# **Electronic Supplementary Information (ESI)**

## Stabilization of a New Nanocomposite Family by Reduction of Gold

## Nanoclusters with Electron-reservoir Complexes

Fangyu Fu,<sup>a,b</sup> Anthony Dedieu,<sup>b</sup> Wenjuan Wang,<sup>b,c</sup> Tao Chen,<sup>a</sup> Yongbo Song,<sup>a</sup> Eric Fouquet,<sup>b</sup> Jean-René Hamon,<sup>c</sup> Manzhou Zhu,<sup>\*a</sup> and Didier Astruc<sup>\*b</sup>

a. Department of Chemistry and Center for Atomic Engineering of Advanced Materials, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.

b. ISM, UMR CNRS N° 5255, Univ. Bordeaux, 33405 Talence Cedex, France.

c. Institut des Sciences Chimiques, UMR CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, France.

## Table of content:

1. General data	S2
2. Details for the synthesis of Au <sub>25</sub> (SR) <sub>18</sub> <sup>-</sup> metallocenium <sup>+</sup> nanoclusters	S2
3. Details for the synthesis of $Au_{25}(SR)_{18}$ · Na <sup>+</sup> nanocluster	S5
4. Characterization of the Au <sub>25</sub> (SR) <sub>18</sub> <sup>-</sup> metallocenium <sup>+</sup> nanoclusters	S5
5. References	.S10

#### 1. General data

All solvents and chemicals were used as purchased, unless otherwise noted.

- UV-vis. absorption spectra were measured with a Perkin-Elmer Lambda 19 UV-vis. spectrometer.

- NMR spectra were recorded at 25 °C with a Bruker AC 400, or 300 (400 or 300 MHz). All the chemical shifts are reported in parts per million ( $\delta$ , ppm) with reference to Me4Si for the <sup>1</sup>H NMR spectra.

- 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 (337 nm). The mass spectra of negative ions were collected in the linear mode at an acceleration voltage of 25 kV and a delay time of 350 ns. Trans - 2 - [3 - (4 - tert - Butyl - phenyl) - 2 - methyl - 2 propenylidene] malononitrile (DCTB) was used as the MALDI matrix.

- Electrospray ionization (ESI) mass spectra were acquired using a Bruker Q-TOF mass spectrometer equipped with ESI source.

#### 2. Details for the synthesis of Au<sub>25</sub>(SR)<sub>18</sub><sup>-</sup> metallocenium<sup>+</sup> nanoclusters

Synthesis of the nanocluster  $[1^{-}, 2^{+}]$  from the 19e complex 2 as example:

In a Schlenk flask, Na/Hg amalgam was prepared in dry THF under N<sub>2</sub> at r.t., then 10 mg of cobalticenium hexafluorophosphate [CoCp<sub>2</sub>] [PF<sub>6</sub>] (Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>) and THF (10 mL) were added, and the mixture was allowed to stir for 2 h. The solution progressively changed color from yellow to brown indicating the formation of cobaltocene **2**. The solvent was removed *in vacuo* providing the crude product that was redissolved in 10 mL dry pentane to eliminate the insoluble NaPF<sub>6</sub> salt by cannula filtration. Finally, pentane was removed *in vacuo*, and the product was redissolved again in dry THF (10 mL) for further use. 5 mg **1** (which was synthesized according to ref 1) was dissolved in 10 mL dry THF under nitrogen in a standard Schlenk flask and stirred at room temperature. Then a fresh **2** solution (1 equivalent was required) was quickly injected into the Schlenk flask after 5 min degassed, the color change of the solution from yellow brown to red brown (Figure S1) indicating the formation of the [**1**<sup>-</sup>, **2**<sup>+</sup>] from **1**. The THF solvent was removed in *vacuo* and the products were extracted by toluene and then filtered, and the toluene solution was dried in *vacuo* at 30 °C to get the pure [nanocluster composite **1**<sup>-</sup>, **2**<sup>+</sup>]. The nanocluster nanocomposites [**1**<sup>-</sup>, **3**<sup>+</sup>], [**1**<sup>-</sup>, **4**<sup>+</sup>] and [**1**<sup>-</sup>, **5**<sup>+</sup>] were synthesized from the other organometallic 19e complexes by a similar process.

