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# **Supporting Information**

### 1. Experimental Section

# Synthesis of AuC≡CR (R = 2,4-2CH<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)

1 g (Me<sub>2</sub>SAu)Cl dissolved in 60 mL acetone and 800  $\mu$ L 1-ethynyl-2,4dimethylbenzene was added successively under vigorously stirring. After the clear solution became cloudy, 603  $\mu$ L triethylamine was added and the suspension turned to clear immediately. The reaction was carried out in the dark at room temperature for 2 hours. The solvent was removed by rotary evaporation to obtain orange solids that were washed with water (10 mL×1), ethanol (15 mL×2) and ether (15 mL×2) in turn to remove the excess ligand. Finally, after dried in an atmosphere of nitrogen, yellow powder was obtained.

### Synthesis of Au<sub>28</sub>(DMPA)<sub>20</sub>

Au<sub>28</sub>(DMPA)<sub>20</sub> was synthesized by the direct reduction of the AuC=CR precursor with tert-butylamine borane (C<sub>4</sub>H<sub>11</sub>NBH<sub>3</sub>). Firstly, AuC=CR was synthesized as described above. Next, 60 mg AuC=CR dissolved in mixture of 10 mL dichloromethane and 5 mL methanol and stirred vigorously. When the solution turned turbid orange, 1.0 mg of C<sub>4</sub>H<sub>11</sub>NBH<sub>3</sub> was added. The reaction was carried out at room temperature for 9 hours. After that, the solvent was removed by rotary evaporation and the obtaining solids were extracted with thimbleful dichloromethane (1 mL). Excess methanol was then added to precipitate the product that was washed several times with methanol and n-hexane. The crude products were separated and purified by thin layer chromatography with dichloromethane/petroleum ether as developing agent. Finally, n-hexane was diffused into a solution of dichloromethane for a week to obtain Au<sub>28</sub>(DMPA)<sub>20</sub> single crystal.

## Synthesis of Au<sub>28</sub>(TBBT)<sub>20</sub>

Au<sub>28</sub>(TBBT)<sub>20</sub> was synthesized based on the reported literature.<sup>S1</sup> First Au<sub>25</sub>(PET)<sub>18</sub> Au<sub>25</sub>(PET)<sub>18</sub> (PET = 2-phenylethanethiol) was synthesized.<sup>S2</sup> 500 mg HAuCl<sub>4</sub>·4H<sub>2</sub>O and 675 mg TOAB (tetraoctylammonium bromide) were dissolved in 35 mL tetrahydrofuran. After stirring for 30 min, 1020  $\mu$ L 2-phenylethanethiol was added immediately the above solution. The mixture was slowly stirred for about 3 hours until the solution became colorless and transparent, then cool the reaction solution to 0 °C. Whereafter, 538 mg NaBH<sub>4</sub> in 8 mL cold water was quickly added. Then, the mixture solution was stirred overnight in an ice bath. The obtained product was washed with methanol three times. The Au<sub>25</sub>(PET)<sub>18</sub> was extracted with toluene. Then 10 mg Au<sub>25</sub>(PET)<sub>18</sub> was dissolved in 0.5 mL toluene, then 0.5 mL 4-tert-butylbenzenethiol was added. The reaction solution was heated at 80 °C oil bath for 2 hours. The product was washed with methanol three times. Finally, the Au<sub>28</sub>(TBBT)<sub>20</sub> was extracted with dichloromethane purified by thin-layer chromatography and with the dichloromethane/petroleum ether as the developing solvent.

#### Synthesis of Au<sub>28</sub>(CPT)<sub>20</sub>

 $Au_{28}(CPT)_{20}$  was synthesized based on the reported literature.<sup>S3</sup> 10 mg  $Au_{25}(PET)_{18}$  was dissolved in 0.5 mL toluene, and then 0.5 mL cyclohexanethiol was added. The reaction solution was heated at 80 °C oil bath for 2 hours. The product was washed with methanol three times. Finally, the  $Au_{28}(CPT)_{20}$  was extracted with dichloromethane and purified by thin-layer chromatography with the dichloromethane/petroleum ether as the developing solvent.

#### Catalytic test

All electrochemical tests were implemented on the electrochemical workstation CHI660D using a standard three-electrode system with glassy carbon electrode (GCE) (diameter: 5 mm, area:  $0.196 \text{ cm}^2$ ) as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode. The obtained nanoclusters and multiwalled carbon nanotube were added into CH<sub>2</sub>Cl<sub>2</sub> and treated under ultrasonication for 30 min. Then the solvent was blown dry with nitrogen to obtain the supported catalysts. The catalyst was dispersed in a mixture containing isopropanol, ultrapure water and 0.5 wt% Nafion solution to prepare a 0.48 mg<sub>gold</sub>/mL catalyst suspension. Then, 5.0  $\mu$ L suspensions of nanoclusters on multiwalled carbon nanotube (0.96 mg<sub>gold</sub>/mL) were dropped on the GC electrode and then dried at room temperature. The electrocatalytic EOR performance was determined by cyclic voltammograms (CVs) conducted in a mixture solution of 1.0 M KOH and 1.0 M C<sub>2</sub>H<sub>5</sub>OH from -0.8 to 0.8 V

vs Ag/AgCl with a sweep rate of 50 mV/s at room temperature. Chronoamperometry tests were performed at 0.10 V vs Ag/AgCl for 2 hours.

