)_3$ , respectively. Absolute PL quantum yields were estimated using a Hamamatsu Photonics C9920-02G assembly with an integration sphere. An Ar-saturated solution was used for the measurement. As for  $2 \cdot (PF_6^-)_3$ , the quantum yield was estimated by the reference method using ICG in EtOH as the standard.<sup>6</sup> PL lifetime measurements at room temperature were performed using a picosecond fluorescence lifetime measurement system (Hamamatsu Photonics). A 371 nm laser diode with a pulsed width of 103 ps was used for the excitation light, while a C4780 streak camera with a monochromator was used for the 2D detection of PL from the samples. The obtained PL decay curves were fitted by a single exponential function.

<sup>1</sup>H (400 MHz) and <sup>31</sup>P{<sup>1</sup>H} (160 MHz) NMR charts were recorded at 298 K using a Jeol JNM-ECS400 spectrometer. The chemical shifts in the <sup>1</sup>H NMR chart were referenced to the residual proton signal of the solvent (CD<sub>2</sub>Cl<sub>2</sub>:  $\delta$  5.32). The chemical shifts in the <sup>31</sup>P{<sup>1</sup>H} NMR chart were referenced to the signal of 85 % H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0.00) as an external standard.

Voltammetric measurements were conducted using a BAS model 720B potentiostat equipped with a Faraday cage. TBAPF<sub>6</sub> recrystallized from EtOH was used as the supporting electrolyte. Crystals of the samples were directly dissolved in a 0.1 M TBAPF<sub>6</sub> solution in DCM at a concentration of ~0.5 mM, and the solution was bubbled with Ar gas for 5 min prior to the measurements. The electrochemical cell consisted of a Pt wire counter electrode, an Ag wire soaked in the supporting electrolyte solution separated by ion permeable glass as the reference electrode, a glassy carbon working electrode ( $\varphi$ 1 mm), an Ar gas inlet, and a gas outlet. The glassy carbon electrode was successively polished using 1 µm diamond paste and 0.05 µm Al<sub>2</sub>O<sub>3</sub> paste. The polished electrode was rinsed with water and EtOH and sonicated in EtOH for 5 min. After sonication, the electrode was rinsed with acetone and dried under a stream of Ar. Differential pulse voltammograms (DPVs) were recorded under the following conditions: potential increments: 4 mV; pulse amplitude: 50 mV; pulse width: 50 ms; sampling width: 40 ms; pulse period: 200 ms.

Variable-temperature (VT) optical measurements were conducted using an Oxford Instruments OptistatDN liquid nitrogen cryostat in the range from 80 to 300 K. A solution in a MeOH/EtOH mixture (1:1) was degassed through freeze-pumps-thaw cycling (5 times) and set in the cryostat. The degassed sample (1 mm optical path) in the cryostat was subjected to VT absorption and PL spectral measurements by a Jasco V-760 spectrophotometer and a Jasco FP-8500 spectrofluorometer, respectively. VT PL lifetime measurement was also performed on the sample in the cryostat using the C4780. The excitation source was generated by a Nd:YVO<sub>4</sub> laser (Coherent, Verdi) pumped Ti:Sapphire laser system (Coherent, Mira-900) equipped with a cavity dumper (Coherent, PulseSwitch). This delivers 100 fs pulse trains at 800 nm. After doubling the frequency with a LiB<sub>3</sub>O<sub>5</sub> (LBO) crystal, the incident pulses were focused on the sample ( $\lambda_{ex} = 400$  nm). The PL decay curves were extracted from the 2D streak images in the  $\Delta\lambda$  range of 95 nm centered at the PL peak of each temperature.