### Synthesis of the nanocluster [1, 2<sup>+</sup>] from the hydride reservoir 7 as example:

10 mg of cobalticenium hexafluorophosphate [CoCp<sub>2</sub>] [PF<sub>6</sub>] and dry THF (10 mL) were added into a Schlenk flask under N<sub>2</sub> at r.t., then 5 eq NaBH<sub>4</sub> was added, and the mixture was allowed to stir for 2 h. The solution progressively changed color from yellow to red indicating the formation of **7**. The solvent was removed *in vacuo* providing the crude product that was redissolved in pentane to eliminate the insoluble NaPF<sub>6</sub> salt by cannula filtration. Finally, pentane was removed *in vacuo*, and the product was redissolved again in dry THF (10 mL) for further use. 5 mg **1** was dissolved in 10 mL dry THF under nitrogen in a standard Schlenk flask and stirred at room temperature. Then a fresh **7** solution (1 equivalent was required) was quickly injected into the Schlenk flask after 5 min degassed, the color change of the solution from yellow brown to red brown (Figure S1) indicating the formation of the composite [**1**<sup>-</sup>, **2**<sup>+</sup>] from **1**. The THF solvent was removed in *vacuo* and the products were extracted by toluene and then filtered, and the toluene solution was dried in *vacuo* at 30 °C to get the pure nanocluster composite [1<sup>-</sup>, 2<sup>+</sup>]. Similarly the nanocluster composites [1<sup>-</sup>, 3<sup>+</sup>] and [1<sup>-</sup>, 4<sup>+</sup>] were synthesized from the other organometallic hydride complexes (8 was synthesized from [CpFe( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)][PF<sub>6</sub>] as starting material at 50 °C, and 9 was synthesized from [CoCp\*<sub>2</sub>][PF<sub>6</sub>] as starting material at 50 °C overnight. See the characterizations of **9** below.



Figure S1. Photographs of the: a,  $[Au_{25}(SR)_{18}]^0$  and b,  $[Au_{25}(SR)_{18}]^-$  [metalloceniums]<sup>+</sup>.



Figure S2. <sup>1</sup>H NMR of the [CoCp\*( $\eta^4$ -C<sub>5</sub>Me<sub>5</sub>H)] **9**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub> \*)  $\delta$  2.10 (dd, J = 12.3, 5.7 Hz, 1H), 1.86 (s, 6H), 1.64 (s, 15H), 1.40 (d, J = 6.6 Hz, 3H), 0.70 (d, J = 1.5 Hz, 6H). \$ ,# and ^ are the solvents.



Figure S3. <sup>13</sup>C NMR of the [CoCp\*( $\eta^4$ -C<sub>5</sub>Me<sub>5</sub>H)] **9**: <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub> \*)  $\delta$  87.70, 51.61, 17.00, 11.32, 10.24, 9.48, 1.08, 0.95. \$,# and ^ are the solvents.

### 3. Details for the synthesis of Au<sub>25</sub>(SR)<sub>18</sub> Na<sup>+</sup> nanocluster

A Schlenk flask was charged with 5 mg Au\_{25}(SR)\_{18} and 10 mL dry THF under N\_2 at r.t., then 2 equivalent NaBH<sub>4</sub> dissolved in 1 mL ethanol was added immediately after 5 min degassed and the color change of the solution from yellow brown to red brown. The solvent was removed in vacuo and the products were extracted by toluene and then filtered under  $N_2$  by cannula to remove the excess NaBH<sub>4</sub>. The toluene solution was dried in vacuo at 30 °C to get the pure nanocluster composite [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>-</sup> Na<sup>+</sup>.



