

## Supporting Information

### Surface engineering of linearly fused Au<sub>13</sub> units using diphosphine and Cd doping

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## Section 1. Experimental Procedures

### 1. Materials.

All materials used in this work were obtained from commercial suppliers and used directly without further purification. Tetrachloroauric (III) acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ , >99.9% metals basis) were purchased from the China Nonferrous Metal Mining (Group) Co.,Ltd. (Shenyang, China). The reagents including the cadmium chloride hemi(pentahydrate) ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , 98%), D-penicillamine (>98.0%(T)), cyclohexanethiol ( $\text{HS-}c\text{-C}_6\text{H}_{11}$ , 98%), 4-tert-butylbenzenethiol (TBBT, 99%), 1,3-bis(diphenylphosphino)propane (DPPP, 97%), 1,1'-bis(diphenylphosphino)ferrocene (DPPF, 97%), sodium borohydride ( $\text{NaBH}_4$ , 98.0%), borane - tert-butylamine complex ( $\geq 95.0\%$ ), Sodium hydroxide ( $\text{NaOH}$ , 96%), sodium tetraphenylboron (AR, 99%) were all purchased from the Sigma-Aldrich (Shanghai, China). Toluene ( $\text{C}_7\text{H}_8$ ,  $\geq 99.9\%$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ,  $\geq 99.9\%$ ), methanol ( $\text{CH}_3\text{OH}$ ,  $\geq 99.9\%$ ), ethanol ( $\text{EtOH}$ ,  $\geq 99.9\%$ ), and n-hexane ( $\text{C}_6\text{H}_{14}$ ,  $\geq 99.9\%$ ) were purchased from Guangfu (Tianjin, China).

### 2. Synthesis and purification the $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$ nanocluster.

The synthesis of  $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  nanocluster was performed using a two-phases exchange method via two steps. The first step is to prepare the water-soluble gold nanoclusters. 60 mg of water-soluble D-penicillium was dissolved in 10 mL of water, then 400  $\mu\text{L}$  of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (0.2 g/mL) was added. After the color of the aqueous solution turned into light yellow, 2 mL of  $\text{NaOH}$  (1 M) was added to adjust the pH of the solution to be alkaline. After about 5 min, 20 mg of  $\text{NaBH}_4$  (dissolved into 2 mL of cold water) was added and the color of solution changed from light yellow to brown red. The second step is ligand exchange: 75  $\mu\text{L}$  cyclohexanethiol was dissolved in 10 mL of DCM and added into the above solution. Then stirred for 20 min until the upper layer of solution became colorless. 30 mg of  $\text{CdCl}_2$  was added and stirred for 5 min, 6 mg of 1,3-bis (diphenylphosphine) propane was added. The crude product was obtained by stirring for 20 min. Then remove the aqueous solution and collect the crude products by centrifugation by adding sodium tetraphenylboron. After rotary evaporation, the excess ligands were washed and removed with methanol, and the nanoclusters were separated by thin layer chromatography (TLC, DCM:  $\text{CH}_3\text{OH}$ = 10:1).

### 3. Synthesis and purification of the $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$ nanocluster.

The one-pot method was used to synthesize the  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  alloy cluster. 30 mg of  $\text{CdCl}_2$  mixed with 400  $\mu\text{L}$  of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (0.2 g/mL). After all the  $\text{CdCl}_2$  being dissolved, 10 mL of ethanol and 15 mL of toluene were added to the system under 60 °C. Then 20 mg 1, 1'-bis(diphenylphosphino)ferrocene and 150  $\mu\text{L}$  4-tert-butylbenzenethiol were added and stirred for about 30 min. Then, 120 mg of borane-tert-butylamine complex was added. After about 4 hours, the products including the  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  nanocluster were synthesized. The excess ligands and other by-product were washed and removed with methanol for several times, and the nanoclusters were separated by thin layer chromatography (TLC, DCM : n-hexane= 1 : 2).

### 4. X-ray Crystallographic Determination of $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$ and $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$ nanoclusters.