#### Analysis

The phosphorescence lifetimes ( $\tau$ ) and the PLQY ( $\Phi$ ) at a given [O<sub>2</sub>] are expressed as

follows by assuming that the ISC is much faster than the fluorescence from the S<sub>1</sub> state:

$$\tau = \frac{1}{k_r + k_{\rm nr} + k_{\rm q}[0_2]} \tag{1}$$

$$\Phi = \tau k_{\rm r} = \frac{k_{\rm r}}{k_{\rm r} + k_{\rm nr} + k_{\rm q}[0_2]} \tag{2}$$

where  $k_r$ ,  $k_{nr}$ , and  $k_q$  denote the rate constants of the phosphorescence, nonradiative decay, and quenching, respectively. By using the experimental values of  $\tau$  and  $\Phi$  at  $[O_2] = 0$  and 2.2 mM, the  $k_r$ ,  $k_{nr}$ , and  $k_q$  were estimated to be 6.4 × 10<sup>4</sup> s<sup>-1</sup>, 1.1 × 10<sup>5</sup> s<sup>-1</sup>, and 2.0 × 10<sup>9</sup> s<sup>-1</sup>M<sup>-1</sup>, respectively.

#### **Synthesis**

Unless otherwise noted, syntheses were conducted under air.

#### [RuAu<sub>12</sub>(dppm)<sub>6</sub>](B<sub>5</sub>O<sub>10</sub>H<sub>4</sub>)<sub>2</sub> (1·(B<sub>5</sub>)<sub>2</sub>)

The optimized synthesis procedure of  $1 \cdot (B_5)_2$  is summarized in Scheme S1. A 200 mL twonecked round-bottomed flask equipped with a magnetic stir bar, a reflux condenser with an Ar inlet, and glass stopper was charged with (AuCl)<sub>2</sub>dppm (510 mg: 1.2 mmol Au) with a counter flow of Ar. One hundred milliliters of degassed and dry DCM was added in and the solution was refluxed (45 °C) for 10 min with stirring. To the colorless solution was added [RuCl<sub>2</sub>(dmod)]<sub>2</sub> (30.8 mg: 0.1 mmol Ru) and the mixture was stirred for 1 min giving a pale-purple solution. Then, 5 mL of freshly prepared ethanolic solution of NaBH<sub>4</sub> (111.5 mg: 3 mmol) was added to the flask at once, resulting in an effervescence and quick color change to black. The reaction mixture was refluxed for another 30 min and the solution was cooled by immersion in an ice bath. The solution was evaporated to dryness using a rotary evaporator. The obtained black residue was extracted with a total of 15 mL of DCM (12 + 3 mL) by centrifugation and toluene (75 mL) was added to the supernatant. The mixture was centrifuged and the precipitate was washed with 10 mL of the toluene/DCM mixture (5:1; v:v) and n-pentane. The dried crude product (~300 mg) was extracted with 10 mL of DCM and the extract was filtered through a 0.2  $\mu$ m syringe filter. The filtrate was layered with 40 mL of cyclopentylmethyl ether (CPME) and the bilayer solution was left to stand at room temperature under dark. After 1-2 days, the black supernatant was decanted and the formed crystals were washed with diethyl ether and *n*pentane. The black microcrystals were dried in vacuo, giving the title compound. Yield: 212.8 mg (41% based on total metal). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.56 (s(br), 4H), 7.06 (t, *J* = 7.55 Hz, 2H), 6.61 (t, J = 7.72 Hz 4H), 3.53 (s(br), 1H); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 12.4 (s). ESI-MS(pos): calcd. for [RuAu12(dppm)6]2+: 2382.112 (monoisotopic); found: 2382.157. ESI-MS(neg): calcd. for  $[B_5O_{10}H_4]$ -: 218.034 (most abundant); 218.022. UV-Vis (DCM)  $\lambda_{max}$  (nm) = 279(sh), 298, 336, 385, 433, 510(sh). Redox potentials (V) from DPV measurement (vs. Fc+/Fc0): 0.152 (7e/8e); 0.140 (6e/7e).



Scheme S1. Synthesis procedure of  $1 \cdot (B_5)_2$  and  $1 \cdot (PF_6)_2$ .