400

600

Wavelength (nm)

800

700

800

900

600

1000

400

C 1.0

Abs.

0.5

0.0

400

600

600

Wavelength (nm)

800

800

### 4. Characterization of the nanocluster composites Au<sub>25</sub>(SR)<sub>18</sub> metallocenium<sup>+</sup>.



1000

d

SqP 0.5

0

400

500

[1<sup>-</sup>, 5<sup>+</sup>].



Figure S5. 1H NMR (in CD<sub>2</sub>Cl<sub>2</sub>) of the nanocluster composites a,  $[1,5^+]$ ; b,  $[1,4^+]$  c,  $[1,3^+]$  and  $[1,2^+]$ . \* indicates the organic solvent and water. For instance, in  $[1,5^+]$  (Figure S2a), the peaks at 7.04-7.22 ppm are attributed to the phenyl groups (AuNC-SCH<sub>2</sub>CH<sub>2</sub>Ph); the  $\beta$ -CH<sub>2</sub> (AuNC-SCH<sub>2</sub>CH<sub>2</sub>Ph) triplet at 3.57 and 2.95 ppm are distinct because of the different ligand sites and configurations. The  $\alpha$ -CH<sub>2</sub> (AuNC-SCH<sub>2</sub>CH<sub>2</sub>Ph) of the 18 thiolate ligands are located at 3.09 ppm as a broad multiplet. The single peak at 2.16 ppm is assigned to -CH<sub>3</sub> on the benzene ring of 5<sup>+</sup> and anther single peak at 1,56 ppm is contributed to -CH<sub>3</sub> on the Cp\* ring of 5<sup>+</sup>. In addition  $[1,2^+]$ ,  $[1,3^+]$  and  $[1,4^+]$  show analogous <sup>1</sup>H NMR spectra; however the Cp signals of 2<sup>+</sup> and 3<sup>+</sup> are located at 5.62 and 4.50 ppm, respectively, and the -CH<sub>3</sub> signal of 3<sup>+</sup> is located at 2.47 ppm and the -CH<sub>3</sub> on the Cp\* ring of 4<sup>+</sup> is located at 1.69 ppm.



Figure S6. MALDI-MS (left) and ESI-MS (right) analysis of the: a,  $[1^-, 2^+]$ ; b,  $[1^-, 3^+]$  and c,  $[1^-, 4^+]$ 



Figure S7. UV-vis. spectra tracked the [1<sup>-</sup>, 2<sup>+</sup>] (a) and [1<sup>-</sup>, 3<sup>+</sup>] (b) nanoclusters exposed to air in THF solution.



Figure S8. UV-*vis.* spectra tracked the nanocluster composite [1-, 4+] exposed to air in THF solution.



Figure S9. UV-vis. spectra showing the oxidation of  $[Au_{25}(SR)_{18}]^{-} Na^{+}$  to  $[Au_{25}(SR_{18}]^{0}$  in air in THF solution within several minutes.



Figure S10. UV-vis. spectra of: a,  $[1^-, 2^+]$ ; b,  $[1^-, 3^+]$  and c,  $[1^-, 4^+]$  obtained from 3 hydride-reservoir sandwich complexes.



Figure S11. ESI-MS analysis of: a, [1<sup>-</sup>, 2<sup>+</sup>]; b, [1<sup>-</sup>, 3<sup>+</sup>] and c, [1<sup>-</sup>, 4<sup>+</sup>] obtained from 3 hydride-reservoir sandwich complexes.

## References

1. Manzhou Zhu, Eric Lanni, Niti Garg, Mark E. Bier, and Rongchao Jin. Kinetically Controlled, High-Yield Synthesis of Au<sub>25</sub> Clusters. *J. Am. Chem. Soc.* 2008, **130**, 1138-113.