Crystals of  $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  were obtained by layering n-hexane onto a  $\text{CH}_2\text{Cl}_2$  solution of the freshly purified  $\text{Cd}_2\text{Au}_{17}$  nanocluster and leaving it to stand at room

temperature for 2-3 days. The crystallizations of the pure  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  were performed in DCM/methanol for about 3-5 days. Single crystal X-ray diffraction (SCXRD) of them were carried out on a Stoe Stadivari diffractometer at 293 K, using a  $\text{MoK}\alpha$  ( $\lambda = 0.71073$ ) and  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54186 \text{ \AA}$ ) for  $\text{Cd}_2\text{Au}_{17}$  and  $\text{Cd}_2\text{Au}_{29}$ , respectively. Data reductions were performed using SAINT (Bruker), and absorption corrections using SHELXTL (Bruker, 2008). The structure was solved by direct methods and refined with full-matrix least-squares on F2 using the SHELXL-2014/7 (Sheldrick, 2014) suite of programs. The placement of the heteroatoms was ascertained by the method of modifying the disorderly free variables. All the refinement parameters are summarized in Table S1 and S2.

### **5. Characterization.**

Ultraviolet-visible (UV-vis) absorption spectra were recorded on an Agilent 8453 spectrophotometer. Fluorescence spectra were obtained using an F-7000 fluorescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a thermal ESCALAB 250, equipped with a monochromated  $\text{Al K}\alpha$  (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, and a flood gun (to counter charging effects). The analysis chamber base pressure was lower than  $1 \times 10^{-9}$  mbar, and data were collected with  $\text{FAT} = 20$  eV. Electrospray ionization mass spectra (ESI-MS) were recorded using a Waters Xevo G<sup>2</sup>-XS mass spectrometer. The source temperature was maintained at 80 °C. The sample was directly infused into the chamber at 1.5  $\mu\text{L}/\text{min}$ . ESI sample was prepared by dissolving it in dichloromethane (0.1 mg/mL). The Matrix-Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS) was performed on an Applied Biosystems Voyager DE-STR MALDI-TOF equipped with a nitrogen laser. Trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as MALDI matrix.

## Section 2. Supplementary Figures

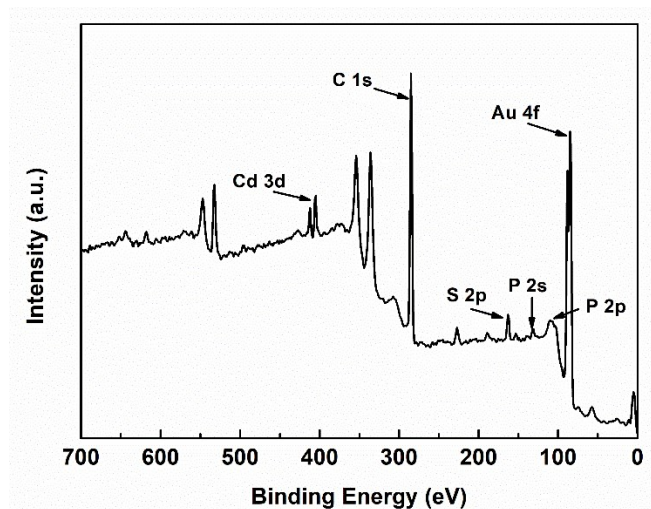


Figure S1. The full X-ray photoelectron spectroscopy (XPS) of  $[\text{Cd}_2\text{Au}_{17}(\text{S-c-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  nanocluster.

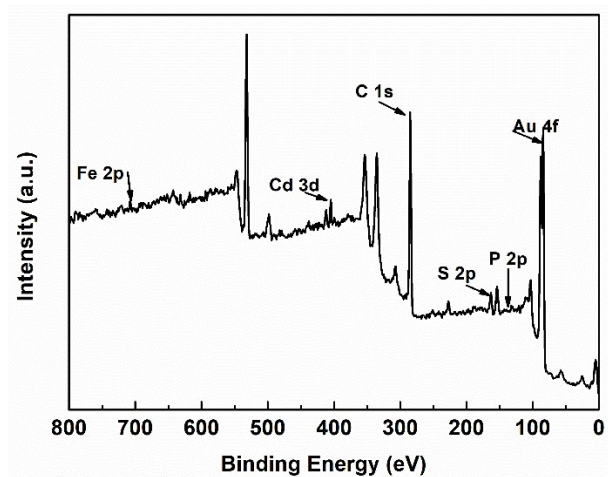


Figure S2. The full X-ray photoelectron spectroscopy (XPS) of  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  nanocluster.