## $[RuAu_{12}(dppm)_{6}](PF_{6})_{2}(1\cdot(PF_{6})_{2})$

The synthesis procedure of  $1 \cdot (PF_6)_2$  is summarized in Scheme S1. One hundred and eighty milligrams of  $1 \cdot (B_5)_2$  (~34 µmol) was placed in a 30 mL vial with a magnetic stir bar. Eighteen milliliters of EtOH was added to the vial and stirring gave a black solution. Then, an ethanolic solution of NaPF<sub>6</sub> (16.8 mg: 0.1 mmol in 1.5 mL EtOH) was added dropwise to the stirring solution of **1**. After 30 min, the formed precipitate was collected by centrifugation and the precipitate was washed with diethyl ether. Yield: 164 mg (95%). For spectroscopic measurement, the part of the product (80 mg) was recrystallized from DCM (10 mL) and CPME (40 mL) at room temperature under dark. After three days, the formed crystals were washed with *n*-pentane and dried *in vacuo*. Yield: 51.5 mg.

# [RhAu<sub>12</sub>(dppm)<sub>6</sub>](PF<sub>6</sub>)<sub>3</sub> (2·(PF<sub>6</sub>-)<sub>3</sub>)

A test tube equipped with a magnetic stir bar was charged with (AuCl)<sub>2</sub>dppm (212 mg: 0.5 mmol Au) and [Rh(cod)Cl]<sub>2</sub> (12.4 mg: 0.05 mmol) complexes. Fifty milliliters of dry DCM was added to the tube and the yellow solution was stirred at the reflux temperature (45 °C) for several minutes. To the reflux solution was added 1.5 mL of a freshly prepared ethanolic solution of NaBH<sub>4</sub> (30.3 mg: 0.8 mmol in 2 mL). The solution turned into black and gas evolved. After 1 h of stirring at the reflux temperature (45 °C), the remaining NaBH<sub>4</sub> solution (0.5 mL) was added to the solution and stirring was continued overnight (~18 h). The solution was cooled to room temperature and then evaporated to dryness. The residue was extracted with 4 mL of DCM and the insoluble solid was removed by centrifugation. To the supernatant was added 25 mL of toluene and the precipitate was collected by centrifugation. The obtained solid was washed with *n*-pentane and the crude product ( $\sim$ 130 mg) was obtained. The crude product was dissolved in 7 mL of EtOH and a methanolic solution of NaPF<sub>6</sub> (34 mg: 0.2 mmol in 1 mL) was added to the stirred solution. After 1 h of stirring, the precipitate was collected by centrifugation, giving a green solid. The solid was extracted with 7 mL of DCM and the mixture was filtered through a 0.2 µm pore syringe filter. Twenty-one milliliters of CPME was layered on the filtrate and the solution was left to stand at room temperature under dark. After four days, the supernatant was removed and the formed crystals were washed with diethyl ether and *n*-pentane. The black crystals were dried in vacuo. Yield: 37.8 mg (15% based on Rh). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.48 (s(br), 4H), 7.18 (t, J = 7.72 Hz, 2H), 6.69 (t, J = 7.72 Hz 4H), 3.85 (s(br), 1H); <sup>31</sup>P{<sup>1</sup>H} NMR (DCM) δ: 15.9 (s). ESI-MS(pos): calcd. for [RhAu<sub>12</sub>(dppm)<sub>6</sub>]<sup>3+</sup>: 1590.407 (monoisotopic); found: 1590.414. UV-Vis (DCM)  $\lambda_{max}$  (nm) = 302, 335, 363(sh), 406(sh), 450(sh), 563.