### Characterization

The UV-vis spectra were characterized by a Shimadzu UV-1800 UV-vis spectrometer. The single crystal X-ray diffraction data of Au<sub>28</sub>(DMPA)<sub>20</sub> were collected on a Bruker D8 VENTURE with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 173 K. Electrospray ionization (ESI) mass spectra of Au<sub>28</sub>(DMPA)<sub>20</sub> were collected using a Z spray source on a Waters Q-TOF mass spectrometer. The cluster sample was dissolved in toluene (0.5 mg/mL) and then the solution was diluted with methanol solution containing 50 mmol/L Cs<sub>2</sub>CO<sub>3</sub> (2:1 V/V). The electrochemically active surface areas (ECSAs) were determined by integrating the hydrogen adsorption charge on CVs, which was conducted in a 1.0 M KOH solution with a sweep rate of 50 mV/s under room temperature. Electrochemical impedance spectroscopy (EIS) tests were carried out on the electrochemical workstation CHI660D using a standard three-electrode system with glassy carbon electrode as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The electrolyte was 1.0 M KOH + 1.0 M C<sub>2</sub>H<sub>5</sub>OH, and the EIS tests were carried out at room temperature. The liquid products were determined by <sup>1</sup>H NMR on BRUKER AVANCE III 400 MHz with Dimethyl sulfoxide (DMSO) as internal standard.

# 2. Supporting Figures and Tables



**Figure S1.** The coordination numbers of Au atoms in  $Au_{28}(DMPA)_{20}$  (a),  $Au_{28}(TBBT)_{20}$  (b) and  $Au_{28}(CPT)_{20}$  (c) except for the outermost surface layer. Color code: green, Au in kernels; dark blue/wathet: Au in staples; yellow: S; gray, C. The H atoms are omitted for clarity. (Only the Au-Au bonds less than 2.880 Å are counted).



**Figure S2.** CV curves of the three catalysts in 1 M KOH solution and the shaded areas are used to calculate the ECSAs of  $Au_{28}(DMPA)_{20}$  (a),  $Au_{28}(TBBT)_{20}$  (b) and  $Au_{28}(CPT)_{20}$  (c).



Figure S3. UV-Vis spectra of  $Au_{28}(DMPA)_{20}$  (a),  $Au_{28}(TBBT)_{20}$  (b) and  $Au_{28}(CPT)_{20}$  (c) clusters before and after the EOR.



**Figure S4.** <sup>1</sup>H NMR spectra obtained from the liquid products of EOR reactions catalyzed by the three  $Au_{28}$  clusters.



**Figure S5.** Cyclic voltammogram curves of EOR on  $Au_{28}(DMPA)_{20}$  (a),  $Au_{28}(TBBT)_{20}$  (c) and  $Au_{28}(CPT)_{20}$  (e) at different scan rates. The corresponding plot of forward peak current density versus the square root of the scan rate  $(v^{1/2})$  for  $Au_{28}(DMPA)_{20}$  (b),  $Au_{28}(TBBT)_{20}$  (d) and  $Au_{28}(CPT)_{20}$  (f).

Table S1. Crystal data and structure refinement for the  $Au_{28}(DMPA)_{20}$  nanocluster.

Empirical formula	C200H180Au28	
Formula weight	8098.49	
Temperature	173.00 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 21.1424(6) Å	α=90°
	b = 46.1033(15) Å	β= 96.5300(10)°
	c = 21.8744(7) Å	$\gamma=90^\circ$
Volume	21183.4(11) Å <sup>3</sup>	
Z	4	
Density (calculated)	2.539 g/cm <sup>3</sup>	
Absorption coefficient	19.344 mm <sup>-1</sup>	
F(000)	14368.0	
Theta range for data collection	3.888 to 54.998°	
Index ranges	-27<=h<=26, -59<=k<=59, -25<=l<=28	
Reflections collected	153423	
Independent reflections	48410 [Rint = 0.0585, Rsigma = 0.0645]	
Absorption correction	Multi-Scan	
Data / restraints / parameters	48410/3077/2270	
Goodness-of-fit on F <sup>2</sup>	1.046	
$\Delta \sigma_{max}$	0.008	
Final R indices [I>2sigma(I)]	R1 = 0.0502, $wR2 = 0.1216$	
R indices (all data)	R1 = 0.0822, $wR2 = 0.1360$	
Largest diff. peak and hole	5.11 and -6.88 eÅ <sup>-3</sup>	

# 3. Supporting References

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- S2 Z. Wu, J. Suhan and R. Jin, J. Mater. Chem., 2009, 19, 622-626.
- S3 N. Xia, J. Yuan, L. Liao, W. Zhang, J. Li, H. Deng, J. Yang and Z. Wu, J. Am. Chem. Soc., 2020, 142, 12140-12145.