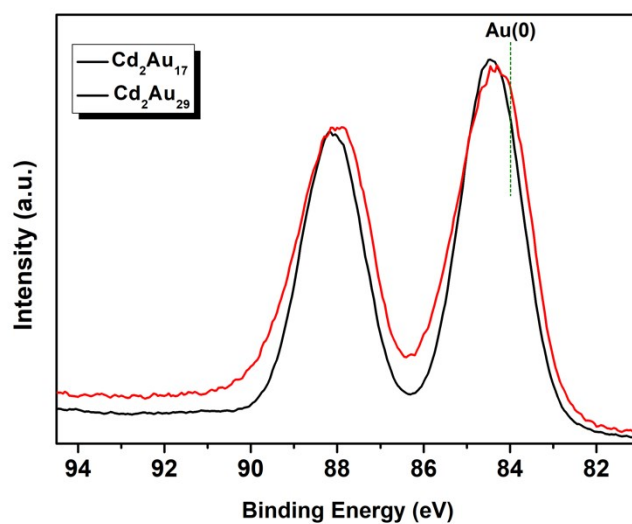


Figure S3. The Au  $4f$  XPS of  $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  (black line) and  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  (red line) nanoclusters.

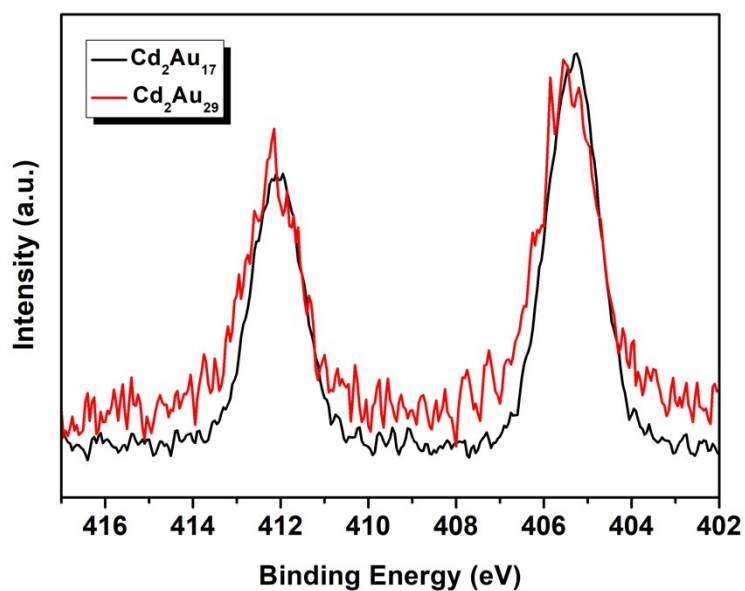


Figure S4. The Cd  $3d$  XPS of  $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  (black line) and  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  (red line) nanoclusters.

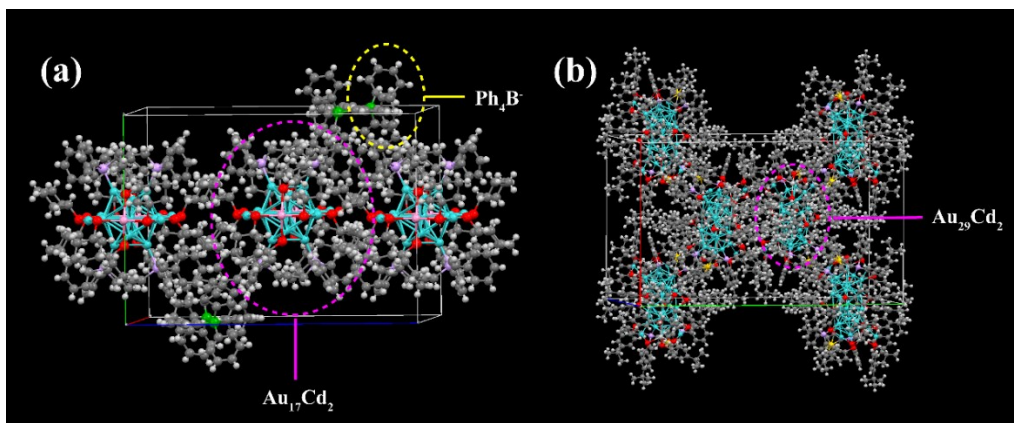


Figure S5. The unit cell of (a)  $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  and (b)  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  nanoclusters (dotted pink circle for nanocluster and dotted pink circle for counterions) (color label: Au = blue; Cd = pink; S = red; P = purple; Fe = yellow; B = green; C = gray; H = white).