## $[IrAu_{12}(dppm)_6](PF_6)_3 (3 \cdot (PF_6^{-})_3)$

A 200 mL two-necked round-bottomed flask equipped with a magnetic stir bar, a reflux condenser, and a glass stopper was charged with  $(AuCl)_2$ dppm (425 mg: 1 mmol Au) and 100 mL of dry DCM was added to the flask. The solution was heated at reflux (45 °C) for 10 min. Then, 33.6 mg of [Ir(cod)Cl]<sub>2</sub> (0.1 mmol Ir) was added to the flask, giving an intense yellow solution. After 1 min of stirring, a freshly prepared ethanolic solution of NaBH<sub>4</sub> (76 mg: ca. 2 mmol in 5 mL) was quickly added to the reflux solution, resulting in a fast color change from yellow to black. After 2 h of reflux, the reaction mixture was cooled to room temperature and the solution was evaporated to dryness. The residue was extracted by a total of 15 mL of DCM (12+3 mL) and the insoluble materials were removed by centrifugation. To the supernatant was added 35 mL of *n*-hexane and the precipitate was collected by centrifugation. The precipitate was dried *in vacuo* and the crude product was extracted by 50 mL of EtOH. The EtOH solution was placed in a 100 mL round-bottomed flask with a magnetic stir bar. To the stirred extract was added conc.

HCl (1 mL) and the mixture was stirred for 1 h. The mixture was evaporated to dryness and the residue was dissolved in 10 mL of DCM. Twenty milliliters of diethyl ether was added to the DCM solution and the precipitate was collected by centrifugation. The precipitate was extracted again by 10 mL of DCM and the target clusters were precipitated by the addition of 10 mL of *n*-hexane. The crude product (~270 mg) was dissolved in 25 mL of EtOH and to the stirred solution was added NaPF<sub>6</sub> (84 mg: 0.5 mmol). After 2 h of stirring, the precipitate was collected by centrifugation and then washed with 10 mL of EtOH. The obtained solid was twice recrystallized from the DCM/CPME mixture (10:30 mL and 4:20 mL) at room temperature under dark. The formed crystals were washed with diethyl ether and *n*-pentane and dried *in vacuo*. Yield: 74.8 mg (14% based on Ir). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 7.50 (s(br), 4H), 7.17 (t, *J* = 7.39 Hz, 2H), 6.68 (t, *J* = 7.72 Hz 4H), 3.74 (s(br), 1H); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 25.6 (s). ESI-MS(pos): calcd. for [IrAu<sub>12</sub>(dppm)<sub>6</sub>]<sup>3+</sup>: 1619.759 (monoisotopic); found: 1619.766. UV-Vis (DCM)  $\lambda_{max}$  (nm) = 293, 316, 349(sh), 381(sh), 406(sh), 490(sh), 517(sh), 574(sh).

#### X-ray crystallography

Single crystals for the X-ray diffraction experiment on 1-3 were grown from the DCM/CPME mixture at room temperature. The crystals were immersed in Paratone-N oil with the mother liquor, scooped up with the oil, and rapidly frozen by a cooled  $N_2$  stream. A diffraction experiment was performed using a Rigaku Varimax dual diffractometer with a Pilatus 200K hybrid pixel array detector and MoK $\alpha$  radiation. The data was corrected for Lorentz polarization and absorption correction was performed analytically using CrysAlisPro software. The initial phase trials were conducted by means of a direct method using SHELXS-2014, and the structures were refined using the full-matrix least-squares method on  $F^2$  by SHELXL-2018.<sup>7</sup> One PF<sub>6</sub> anion showed highly disordered electron densities of crystals  $2 \cdot (PF_6^-)_3$  and  $3 \cdot (PF_6^-)_3$ , and those were treated by SQUEEZE on the PLATON platform.<sup>8,9</sup> The location of Ir was assumed only at the central position. All non-hydrogen atoms were anisotropically refined and the hydrogen atoms were treated as riding models. All aromatic rings were treated using rigid constraints (AFIX 66). Some of the phenyl rings showed disordered electron densities, which were treated by dividing the moieties into several parts to construct reasonable models. CheckCif programs for  $1 \cdot (B_5)_2$  generated a B-level alert regarding the absence of a hydrogen bond acceptor of one of the hydroxy groups (040) in the pentaborate anion. We carefully checked the residual electron density around this OH group; however, no reasonable density was found. Despite this anomaly, the structure of the cluster unit is unequivocal. Therefore, this alert does not affect the conclusions of this study. The structure data were deposited at the Cambridge Crystallographic Data Center (CCDC) and the deposition numbers are summarized in Table S4.

#### **Theoretical calculation**

Geometry optimizations for the S<sub>0</sub>, S<sub>1</sub>, and T<sub>1</sub> states of a model system [RuAu<sub>12</sub>(dmpm)<sub>6</sub>]<sup>2+</sup> (**1**<sup>Me</sup>) (dmpm = (Me)<sub>2</sub>PCH<sub>2</sub>P(Me<sub>2</sub>)) were performed by density functional theory computations using TURBOMOLE<sup>10,11</sup> under the resolution of the identity (RI) approximation with the PBE functional<sup>12</sup> using the def-SV(P) basis sets<sup>13</sup> along with the relativistic effective core potential for Ru.<sup>14</sup>

# Supplemental data



**Figure S1.** Positive- (left) and negative-mode (right) ESI mass spectra of  $1 \cdot (B_5)_2$ . Inset shows the experimental (red) and calculated (black) isotope patterns of  $[RuAu_{12}(dppm)_6]^{2+}$  (left) and  $[B_5O_{10}H_4]^{-}$ , respectively.



**Figure S2.** Positive-mode ESI mass spectrum of  $2 \cdot (PF_6^-)_3$ . Inset of the mass spectrum show the experimental (red) and calculated (black) patterns of  $[RhAu_{12}(dppm)_6]^{3+}$  (left) and  $[RhAu_{12}(dppm)_6]^{3+}(PF_6^-)$  (right).



**Figure S3.** Positive-mode ESI mass spectrum of  $3 \cdot (PF_6^-)_3$ . Inset of the mass spectrum show the experimental (red) and calculated (black) patterns of  $[IrAu_{12}(dppm)_6]^{3+}$  (left) and  $[IrAu_{12}(dppm)_6]^{3+}(PF_6^-)$  (right).



**Figure S4.** <sup>1</sup>H (left) and <sup>31</sup>P{<sup>1</sup>H} (right) NMR charts of  $1 \cdot (B_5)_2$ . Asterisks correspond to residual solvent (\*) and CPME (\*\*), respectively.



**Figure S5.** <sup>1</sup>H (left) and <sup>31</sup>P{<sup>1</sup>H} (right) NMR charts of  $2 \cdot (PF_{6})_{3}$ . Asterisks correspond to residual solvent (\*), CPME (\*\*), and PF<sub>6</sub> (\*\*\*), respectively.



**Figure S6.** <sup>1</sup>H (left) and <sup>31</sup>P{<sup>1</sup>H} (right) NMR charts of  $3 \cdot (PF_{6})_{3}$ . Asterisks correspond to residual solvent (\*), CPME (\*\*), and PF<sub>6</sub> (\*\*\*), respectively.



**Figure S7.** DPV chart of  $1 \cdot (B_5)_2$  in 0.1 M TBAPF<sub>6</sub>/DCM at 298 K. Downward arrow indicates the corresponding open circuit potential.



**Figure S8.** PL emission spectra of  $1 \cdot (B_5)_2$  for the estimation of PLQY by the absolute method. Black and red lines correspond to the observed signal without and with samples, respectively.



**Figure S9.** PL emission spectra of  $1 \cdot (PF_6)_2$  for the estimation of PLQY by the absolute method. Black and red lines correspond to the observed signal without and with samples, respectively.



**Figure S10.** (a) PL emission spectra of  $3 \cdot (PF_6^-)_3$  for the estimation of PLQY by the absolute method. Black and red lines correspond to the observed signal without and with samples, respectively. (b) PL lifetime decay curves of  $3 \cdot (PF_6^-)_3$  under Ar (red) and  $O_2$  (green). The dots correspond to the experimental data and the solid lines represents the curve fitted by a single exponential function.



**Figure S11.** Temperature-dependent PL emission spectra of  $1 \cdot (B_5)_2$  in DCM. Since the DCM does not form transparent glass at low temperatures, the intensity of the emission spectra was normalized. Inset shows the peak top wavelength of the emission spectra as a function of the temperature.