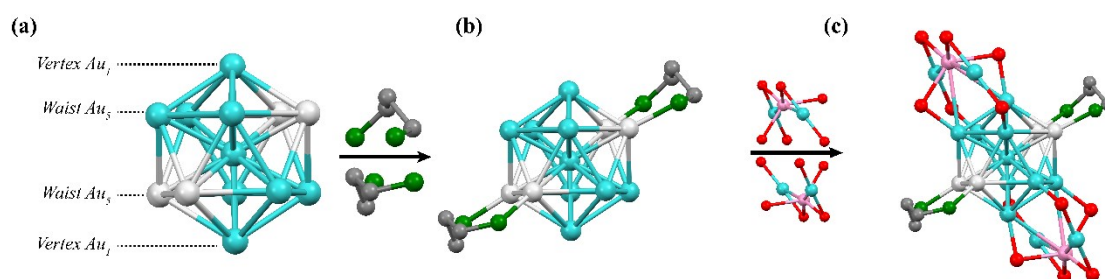


Figure S6. The structural analysis of  $[\text{Cd}_2\text{Au}_{17}(\text{S-}c\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  nanocluster: (a) the  $\text{Au}_{13}$  core; (b) the  $\text{Au}_{13}$  core with two diphosphine; (c) the framework of  $\text{Cd}_2\text{Au}_{17}$  (color label: Au = blue/light gray; Cd = pink; S = red; P = green; all C and H atoms are omitted).

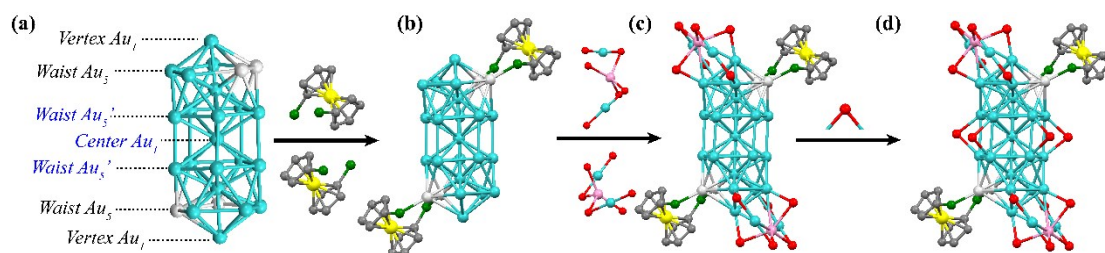


Figure S7. The structural analysis of  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  nanocluster: (a) the  $\text{Au}_{25}$  core; (b) the  $\text{Au}_{25}$  core with two diphosphine; (c) the  $\text{Au}_{25}$  core with two diphosphine as well as two  $\text{Au}_2\text{CdS}_6$  motifs (d) the framework of  $\text{Cd}_2\text{Au}_{29}$  (color label: Au = blue/light gray; Cd = pink; S = red; P = green; Fe = yellow; all C and H atoms are omitted).