**Figure S12.** Deconvoluted spectra of the temperature-dependent PL emission spectra of  $1 \cdot (B_5)_2$ . Red, blue, green, and black curves represent the contribution of the high-temperature component (~14300 cm<sup>-1</sup>), that of the low-temperature component (~15230 cm<sup>-1</sup>), the sum of the two curves, and the experimental data, respectively. For the fitting, the peak wavenumber of the high-temperature component was fixed at a value of 160 K. Even at 80 K, a small contribution of the high-temperature state was needed to reproduce the experimental curve.



**Figure S13.** Temperature-dependent PL spectra of  $1 \cdot (B_5)_2$  in EtOH/MeOH mixture under an  $O_2$  atmosphere. The solution and head space gases are saturated by pure  $O_2$ . Inset shows the same spectra in logarithmic scale.



**Figure S14.** Temperature-dependent PL lifetime data of  $1 \cdot (B_5)_2$  in EtOH/MeOH mixture. Red circles, solid black lines, and dotted black lines correspond to the observed PL decay curve, single exponential fit data, and instrument response functions, respectively.

Temperature (K)	τ1 (µs)@PL peak	Decay (µs) @ 660 nm	Rise (µs) @700 nm	Decay (µs) @ 700 nm
80	24.4	-	-	-
100	22.1	-	-	-
120	20.6	-	-	-
130	$16.6^{a}$	13.6	6.98	14.5
140	14.2	-	-	-
150	13.5	-	-	-
160	12.4	-	-	-
180	11.9	-	-	-
200	11.2	-	-	-
220	10.6	-	-	-
240	10.1	-	-	-
260	8.58	-	-	-
280	8.24	-	-	-
300	7.29	-	-	-

**Table S1.** Fitting results of PL lifetime data of  $1 \cdot (B_5)_2$  in EtOH/MeOH mixture at various temperatures.

<sup>*a*</sup>Attempt to fit by single exponential curve.

Table S2. Result of NBO analysis of 1<sup>Me</sup>.

Model	NBO charge on Ru	Average NBO charge on Au <sup>a</sup>
S <sub>0</sub> (DFT)	-1.548	0.138

<sup>*a*</sup>The NBO values on 12 Au atoms are distributed in the range of 0.134 - 0.142.



**Figure S15.** Kohn–Sham orbitals of  $1^{Me}$  (S<sub>0</sub> state) near the HOMO and LUMO levels. Orbitals are depicted at the 0.02e level.

Table S3. Relative energy and structural parameters of the optimized structures of 1<sup>Me</sup>.

	Relative	Excitation	Average bond lengths (Å)				RMSD <sup>c</sup> (Å)	
Model	Energy (eV) <sup>a</sup>	Energy (eV)	Ru-Au	Au–Au	Au-P	CSM <sup>b</sup>	RuAu <sub>12</sub> <sup>d</sup>	RuAu <sub>12</sub> P <sub>12</sub> <sup>e</sup>
S <sub>0</sub> (DFT)	0	0	2.806±0.002	2.951±0.041	2.3799	0.028	0	0
S <sub>1</sub> (DFT)	1.822	1.49	2.817±0.035	2.963±0.064	2.383±0.016	0.068	0.0931	0.1818
T <sub>1</sub> (DFT)	1.786	1.23	2.828±0.062	2.951±0.063	2.385±0.010	0.178	0.1016	0.2722
T <sub>1</sub> (TDDFT)	1.791	1.45	$2.814 \pm 0.027$	2.959±0.063	$2.385 \pm 0.010$	0.059	0.0616	0.2032

<sup>*a*</sup>Calculated total energy difference from that of the S<sub>0</sub> state. <sup>*b*</sup>Continuous symmetry measure. <sup>*c*</sup>Root mean square deviation values from the S<sub>0</sub> structure. <sup>*d*</sup>Ru@Au<sub>12</sub> core and <sup>*e*</sup>Ru@Au<sub>12</sub> core with P atoms are taken into consideration.

	<b>1</b> ·( <b>B</b> 5) <sub>2</sub>	<b>1</b> ·(PF <sub>6</sub> -) <sub>2</sub>	<b>2</b> •(PF <sub>6</sub> −) <sub>3</sub>	<b>3</b> •(PF <sub>6</sub> −) <sub>3</sub>
Formula <sup>a</sup>	$\begin{array}{c} C_{166}H_{172}Au_{12}B_{10}Cl_8\\ O_{22}P_{12}Ru \end{array}$	C <sub>150</sub> H <sub>132</sub> Au <sub>12</sub> F <sub>12</sub> P <sub>14</sub> Ru	$C_{150}H_{132}Au_{12}F_{12}P_{14}$ Rh	C150H132Au12F12P14 Ir
FW <sup>a</sup> (g mol <sup>-1</sup> )	5747.03	5060.80	5062.64	5151.93
Crystal size	0.182 x 0.151 x	0.100 x 0.075 x	0.082 x 0.068 x	0.059 x 0.037 x
(mm)	0.097 Monoclinic	0.074 Cubic	0.050 Triclinic	0.021 Triclinic
Space group 7	$P2_{1}/n_{2}$	$D_{2}\overline{2}$		$\vec{D1}$ 1
space group, z	r 21/11, 2	1 d3, 4	11,1	<i>I</i> 1, 1
a (A)	20.09083(19)	24.1905(2)	16.56435(17)	16.6056(2)
b (Å)	16.46782(15)	24.1905(2)	16.9676(2)	17.0015(2)
<i>c</i> (Å)	26.0406(2)	24.1905(2)	17.0633(3)	17.0194(3)
α (°)	90	90	70.2075(14)	70.1635(14)
β (°)	93.4636(9)	90	62.3430(14)	62.3690(14)
γ (°)	90	90	83.3307(10)	82.9846(11)
V (Å3)	8599.83(14)	14155.8(4)	3992.01(11)	4000.76(11)
Т(К)	105(2)	103(2)	103(2)	93(2)
$ ho_{ m calc}$ (g cm <sup>-3</sup> )	2.219	2.375	2.106	2.138
μ (mm-1)	10.395	12.699	11.292	12.004
$\theta$ range (°)	1.754 - 25.242	1.882 - 25.242	1.670 - 25.242	1.842 - 25.242
Measured reflections	90065	48658	77482	90872
Unique reflections	15754 ( <i>R</i> <sub>int</sub> = 0.0304)	$4332 (R_{int} = 0.0374)$	14614 ( <i>R</i> <sub>int</sub> = 0.0446)	14636 ( <i>R</i> <sub>int</sub> = 0.0503)
Data/paramet ers/restraints	15754/1014/487	4332/321/504	14614/709/36	14636/751/360
$R^{b,c}$ indices $[I > 2\sigma(I)]$	$R_1 = 0.0275, wR_2 = 0.0674$	$R_1 = 0.0189, wR_2 = 0.0462$	$R_1 = 0.0185, wR_2 = 0.0447$	$R_1 = 0.0240, wR_2 = 0.0475$
R <sup>b,c</sup> indices [all data]	$R_1 = 0.0310, wR_2 = 0.0684$	$R_1 = 0.0227 wR_2 = 0.0473$	$R_1 = 0.0208, wR_2 = 0.0455$	$R_1 = 0.0342, wR_2 = 0.0497$
Goodness-of-fit on F <sup>2</sup>	1.117	1.053	1.004	1.028
CCDC depository No.	2076179	2076176	2076177	2076178

Table S4. Crystal data.

<sup>*a*</sup>Solvent molecules included. <sup>*b*</sup>R<sub>1</sub> =  $\Sigma(||F_0| - |F_c||)/\Sigma|F_0|$ . <sup>*c*</sup>*w*R<sub>2</sub> =  $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$ , *w* =  $1/[\sigma^2(F_0^2) + (ap)^2 + bp]$ , where *p* =  $[\max(F_0^2, 0) + 2F_c^2]/3$ .

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