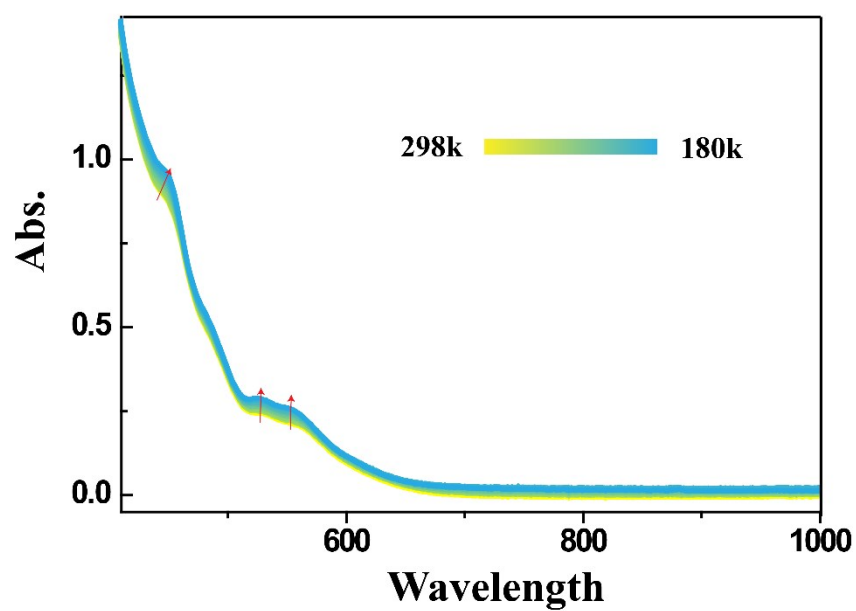


Figure S8. The time-dependent UV-vis spectra of  $[\text{Cd}_2\text{Au}_{17}(\text{S-}i\text{-C}_6\text{H}_{11})_{12}(\text{DPPP})_2](\text{BPh}_4)$  nanocluster.

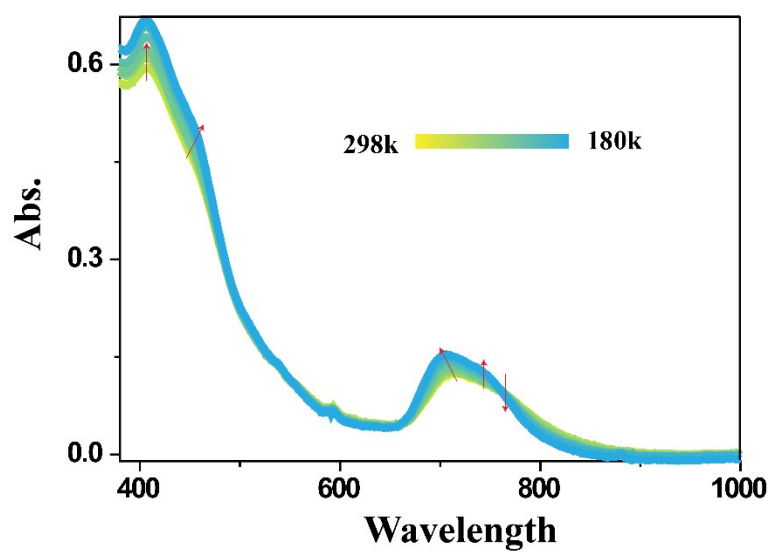


Figure S9. The time-dependent UV-vis spectra of  $\text{Cd}_2\text{Au}_{29}(\text{TBBT})_{17}(\text{DPPF})_2$  nanocluster.

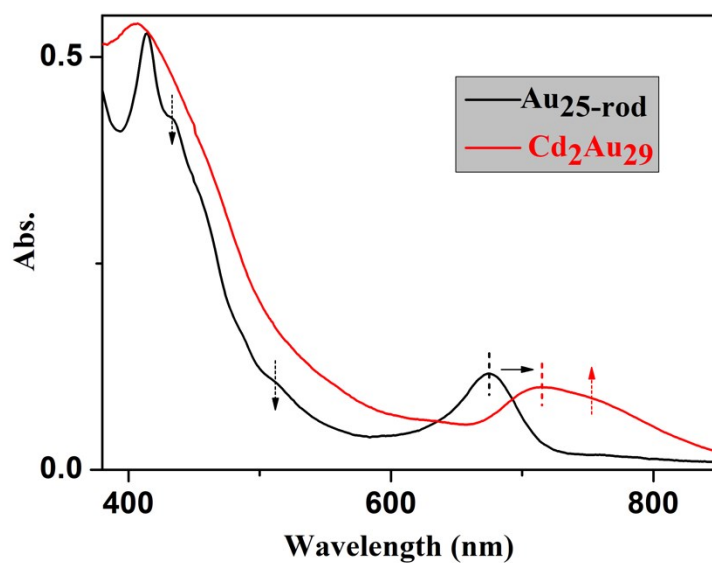


Figure S10. The optical absorption spectra of rod-Au<sub>25</sub> and Cd<sub>2</sub>Au<sub>29</sub>(TBBT)<sub>17</sub>(DPPF)<sub>2</sub> nanoclusters.

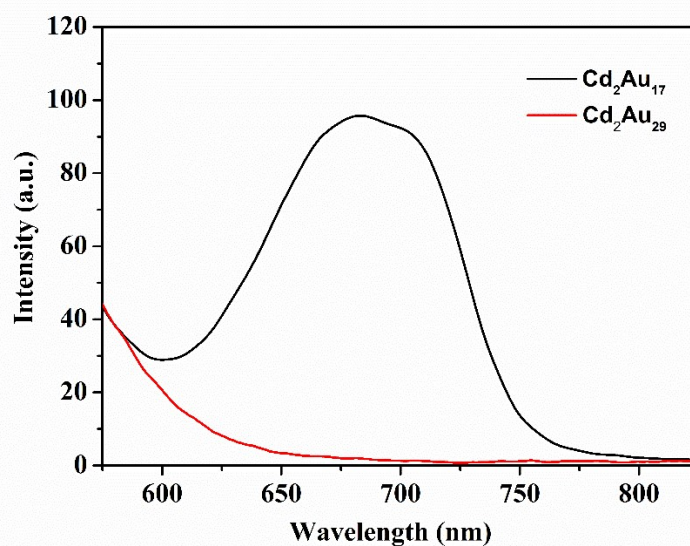


Figure S11. Fluorescence spectra of [Cd<sub>2</sub>Au<sub>17</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>12</sub>(DPPP)<sub>2</sub>](BPh<sub>4</sub>) (black curve) and Cd<sub>2</sub>Au<sub>29</sub>(TBBT)<sub>17</sub>(DPPF)<sub>2</sub> (red curve) excited at 467 nm.



### Section 3. Supplementary Tables

**Table S1 Crystal data and structure refinement for Cd<sub>2</sub>Au<sub>17</sub>.**

CCDC	2056813
Empirical formula	C <sub>150</sub> H <sub>204</sub> Au <sub>17</sub> BCd <sub>2</sub> P <sub>4</sub> S <sub>12</sub>
Formula weight	6099.76
Temperature/K	120
Crystal system	orthorhombic
Space group	P222 <sub>1</sub>
a/Å	19.544(4)
b/Å	18.626(4)
c/Å	26.122(5)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	9509(3)
Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	2.130
μ/mm <sup>-1</sup>	13.476
F(000)	5600.0
Crystal size/mm <sup>3</sup>	0.25 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.75 to 50.576
Index ranges	-23 ≤ h ≤ 22, -21 ≤ k ≤ 22, -13 ≤ l ≤ 30
Reflections collected	71306
Independent reflections	17007 [R <sub>int</sub> = 0.0634, R <sub>sigma</sub> = 0.0492]
Data/restraints/parameters	17007/1198/856
Goodness-of-fit on F <sup>2</sup>	0.968
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0734, wR <sub>2</sub> = 0.1965
Final R indexes [all data]	R <sub>1</sub> = 0.0948, wR <sub>2</sub> = 0.2182
Largest diff. peak/hole / e Å <sup>-3</sup>	6.76/-4.63
Flack parameter	0.501(9)

**Table S2 Crystal data and structure refinement for Cd<sub>2</sub>Au<sub>29</sub>.**

CCDC	2056824
Empirical formula	C <sub>238</sub> H <sub>277</sub> Au <sub>29</sub> Cd <sub>2</sub> Fe <sub>2</sub> P <sub>4</sub> S <sub>17</sub>
Formula weight	9855.01
Temperature/K	120
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
a/Å	27.2386(12)
b/Å	44.9120(15)
c/Å	25.7433(13)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	31493(2)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	2.079
μ/mm <sup>-1</sup>	27.952
F(000)	17904.0
Radiation	CuKα (λ = 1.54186)
2θ range for data collection/°	11.908 to 139.576
Index ranges	-32 ≤ h ≤ 12, -54 ≤ k ≤ 51, -28 ≤ l ≤ 30
Reflections collected	170838
Independent reflections	28819 [R <sub>int</sub> = 0.0604, R <sub>sigma</sub> = 0.0529]
Data/restraints/parameters	28819/828/1369
Goodness-of-fit on F <sup>2</sup>	1.051
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0582, wR <sub>2</sub> = 0.1431
Final R indexes [all data]	R <sub>1</sub> = 0.0746, wR <sub>2</sub> = 0.1500
Largest diff. peak/hole / e Å <sup>-3</sup>	3.99/-3.79